BORON: BORANES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1982

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CONTENTS

A. INTRODUCTION

The role of the organoboranes in organic synthesis continues to grow at an impressive rate. Borane reagents are used in hundreds of hydroborations and reductions each year and this year is no exception. As in the past, this review is focused on reports primarily concerned with developing new organoborane methodology and/or reagents and not to the routine use of well characterized borane or borohydride reagents. Not surprisingly, Professor Brown and his research group are the leading contributors to the field. It is a pleasure to note that many other scientists are now focusing attention on the boranes; a fact that can only lead to greater utilization of these versatile reagents.

I have presented the chemistry in the format which has proved to be successful in previous years. As always, classification of data can be arbitrary but, hopefully, logical. Thus $RBCl_2$ reagents are found in section B.1.b because they generally serve as precursors for RBH_2 in hydroboration reactions.

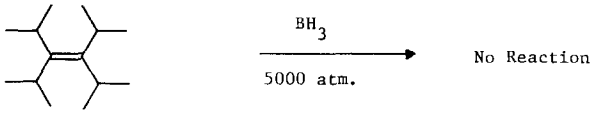
B. BORANE REAGENTS

1. Hydroborating Agents

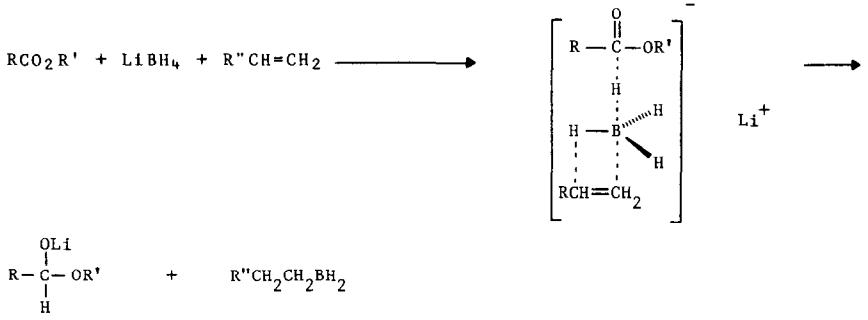
a. BH_3

The hydroboration reaction is the fundamental reaction in the organoborane field. Okamoto reports that highly hindered alkenes can be hydroborated at high pressures [1]. Rearrangements are observed as the pressure is reduced. Thus trithexylborane isomerizes over a period of days after the system is returned to atmospheric pressure.

[The attachment of the boron was determined by oxidation and it is likely that the reaction contains a mixture of isomeric trialkylboranes.] (E)-1,2-Di-tert-butylethylene forms only the corresponding monoalkylborane whereas the highly hindered tetraisopropylethylene does not hydroborate even at 5000 atmospheres.



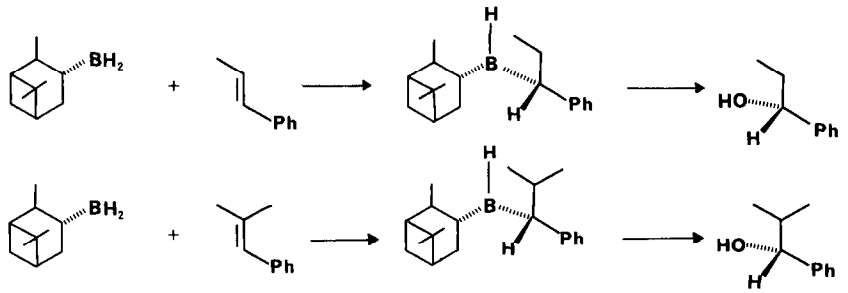
Brown and Narasimhan have reported that $LiBH_4$ can be used to hydroborate alkenes in the presence of carboxylic esters [2]. The reaction can be viewed as an *in situ* generation of BH_3; the evidence indicates that the hydroboration reaction is coupled to the reduction reaction.



The reaction produces the dialkylborinate esters in excellent yields if two equivalents of alkene are utilized. This reaction could prove useful for the synthesis of dialkylborinate esters which are valuable synthetic intermediates.

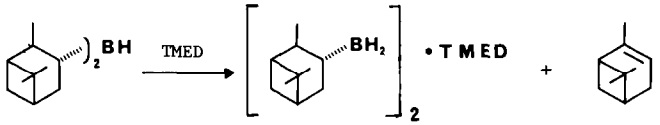
b. RBH_2

Brown has utilized monoisopinocampheylborane as a chiral hydroborating agent for trans-disubstituted and trisubstituted alkenes [3].



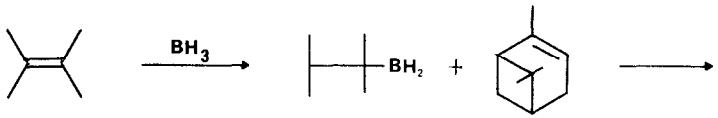
The product alcohols exhibit enantiameric purities in the range of 53-100% ee. The enantiomeric purities of the products increase with increasing steric requirements of the alkyl or phenyl substituents. Brown notes that monoisopinocampheylborane ($IpcBH_2$) complements diisopinocampheylborane (Ipc_2BH) in two respects. (1) Ipc_2BH is a more effective chiral hydroborating agent for cis olefins but fails for trans olefins whereas $IpcBH_2$ hydroborates trans olefins more efficiently than cis olefins. (2) Although both Ipc_2BH and $IpcBH_2$ both hydroborate cis olefins, they provide alcohols of opposite configurations (even though they are prepared from the same enantiomer of α-pinene).

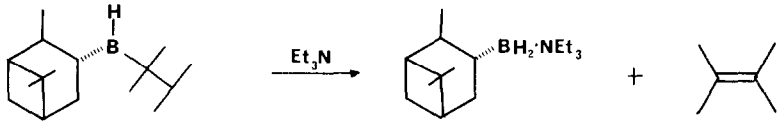
The synthesis of monoisopinocampheylborane can be achieved via a number of routes. One of the most straightforward routes involves the displacement of an α-pinene moiety from diisopinocampheylborane by TMED or triethylenediamine [4,5]. The free borane is liberated from the TMED



complex via the addition of boron trifluoride etherate or an equivalent of $BH_3 \cdot THF$.

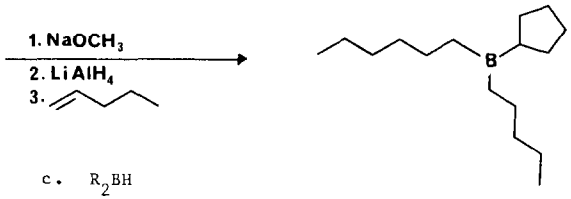
Thexylborane can also be utilized to prepare monoisopinocampheylborane via formation of the thexylisopinocampheylborane followed by elimination of the thexene by triethylamine [4]





The patent literature contains a report of a new chiral monoalkylborane prepared from myrtanyldithiane [6]. The reagent will hydroborate alkenes and reduce ketones asymmetrically.

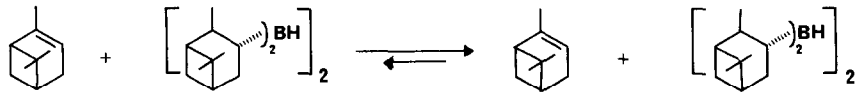
Brown reports that alkyldibromoboranes may be utilized as "masked" monoalkylboranes because of the ready replacement of the bromines [7]. Mixed trialkylboranes are prepared by the controlled hydridation of alkyldibromoboranes in the presence of an alkene; the resultant dialkylbromoborane can be used to hydroborate another alkene via the in-situ generation of a dialkylborane.



c. R_2BH

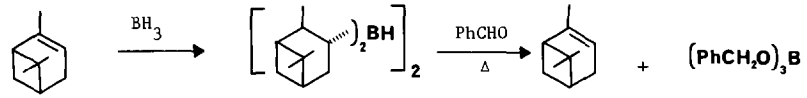
Dialkylboranes continue to play an important role in borane chemistry. They are utilized to increase the efficiency, regioselectivity,

and stereoselectivity of hydroboration and reduction reactions. Brown, Desai and Jadhav reported a significant improvement in the synthesis of diisopinocampheylborane [8]. They found that they could prepare the reagent with an enantiomeric purity of 99.1% from α-pinene of 92% enantiomeric purity! They achieved this seemingly impossible task by simply equilibrating the solid sym-tetraisopinocampheyldiborane with a 15% excess of α-pinene and permitting the apparently less soluble, enantiomerically purer enantiomer to accumulate.



92% ee 92% ee <92% ee 99% ee

Brown and his coworkers used the more enantiomerically pure material to carry out asymmetric hydroborations with essentially quantitative asymmetric induction. Interestingly, they also utilized the process to upgrade the optical purity of commercial α-pinene [9]. The elimination of α-pinene via the reduction of aldehydes has also



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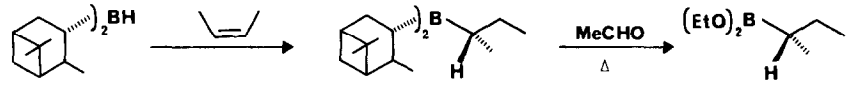
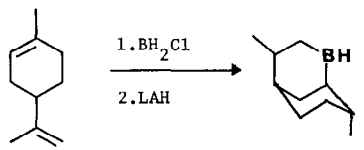
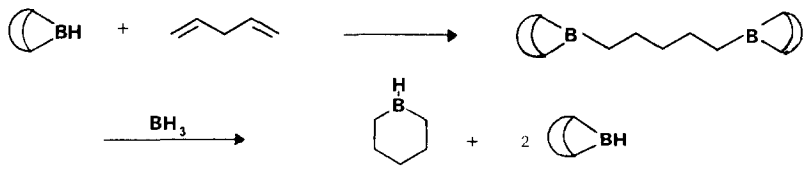
been utilized to prepare optically active boronic esters by Brown and his coworkers [10].



Jadhav and Kulkarni reported that limonylborane can be readily prepared and is an effective hydroborating agent [11].

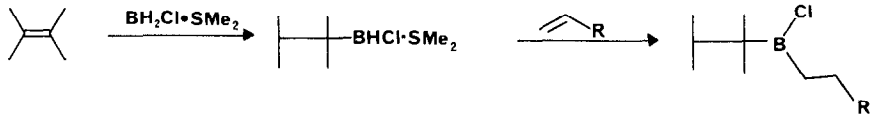


Brown and Pai have reported a greatly improved synthesis of borinane [12]. The process involves hydroborating 1,4-pentadiene with 9-borabicyclo[3.3.1]nonane (which achieves the desired regiochemistry) and then treating the dihydroborated pentane with BH_3•THF to generate borinane and 9-BBN.

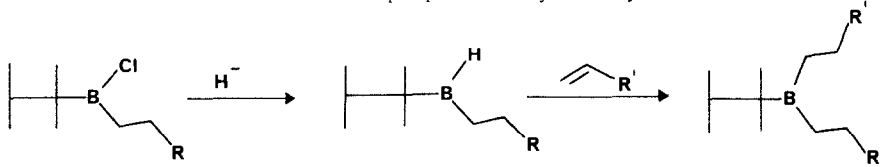


Brown and his coworkers have reviewed the use of dialkylboranes for the hydroboration of alkynes [13]. They have also reviewed the use of alkylhaloboranes and haloboranes in organic synthesis [14].

Brown and Sikorski carried out a thorough investigation of the preparation, reactions, and stability of thexylchloroborane [15]. They found that the dimethyl sulfide complex is readily prepared and stable over extended periods of time [16]. The reagent hydroborates alkenes



with very high regioselectivity and the resulting thexylalkylchloroborane can be reduced and used to prepare thexyldialkylboranes.



Koester, Idelmann, and Dahlhoff are continuing their pioneering studies of organoborane monosaccharides [17].

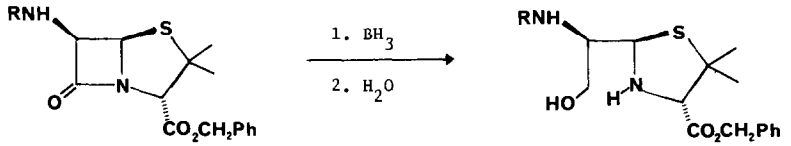
2. Reducing Agents

a. BH_3

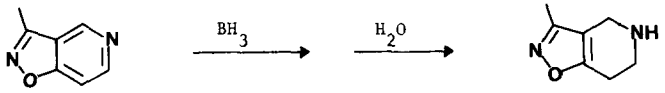
Borane complexes have proven to be efficient reducing agents. Brown, Yong, and Narasimhan have developed a simple procedure for enhancing the rate of reduction of representative functional groups by BH_3•SMe_2 [18]. They report that distilling off the dimethyl sulfide (by heating the THF solutions to reflux) greatly increases the rate of reduction. They successfully reduced carboxylic esters, amides, and nitriles while leaving nitro, chloro, and methoxy groups untouched.

Jung and Cho report that BH_3•THF readily reduces the sodium salts of a variety of carboxylic acids [19]. The BH_3•SMe_2 complex also reacts but at a much slower rate.

Sammes and Smith report that β-lactams are reduced by BH_3•THF to yield the 1,3-aminoalcohol derivatives rather than the expected azetidine [20].



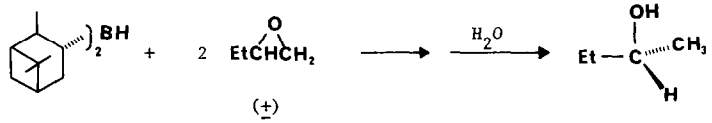
Adembri, Camparini, Ponticelli, and Tedeschi report that BH_3•THF reduces isoxazolopyridine to the tetrahydroisoxazolopyridine rather than attacking the isoxazole ring [21].



Camacho, Uribe, and Contreras report the synthesis of diphenylamineborane complex [22]. The reagent reduces aldehydes and ketones at 0°C and will hydroborate alkenes.

b. R_2BH

Yoon and Soon report that diisopinocampheylborane can be used to selectively reduce one of the 2 enantiomers of 1,2-butylene oxide in the presence of lithium chloride [23]. If the reaction is run using a twofold excess of the racemic butylene oxide, the recovered starting material is enriched in the S-isomer.



(-)-Ipc_2BH

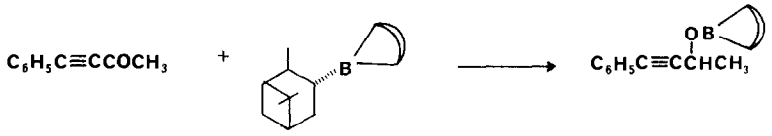
R-2-butanol
(22% ee)

Kim, Kim, and Jin utilized chiral limonylborane to reduce methyl ketones to optically active alcohols [24]. The alcohols were obtained in 2.8-8.6% enantiomeric excess.

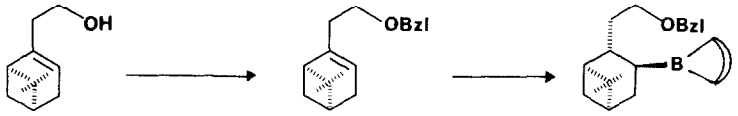
c. R_3B

Midland has investigated the kinetics of the reduction of benzaldehyde with B-octyl-9-BBN [25]. He finds second order rate constants for the reaction of B-octyl-9-BBN with a series of para-substituted benzaldehydes. The rate constants correlate with σ^+ (σ +1.03). The relative rates are consistent with a hydride addition to the carbonyl carbon in the rate determining step. Activation parameters were obtained for the reaction and the major barrier to the reaction is entropy. The large negative entropies of activation (-43 to -49) indicate a highly ordered transition state.

Brown and Pai improved the procedure for asymmetrically reducing prochiral ketones with B-pinanyl-9BBN by carrying out the reactions in the absence of solvent [26].

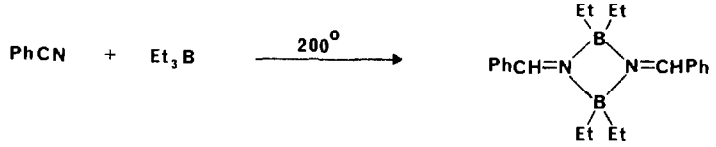


Midland and Kazubski report that the 9-BBN adduct of nopol is an excellent and inexpensive substitute for the β-pinanylborane prepared from (-)-α-pinene [27]. The reduction of prochiral acetylenic ketones



yield the S-propargyl alcohols in high enantiomeric excess (86-96%).

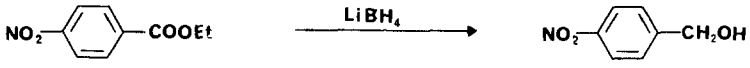
Mikhailova, Tikhomirov, and Matveeva report that triethylborane will reduce nitriles at elevated temperatures with the evolution of ethylene [28].



d. $R_4B^-M^+$

The borohydrides continue to be popular reducing agents and it would be impossible to tabulate each instance when they were used. There have been some useful advances which are noteworthy.

Brown, Narasimhan, and Choi carried out a comparative study of the relative reactivities of the lithium, sodium, and calcium borohydrides toward carboxylic esters [29]. In ether solvents, the reactivity follows the trend $LiBH_4 > Ca(BH_4)_2 > NaBH_4$ but in alcohol solvents the trend is $Ca(BH_4)_2 > LiBH_4 > NaBH_4$. A number of ester derivatives, including compounds containing nitro, cyano, halo, and alkoxy groups were reduced by their procedure. It should be noted, however, that unsaturated esters undergo simultaneous hydroboration.

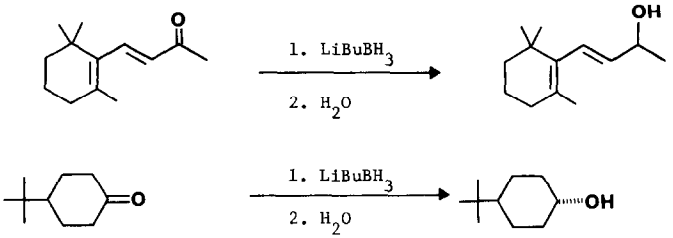


Brown and Narasimhan also report that the reduction of esters is catalyzed by the presence of 10 mole-percent of lithium

triethylborohydride [30]. They note that B-methoxy 9-BBN and trimethylborate also catalyze the $LiBH_4$ reductions.

The reducing properties of tetraalkylammonium borohydrides were reviewed by Guida and Raber [31]. Bram, D'Incan, and Loupy report that tetrabutylammonium borohydride (as well as the lithium and sodium borohydrides) can be adsorbed on alumina, silica, or clays. The solid materials are very effective for the reduction of α,β-unsaturated ketones. The reactions appear to proceed under milder conditions and with high regeospecificity [32].

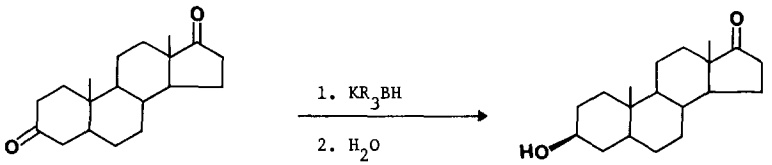
Kin, Moon, and Ahn report that lithium n-butylborohydride is readily prepared via the reaction of n-butyl lithium with borane-dimethylsulfide [33]. They report that it selectively reduces the carbonyl group of most conjugated enones. The reagent is more regioselective and stereoselective than simple borohydrides.



Yoon and Cho synthesized and studied the formation and properties of acyloxyborohydrides [34]. They find that the addition of a Lewis acid to an acyloxyborohydride leads to the formation of the corresponding alcohol.

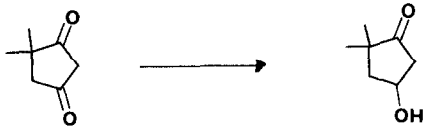
$$RCO_2H + BH_3 \longrightarrow RCO_2BH_3 \xrightarrow[2.\ H_2O]{1.\ BF_3} RCH_2OH$$

Gordon and Orr demonstrated that potassium tri-sec-butylborohydride selectively reduces steroid ketones [35]. As an example 5-β-androstane-3,17-dione is reduced exclusively to the corresponding 3-β-hydroxy-5-β-androstan-17-one. None of the 3-α-hydroxy isomer is formed and the 20-keto group is untouched. Similar reactions occur for the pregnanedione series.

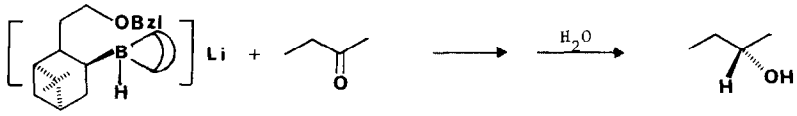


Krishnamurthy and Vreeland found that the lithium trialkylborohydrides reduce cyclic anhydrides to the corresponding lactones [36].

With unsymmetrical anhydrides, the less hindered carbonyl group is reduced.



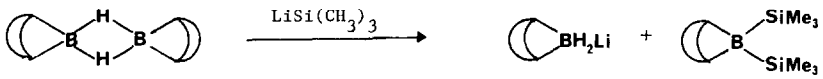
Midland and Kazubski prepared a new chiral trialkylborohydride from the nopol-9-BBN reagent (NB-Enantride) by treating it with t-butyllithium [37]. The reagent efficiently reduces straight chain aliphatic ketones.



Coates, Hedge, and Pearce synthesized lithium triethyltritide by reacting lithium tritide with triethylborane [38]. They used the reagent to introduce tritium into organic compounds via the reduction of functional groups.

Yameda, Takeda, and Iwakuma prepared chiral triacyloxyborohydrides and utilized them to asymmetrically reduce imines [39].

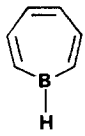
Biffer and Noeth prepared 9-borobicyclo[3.3.1]none hydride along with the disilylated 9-BBN derivative when they attempted to prepare B-trimethylsilyl-9BBN [40].



3. Mechanism and Theory

Bentley calculated molecular geometries of organoborates and their isomerization energies using STO-3G (ab initio), MINDO/3 and MINDO (semiempirical). The calculations model carbonylation, alkynylborate, and cyanoborate reactions in which 1,2-alkyl shifts occur from boron to carbon. For carbonylation, the calculated energies are consistent with a reversible reaction between borane and carbon monoxide, followed by a rate limiting 1,2 shift. Subsequent rearrangements, followed by dimerization and trimerization, are predicted to be highly exothermic [41].

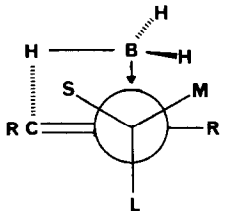
Schulman and his coworkers used STO-3G and 4-31G basis sets to study the structure of borepin [42]. They concluded that borepin has a planar structure and is a weakly conjugated system.



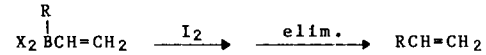
Kosmus and Kolcher carried out ab initio calculations on vinyldifluoroborane [43]. They conclude that a π-contribution of 5.5 kcal/mole is due to the carbon carbon double bond and not the lone pairs of the fluorines. The force field calculations support the ab initio results.

Bews and Glidewell have used MNDO and UHF wavefunctions to calculate the molecular structures and energies for the molecular cation and all fragments of Me_3B obtained via mass spectrometry [44].

Paddon-Row, Nelson, and Houk have calculated the transition structure for the addition of borane to an alkene using ab initio calculations with a split-valence 3-21G basis set and gradient techniques [45]. In the model for the borane addition, the largest allylic substituent takes the sterically least hindered position in each case.



Slayden has continued to investigate the relative migratory aptitudes of alkyl groups in organoborane rearrangements. In this investigation, the iodine-induced rearrangement of bromomagnesium ethenylborates was examined [46]. The overall migratory aptitude is

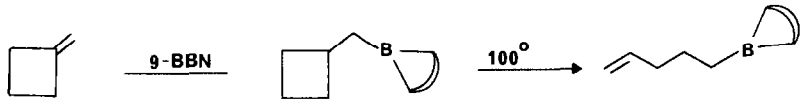


cyclohexyl > s-butyl > i-butyl > n-butyl, bicyclooctyl > thexyl. The data is consistent with a process in which the slow-step involves the formation of a cyclic iodonium ion from which a fast anti alkyl group migration occurs. Thus the migratory aptitude may depend on the relative conformational stabilities of the intermediate.

Brown and Racherla investigated the thermal isomerization of 3-hexyldicycloalkylboranes and found that the rate of isomerization of the larger boranes is much faster than that observed for the smaller boranes [47]. As an example 3-hexyldicyclooctylborane isomerizes 100 times faster than 3-hexyldicyclopentylborane. Racherla and Pai found that a similar situation applied to a series of cyclic borane derivatives [48].

Midland, and his coworkers find that B-3-pinanyl-9BBN undergoes a very facile olefin-alkyl group exchange. The half-life is less than 10 hours as compared to a half-life of four days for the corresponding B-3-methyl-2-butyl-9-BBN derivative. The facility of this reaction has important consequences for asymmetric reductions using B-isopino-campheyl-9BBN (Alpine-borane) [49].

Hill, Nylen, and Fellinger report that cyclobutylmethylboranes undergo a facile ring cleavage rearrangement at 100°C [50]. The



rearrangement can be inhibited via the formation of pyridine complexes.

Singaram and Pai investigated the complexation of boranes by tetramethylenediamine and triethylenediamine [51]. Ikhlov and coworkers investigated complexes of organoboranes with a series of pyrazole derivatives [52].

The kinetics of hydroboration reactions were studied in detail this year. Nelson and Brown measured the rates of hydroboration of a number of haloalkenes [53]. The kinetics parallel those observed for the parent alkenes in that the faster reacting haloalkenes show kinetics which are first order in $(9\text{-BBN})_2$ while the slower reacting ones display kinetics which are three halves order: first order in haloalkene and one-half order in $(9\text{-BBN})_2$. Their studies also revealed the effect of the halogen substituents on the rate of hydroboration: an allylic chlorine reduces the rate of hydroboration by a factor of 25 (bromine by ~20, iodine by ~14).

Wang and Brown measured the kinetics of the hydroboration of alkenes with $(9\text{-BBN})_2$ in noncomplexing solvents as well as in a variety of complexing solvents [54]. Their results lead to the postulation that the complexing agent is not directly involved in the actual hydroboration step but provides an alternative low energy pathway to monomeric boranes. [In essence a high activation energy step is replaced with two parallel lower activation energy steps.]

$$(9\text{-BBN})_2 + 2\text{THF} \rightleftharpoons 2\ 9\text{-BBN}\cdot\text{THF}$$

$$9\text{-BBN}\cdot\text{THF} \rightleftharpoons 9\text{-BBN} + \text{THF}$$

$$9\text{-BBN} + \text{alkene} \rightleftharpoons \text{B-alkyl-9-BBN}$$

instead of

$$(9\text{-BBN})_2 \rightleftharpoons 2\ (9\text{-BBN})$$

$$9\text{-BBN} + \text{alkene} \rightleftharpoons \text{B-alkyl-9BBN}$$

Wang, Scouten, and Brown measured the kinetics of the hydroboration

of alkynes with 9-borobicyclo[3.3.1]nonane [55]. For more reactive alkynes, the reactions exhibit first-order kinetics while the less reactive alkynes exhibit three-halves order kinetics. Thus the alkyne hydroborations exhibit kinetics similar to those observed for alkenes; apparently the reaction proceeds via the same mechanism for alkenes and alkynes. The experimental results are in very good agreement with the calculated values obtained by the Runge-Kutta method.

Nelson, Blue, and Brown also measured the kinetics of the hydroborations of several 1-halo-1-alkynes with 9-BBN [56]. The kinetics complement those observed for the unsubstituted alkynes although some of the 1-halo-1-alkynes display kinetics intermediate between the expected first order and three-halves order.

Sikorsky and Brown measured the relative reactivities of various alkenes toward thexylchloroborane-methyl sulfide. The results were compared to data obtained from hydroborations with 9-BBN, disiamylborane, and dibromoborane. Thexylchloroborane exhibits far higher reactivity towards cis alkenes relative to trans alkenes than any hydroborating reagent examined to date, giving cis/trans reactivity ratios of the order of 100/1 [57].

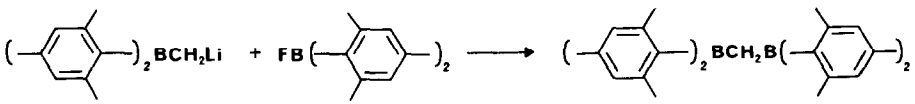
Alyosov, Kuznetsov, Maslennikov, and Aleksandrov measured the rate constants and activation energies for the reactions of organoboranes with hydroperoxides [58]. The rate determining step involves the decomposition of the borane-hydroperoxide complex.

A few NMR investigations of the bonding patterns in a variety of organoboranes were reported. Wrackmeyer and Koester measured the ^{17}O-chemical shifts in a series of 33 cyclic boron-oxygen compounds [59]. Their data indicate that the magnetic screening of oxygen depends on the extent of the boron-oxygen pi-bonding.

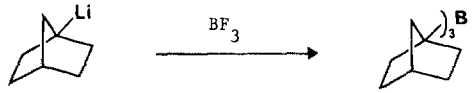
Contreras and Wrackmayer investigated the exchange reactions between trialkylboranes and BH_3 in THF and dimethylsulfide using boron-11 NMR [60]. Cragg and Miller reported the proton and carbon-13 NMR spectra of a series of alkoxyaminophenylboranes which they prepared [61]. Boulton and Prado used NMR to calculate energy barriers for the racemization of tetrahedral boron chelates [62].

4. Synthesis of Organoboranes

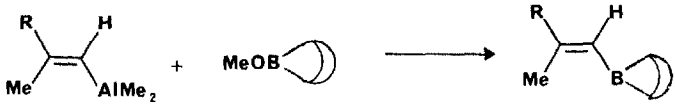
The hydroboration reaction is, of course, not the only method suitable for the preparation of organoboranes. A number of investigators have examined alternative routes to a variety of organoboranes. Garad and Wilson prepared bis(dimesitylboryl)methane via a lithiation reaction [63].



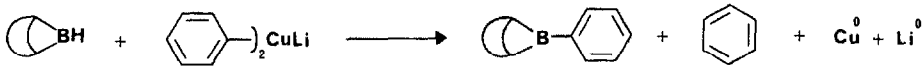
Dimitrov and Zschunke prepared tri-1-norbornyl- and tri-7-norbornylborane via the reaction of the corresponding lithium reagents with $BF_3 \cdot Et_2O$ [64].



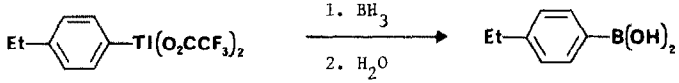
Negishi and Boardman report that alkenylboranes are readily synthesized via reaction of alkenylaluminum derivatives with B-methoxydialkylboranes [65]. The reaction permits the syntheses of β,β-dialkylsubstituted alkenylboranes.



Whiteley developed a synthesis of a series of B-alkyl-9-BBN reagents utilizing the reaction of lithium (or magnesium) dialkylcuprates with 9-BBN [66].



Pickles and coworkers report that arylthallium trifluoroacetates react with BH_3•THF to yield arylboronic acids after hydrolysis in good yields [67].



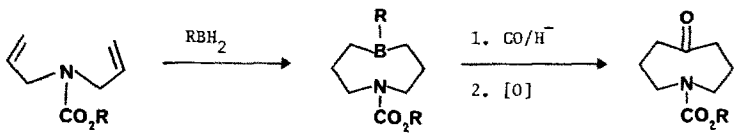
Wrackmeyer reviewed the formation of organoboranes via alkynyltin reagents [68]. Although it couldn't be considered a synthetic procedure, it is interesting to note that Marsella and Caulton detected methylborohydride and dimethylborohydride in reactions of BH_3•THF with dimethylzirconium derivatives [69].

C. CARBON-CARBON BOND FORMATION

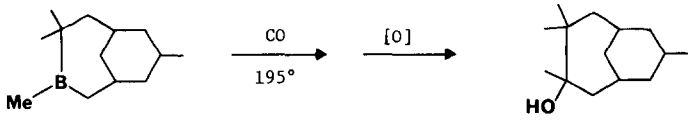
1. Homologation

The synthesis of carbon-carbon bonds is fundamental to organic synthesis. A number of reactions have been developed over the years which involve the transfer of alkyl groups from boron to carbon to create carbon-carbon bonds. Pelter has reviewed the use of organoboranes in carbon-carbon bond synthesis [70].

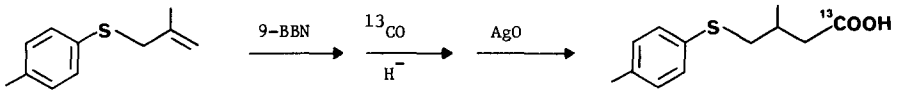
One of the oldest homologation reaction is the carbonylation reaction. Garst, Bonfiglio, and Marks report that a number of bis-olefinic amines can be converted to the corresponding azacycloalkanones via the carbonylation and cyanidation reactions [71].



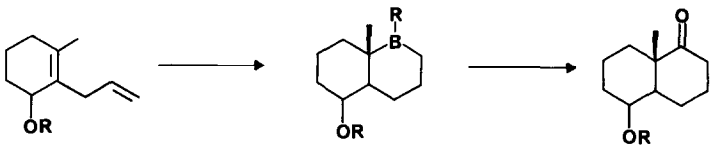
Mikhailov utilized the carbonylation reaction to elucidate the structure of an organoborane rearrangement product [72].



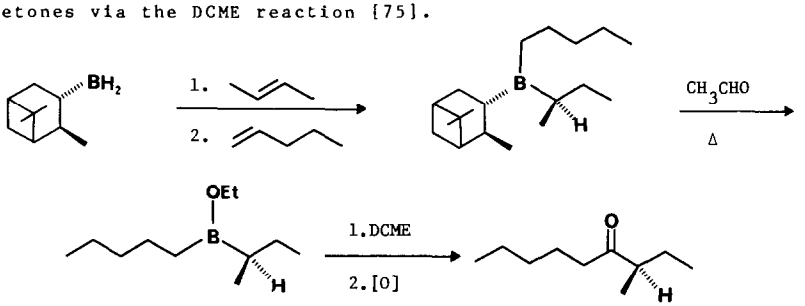
Kabalka utilized the carbonylation reaction to synthesize a series of carbon-13 labeled carboxylic acids [73].



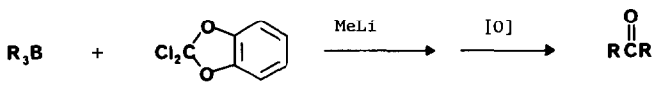
Bryson utilized the annulation reaction to prepare decalin synthons from dienes [74].



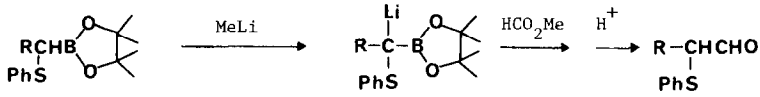
Brown, Jadhav, and Desai prepared optically active borinic acid ester and then converted them to the corresponding optically active ketones via the DCME reaction [75].



Suzuki developed a new symmetrical ketone synthesis utilizing dichlorobenzodioxole [76].



Ray and Matteson have continued to develop the chemistry of substituted alkaneboronic esters. They find that α-lithio-α-(phenylthio)alkaneboronic esters react with methyl formate to yield α-phenylthioaldehydes [77].



Matteson and Moody have reported that 1,1-diboronic esters are efficiently deprotonated with 2,2,6,6-tetramethylpiperide in the presence of tetramethylethylenediamine. The resultant diborylmethide salt was then alkylated with alkyl halides to form 1,1-bis-(1,3,2-dioxaborin-2-yl)alkanes which in turn were alkylated with a second alkyl halide [78]. In addition, they have found that the

$$LiCH(BO_2C_3H_6)_2 \xrightarrow{RBr} RCH(BO_2C_3H_6)_2$$

$$RCH(BO_2C_3H_6)_2 \longrightarrow LiCR(BO_2C_3H_6)_2$$

$$LiCR(BO_2C_3H_6)_2 \xrightarrow{R'Br} RR'C(BO_2C_3H_6)_2$$

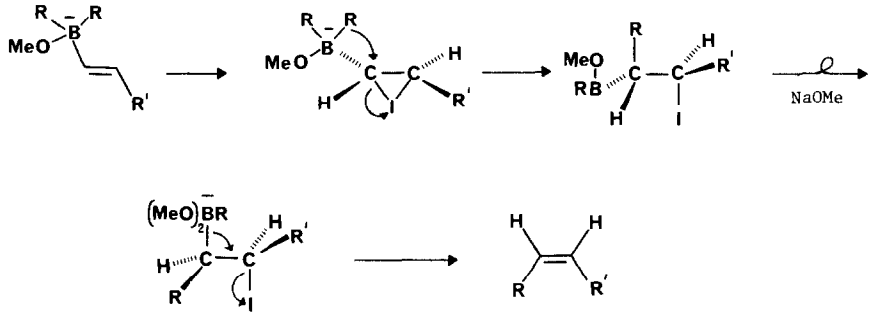
carbanionic intermediates will react with carbonyl compounds to form alkeneboronic esters and with carboxylic esters to form ketones with elimination of boron.

$$LiCR(BO_2C_3H_6)_2 + R'COR'' \longrightarrow R'R''C{=}CR(BO_2C_3H_6)$$

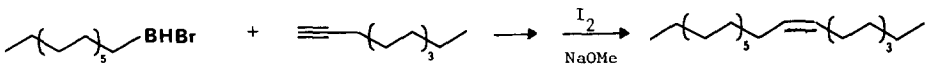
$$R'CO_2CH_3 + LiCR(BO_2C_3H_6)_2 \longrightarrow \longrightarrow RCH_2COR'$$

2. Alkenylborate Rearrangements

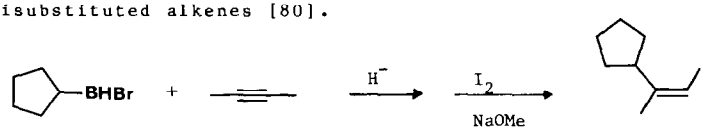
Alkenylborates react with electrophiles to generate a wide variety of rearranged alkenes and alkylborates. One of the more useful reactions involves the iodine induced migration of an alkyl or alkenyl group from boron to carbon to generate a cis-alkene after boron and iodine are eliminated.



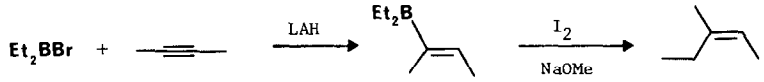
Brown and Basavaiah utilized the reaction to synthesize muscalure (the sex pheromone of the housefly) from an alkylbromoborane [79].



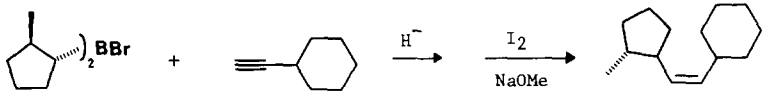
They also applied the reaction to the synthesis of a wide variety of trisubstituted alkenes [80].



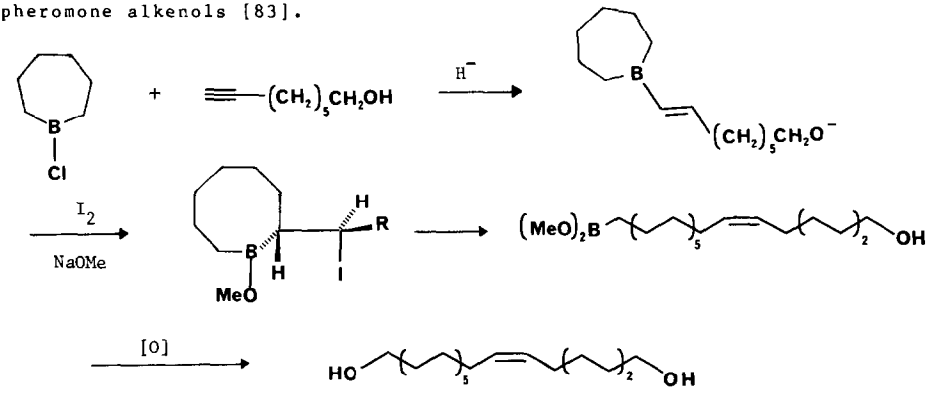
Brown, Basavaiah, and Kulkarni also carried out a related study involving the syntheses of trisubstituted alkenes utilizing the in-situ formation of dialkylboranes from dialkylbromoborane [81].



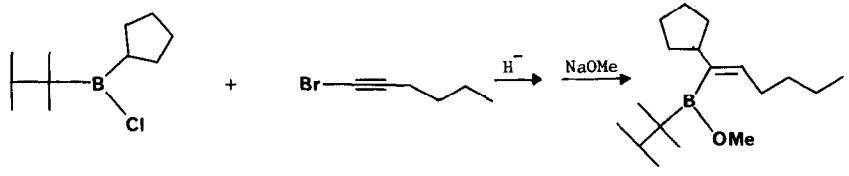
A parallel study centered on the synthesis of cis alkenes via the in-situ hydroboration of 1-alkynes with dialkylbromoboranes was reported by Kulkarni, Basavaiah, and Brown [82].

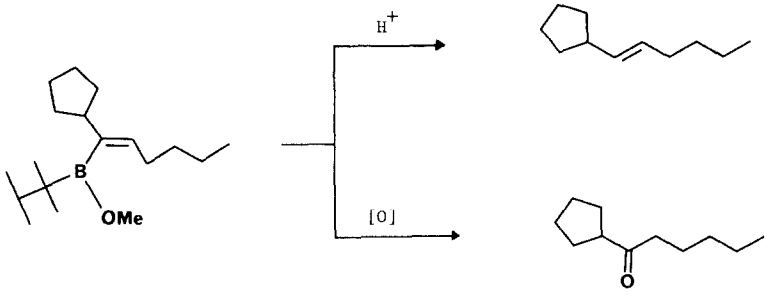


Basavaiah and Brown utilized the procedure to synthesize a series of pheromone alkenols [83].



Brown and Basavaiah also applied the in-situ generation of dialkylboranes to the hydroboration of 1-haloalkynes [84]. The resultant products are known to rearrange to vinylborane which are useful synthetic intermediates [85,86].



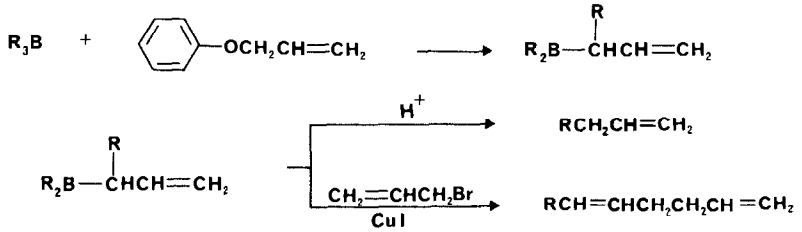


Brown, Basavaiah, and Kulkarni also utilized alkylbromoboranes to hydroborate 1-haloalkynes [87]. The reactions are completely analogous but have the advantage that one alkyl group is not wasted (thexyl normally)

$$RBHBr + BrC{\equiv}CR' \xrightarrow[H_2O_2]{NaOH} R\text{-}\overset{O}{\overset{\|}{C}}CH_2R'$$

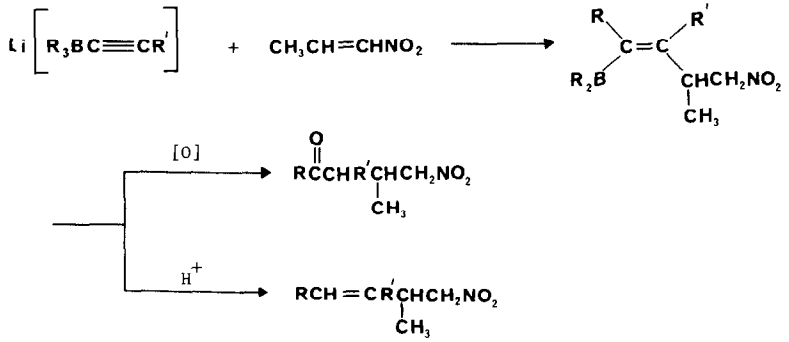
Torregrosa and Baboulene utilized an analogous reaction to synthesize aminodienes from an amino substituted 1-bromoalkyne [88].

Hara, Imai, Hara and Suzuki reported that trialkylboranes react with phenyl allyl ether to yield an intermediate borane which can be readily converted to 1-alkenes or 1,5-alkydienes [89]

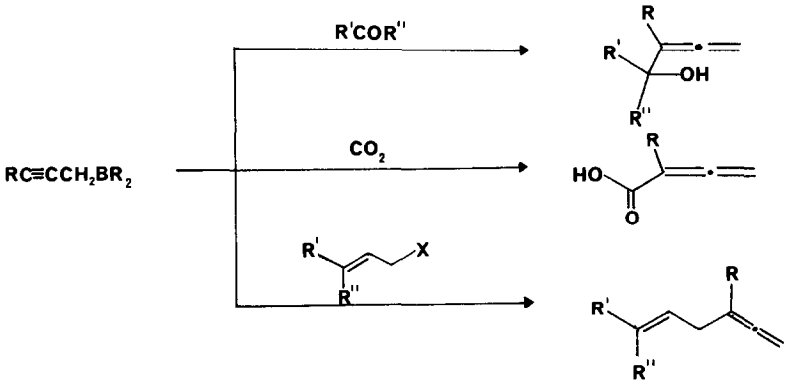


3. Alkynylborate Rearrangements

Alkynylborate complexes undergo rearrangements analogous to the alkenylborate complexes. Pelter, Hughes, and Rao found that lithium trialkylalkynylborates undergo a Michael reaction. The resulting vinylboranes are readily oxided to ketones or hydrolyzed to alkenes [90].

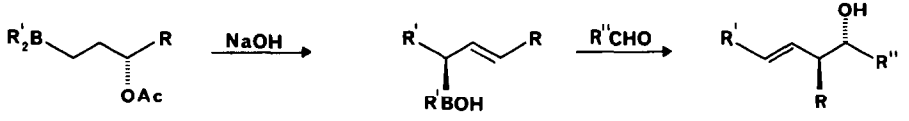


Pearson, Hahn, and Zweifel found that propargylic lithium borates react with a variety of electrophiles to furnish allenic products [91]

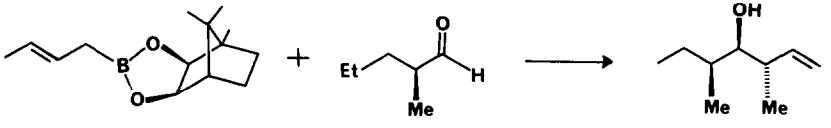


4. Allylboranes

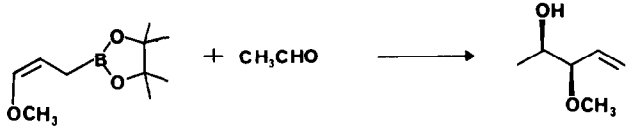
Allylboranes are among the most reactive organoborane intermediates in organic synthesis. Midland and Preston report that condensations of aldehydes with enantiomerically enriched allylboranes provide homoallylic alcohols with a high degree of enantioselectivity and diastereoselectivity (55-85% ee) [92].



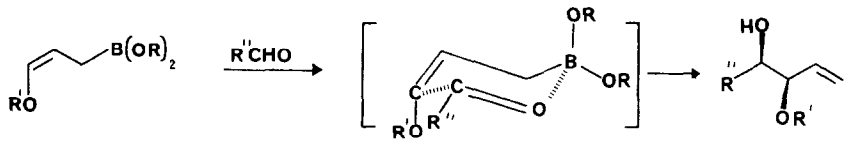
Hoffman, Zeiss, Ladner, and Tabche synthesized alkenols containing multiple asymmetric centers by utilizing chiral crotylboronates and chiral alcohols [93]



Hoffman and Kemper also examined the addition of γ-alkoxy-2-allylboronates to aldehydes [94].

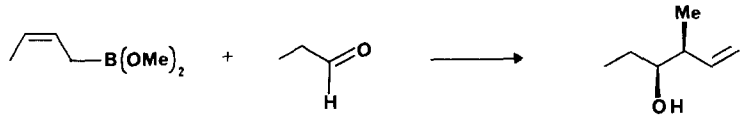


Wuts and Bigelow independently reported the stereoselective formations of monoprotected, threo 1,2-diol derivatives via the reaction of γ-alkoxyallylboronates [95]. They utilized the method to

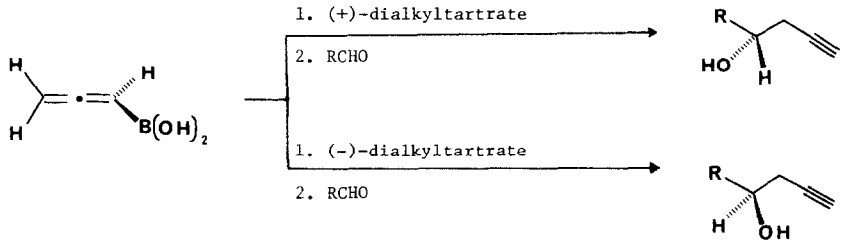


synthesize (+)-exobrevicomin [96].

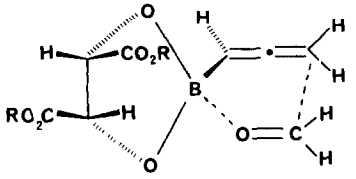
Schlasser and Fujita synthesized an aggregation pheromone via the reaction of a (Z)-2-butenylboronate ester with propanal [97].



Yamamoto and his coworkers prepared chiral allenylboronic esters which react with aldehydes to generate β-acetylenic alcohols with a high degree of enantioselectivity [98]. [The chiral allenylboronic esters are prepared by reaction of the boronic acids with chiral dialkyl tartrates.]

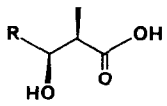


The reaction presumably occurs through a transition state of the following type:

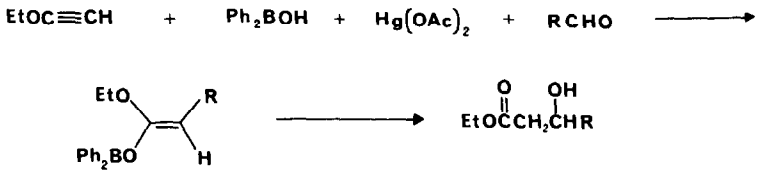


5. Enol Borinates

The condensation of boron enolates with a variety of carbonyl compounds continues to play an important role in the stereoselective syntheses of chiral molecules. Masamune, Kaiho, and Garvey have developed an elegant syntheses of a syn-3-hydroxy-2-methylcarboxylic acid, a fundamental structural unit embedded in numerous natural products of propionate origin, utilizing a dicyclopentylboron enolate [99].

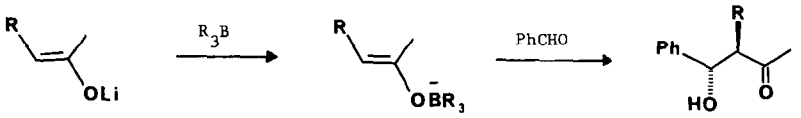


Murakami and Mukaiyama report that boron enolates can be generated in situ by treatment of alkoxy alkynes with $Hg(OAc)_2$ and diphenylboronic acid [100].



Hooz and Oudenes developed a unique 1,3-diketone synthesis via the reaction of enolborinates with nitriles. The reaction proceeds via a boroxazine intermediate [101]

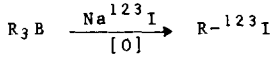
Yamamoto, Yatagai and Maruyama found that adding trialkylboranes to lithium enolates before condensing them with aldehydes increases the percentage of the threo product [102].



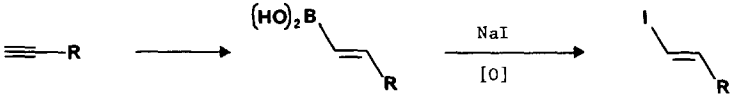
D. CARBON–HETEROATOM BOND FORMATION

1. Group VII

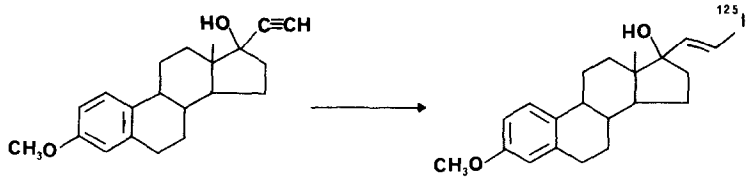
Kabalka, Gooch, Smith, and Sells developed a new radioiodination technique in which sodium [^{123}I]-iodide is oxidized to iodine monochloride in the presence of organoboranes. The synthesis provides a rapid route to radioiodinated materials of very high specific activity [103]



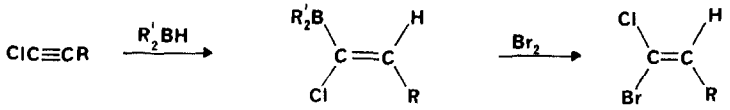
Kabalka, Sastry, and Somayaji utilized the in-situ iodination method to synthesize a variety of (E)-I-iodoalkenes [104].



Kabalka and his coworkers then applied the new reaction to the synthesis of a new series of radioiodinated estrogens which are being developed for differentiation of breast tumors [105].



Zweifel, On, and Snow have extended the reaction of vinylborane derivatives to the syntheses of 1-chloro-1-bromoalkenes via the hydroboration of 1-chloroalkynes [106].



Kabalka, Sastry, and Pagni developed an in-situ bromination reaction analogous to the previously discussed iodination reaction and utilized it to synthesize a variety of bromine-82 labeled materials of high specific activity [107]

$$R_3B \xrightarrow[[O]]{Na^{82}Br} R\text{-}^{82}Br$$

2. Group VI

The oxidation of organoboranes is one of the key transformations in syntheses involving organoboranes. Kulkarni, Rao, and Patil investigated the oxidation of 9-borabicyclo[3.3.1]nonane with pyridinium chlorochromate [108]. They find that a mixture of products is obtained with cyclooctanone being the major constituent.

Alyasov, Maslennikov, Aleksandrov, and Kuznetsov investigated the reaction of organoboranes with alkyl hydroperoxides [109].

Ortiz and Larson reported an interesting and potentially useful synthesis of aryl alkyl sulfides via the reaction of aromatic sulfonyl azides [110].

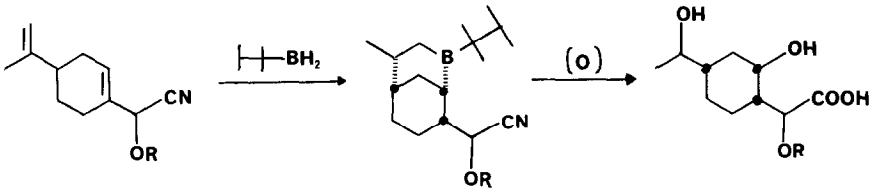
$$Ar\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}N_3 + R_3B \longrightarrow \longrightarrow ArSR$$

The mechanism of the reaction is unknown but a wide variety of sulfides were prepared.

E. HYDROBORATION OXIDATION/PROTONOLYSIS

1. Natural Products

Hydroborations have become routine in organic synthesis. McGuirk and Collum utilized the thexylborane hydroboration of a cyanohydrin derivative of perilla aldehyde to obtain the desired chirality in a diol precursor of a sesquiterpene glucoside [111]



Sonnet utilized a hydroboration with disiamylborane followed by oxidation to prepare 10-methyl-1-dodecanol from the precursor alkene [112].

$$CH_3CH_2CHCH_3(CH_2)_7CH{=}CH_2 \xrightarrow{R_2BH} \xrightarrow{oxid} CH_3CH_2CHCH_3(CH_2)_9OH$$

The material is a precursor of the sex pheromone of the southern corn rootworm.

2. General Synthetic Applications

Zaidlewicz and Sarnowski synthesized tetrahydrofurfuryl alcohols via hydroboration-oxidation of allylic epoxides [113].

Dahlhoff and Koester continue to explore the chemistry of the O-ethylboranedyl groups in carbohydrate chemistry. They have examined Fisher glycosidations and stereoselective glycosylations of O-ethylboranedyl protected carbohydrates [114].

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