BORON: BORANES IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1984 *

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CONTENTS

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A. INTRODUCTION

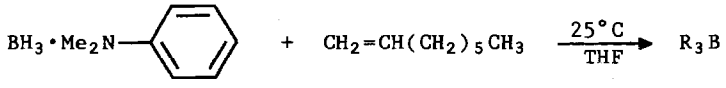
Organoboranes continue to play an expanding role in organic synthesis. The boranes are used in thousands of hydroborations and reductions each year. This review focuses on reports concerning new methodology and/or reagents and not on the routine use of boranes and borohydrides. Traditionally, Professor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

B. BORANE REAGENTS

1. Hydroborating Agents

a. BH_3

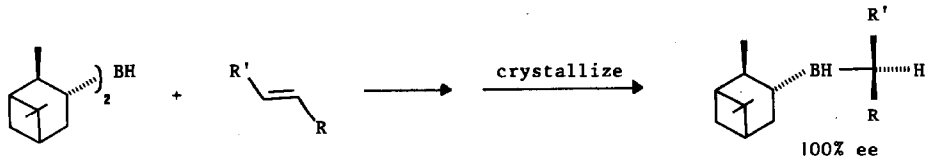
The hydroboration reaction is fundamental to organoborane chemistry and the reaction is used regularly in a number of relatively routine transformations such as the anti-Markovnikov hydration of alcohols or hydrogenation sequences. Two groups studied the use of borane-amine complexes in hydroboration sequences which may prove valuable to researchers active in the organoborane field. Brown and Murray hydroborated 1-octene with a series of borane-amine complexes with widely different structural features in the amine portion of the complex [1]. The BH_3•N-phenylamines, such as the N,N-dialkylanilines, were unique hydroborating agents. The rates of hydroboration of alkenes with the BH_3-amine complexes were inversely related to the stability of the adducts. Thus the N,N-dimethylaniline complex hydroborates 1-octene at room temperature whereas alkylamine complexes require higher temperatures.



The authors propose that the reaction proceeds via the dissociation of the borane-amine complex prior to hydroboration. This postulation is supported by the observation that excess amine suppresses the hydroboration rate. Kafka and Ferles utilized an amine-borane complex to hydroborate 1-(alkenyl)piperidines (2). They observed the formation of spiro intermediates prior to oxidation.

b. RBH_2

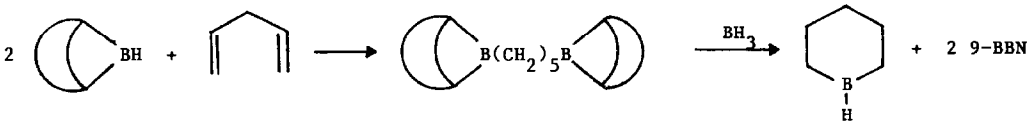
Brown and Singaram reported a simple procedure for obtaining 100% optical induction via the reaction of monoisopinocamphenylborane with prochiral olefins [3]. The optically pure isopinocamphenylboranes were



prepared by hydroborating the alkene with monoisopinocamphenylborane in the usual fashion and then simply crystallizing the product from an appropriate solvent such as ethyl ether. The α-pinene is used both for optical induction and for upgrading the enantiomeric purity of the product dialkylborane. The authors utilized the procedure to synthesize diisopinocamphenylborane of 99% enantiomeric excess [4].

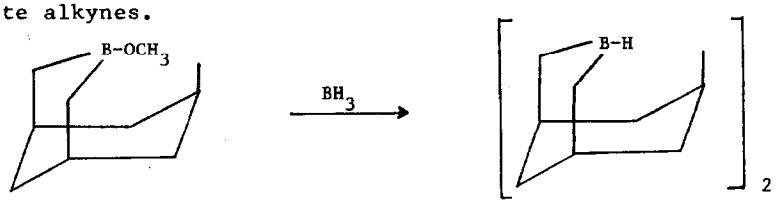
c. R_2BH

Brown, Pai, and Naik reported an improved preparation of borinane and boripane which involves an initial hydroboration of the appropriate α,γ-diene with 9-BBN [5]. The initial dumbell-shaped trialkylboranes then undergo a redistribution reaction with borane to yield the desired product.



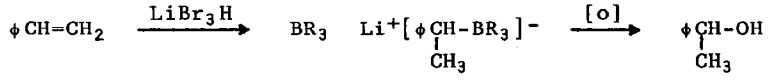
The five membered ring, borolane, undergoes a rapid ring opening under the reaction conditions utilized.

Vasilev, Smirnova, Struchkova, and Mikhailov reported the synthesis and use of 7-methyl-3-borabicyclo[3.3.1]nonane [6]. The reagent will hydroborate alkynes.

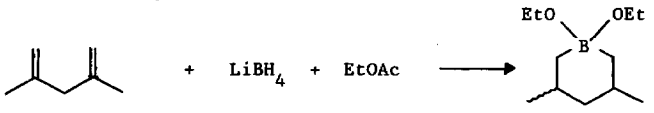


d. $R_3BH^-M^+$

Borohydride reagents are not normally utilized in hydroboration reactions. Two unusual reactions were reported by The Purdue group which may have utility in organic synthesis. Brown and Kim reported that triethylborohydride readily reacts with substituted styrenes to yield the corresponding tetraalkylborates in which the boron is attached to the benzylic carbon [7]. The reaction presumably proceeds via the



nucleophilic addition of the hydride at the styrene double bond followed by the addition of BR_3 to the resultant carbanion. The method provides for the Markovnikov hydroboration of styrenes. Brown, Somayaji, and Narasimhan report that alkenes and alkynes are readily hydroborated by lithium borohydride in the presence of carboxylate esters. The products are generally borinates [8]. The reactions presumably proceed via a



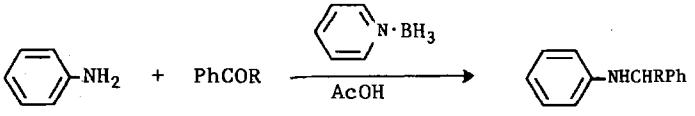
lithium diethoxyborohydride intermediate which then dissociates to $EtOBH_2$ which acts as the hydroborating agent.

2. Reducing Agents

a. BH_3

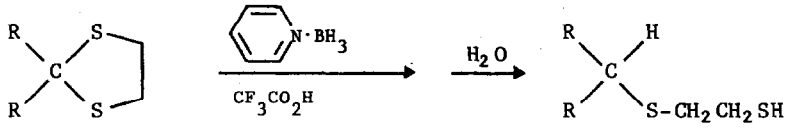
The use of BH_3 for the reduction of carbonyl groups is well documented. A number of investigators have begun to examine the utility of borane complexes for enantioselective reductions. Allwood, Shahriari-Zavareh, Stoddart, and Williams report that an enantioselective reduction of prochiral aromatic ketones can be achieved using adducts of ammonia-borane complexes with optically active tetraphenyl-18-crown-6 [9]. Enantiomeric excesses range from 20-67%. Itsuno, Ito, Hirao, and Nakahama utilized borane complexed to polystyrene-bound prolinol to produce chiral alcohols in 80% optical purity [10].

Other amine-borane complexes have also been investigated. Wong, Osuga, and Feeney reported that pyridine-borane is especially useful for the reductive methylation of amino groups in protein molecules [11]. In addition to the reductive methylation, using formaldehyde, they found that tryptophans are reduced to dihydrotryptophans. Pelter, Tosser, and Mills also reported that the pyridine borane complex produced high yields of amines products in reductive amination sequencs [12]. They

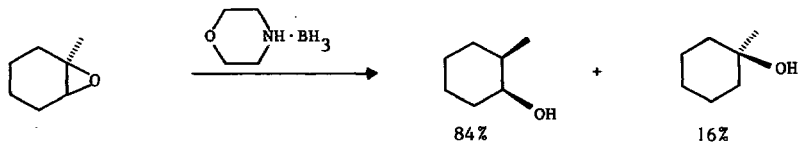


report that the pyridine reagent is less expensive and less toxic than the more traditional reagent, sodium cyanoborohydride. It should also be noted that Morales, Perez-Juarez, Ceullar, Mendoza, Fernandez, and Contreras report that borane-tetrahydrofuran solutions can also be utilized effectively for reductive amination reactions [13].

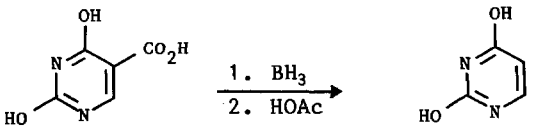
Kikugawa reports that pyridine borane can be used to produce sulfides from dithioacetals [14]. The reaction proceeds in 5 minutes in the presence of trifluoroacetic acid.



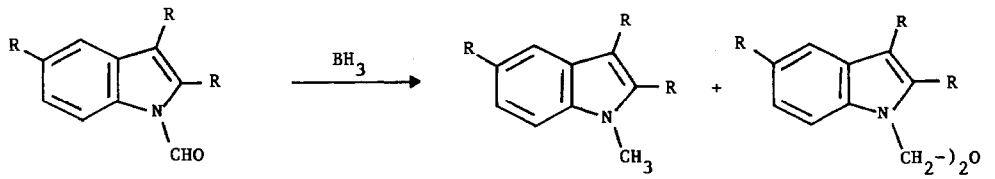
Smith has found that morpholine-borane cleave epoxides in the presence of BF_3 [15]. The BF_3 does not appear to rearrange the epoxide prior to reduction.



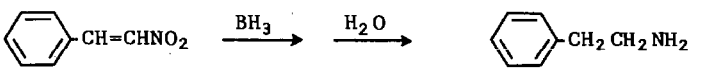
Ghosh, Schmidt, and Pal found an unusual decarboxylation reaction when they attempted to reduce certain uracil derivatives with borane [16]. The reaction appears to be occuring via the conjugate addition of hydride.



Biswas, Mallic, and Roy report that borane reduces 7-methoxy-2,3-diphenylindole-4-carboxaldehyde to the corresponding 4-methyl derivative [17]. Other byproducts were also formed but none of the expected 4-methylol was obtained. Biswas, Dhara, Roy, and Mallik also report that indole-1-carboxaldehydes are reduced to the corresponding methyl derivatives; in addition di(indolylmethyl) ethers are formed [18]. The latter are unique.



Kabalka, Mourad, and Varma report that borane can be utilized to reduce α,β-unsaturated nitroalkenes to the corresponding amines in the presence of sodium borohydride [19]. No reaction is observed in the



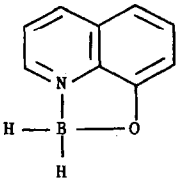
absence of the hydride catalyst. The catalytic effect of borohydride was also reported by Saito, Hasegawa, Inaba, Nishida, Fujii, Nomizu, and

Moriwake. They report that borane-dimethylsulfide reduces α-hydroxy esters in the presence of borohydride [20].

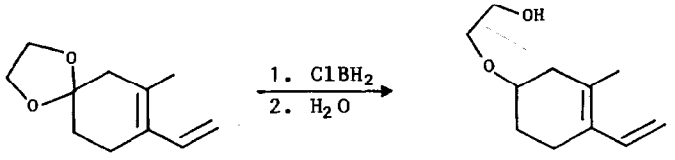
b. RBH_2

Brown and Mandal synthesized monoisopinocampheylborane of high optical purity and investigated its use in asymmetric reductions [21]. They achieved enantiomeric excesses ranging up to 46%.

Itsuno, Ito, Hirao, and Nakahama continued their investigation of (S)-(-)-2-amino-3-methyl-1,1-diphenylbutan-1-ol as an asymmetric ligand in BH_3 reductions. They report that prochiral ketones produce the chiral alcohol products in 78% enantiometic excess [22]. Kim, Kang, and Yang report that the reagent prepared by reacting 8-oxyquinoline with BH_3 effectively reduces aldehydes in the presence of ketones [23,24].



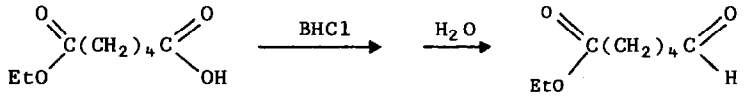
Borders and Bryson investigated the use of monochloroborane complexes in the reductive cleavage of ketals and acetals [25]. They found that chemoselectivity of the reduction can be reversed by using the dimethylsulfide complex in place of the ether complex.



c. R_2BH

Yoon, Kim, and Kim developed a new chiral reducing agent, t-butoxy-isopinocampheylborane, which produces chiral alcohols in 23% enantiomeric excess [26].

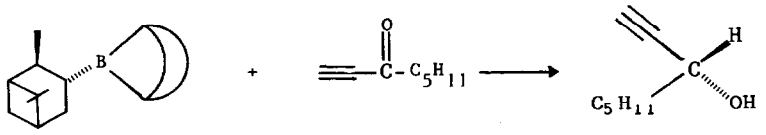
Brown, Cha, Nazer, and Yoon report that thexylchloroborane-dimethylsulfide can be used to reduce carboxylic acids to the corresponding aldehydes in 15 minutes [27]. They find that an acid group can be reduced in the presence of an ester group.



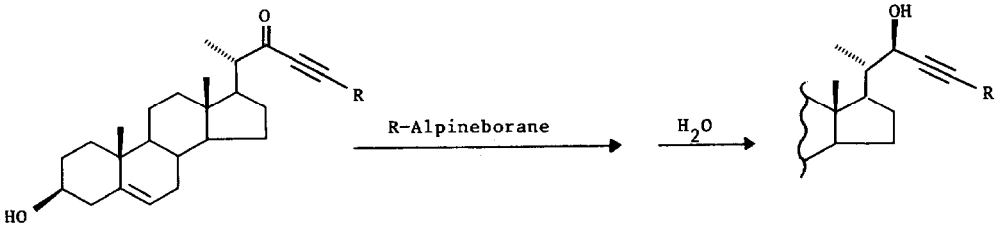
d. R_3B

Midland, Tramontano, Kazubski, Graham, Tsai, and Cardin summarized the use of Alpine-borane (B-3-pinanyl-9-borobicyclo[3.3.1]nonane) to

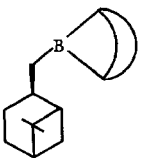
reduce propargyl ketones [28]. Propargylic alcohols are formed in essentially 100% enantiomeric excess.



Midland and Kwon also utilized Alpine-borane to stereoselectively synthesize 22-hydroxy-23-acetrylenic steroids [29].

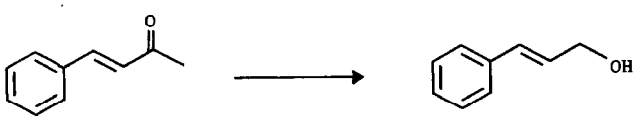


Midland and McLoughlin synthesized cis-myrtanylborane and investigated its use as an asymmetric reducing agent [30]. They found that prochiral ketones of intermediate steric bulk were reduced in moderate to good enantiomeric excess.



e. $R_3B^-M^+$

The use of borohydride reagents in organic reductions has grown at an unbelievable rate. A number of investigators have successfully modified the reactivity of the borohydride anion by complexation and replacement reactions. Sande, Jagdalde, Mane, and Slunkhe find that borohydride exchange resins can be utilized to reduce α,β-unsaturated aldehydes much faster than the corresponding unsaturated ketones [31,32].



Brown and Naarasimhan examined the reduction of a variety of functional groups by lithium borohydride in the presence of a number of Lewis acids [33]. They found that Trimethylborate and B-methoxy-9-BBN had a remarkable catalytic effect on lithium borohydride reductions. Yoon, Oh, Choi, and Lee also reported that triethylborane dramatically accelerates the reduction of epoxides with lithium borohydride [34].

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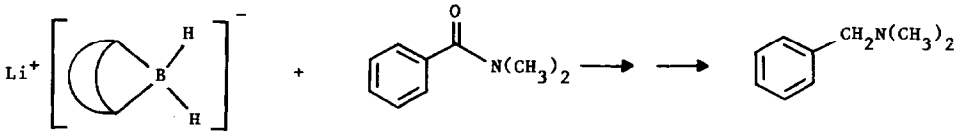
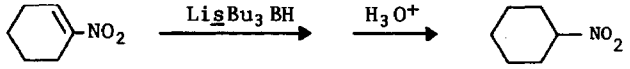
Guida, Entreken, and Guida used sodium borohydride in the presence of 1,2-ethanedithiol to reduce carboxylic acid esters [35]. Hutchins, Learn, El-Telbany, and Stercho also report that esters are readily reduced, as well as amides, by borohydrides in which one of the hydrides has been replaced by an amine functionality [36].

Brown, Cha, and Nazer developed an alkoxy-9-BBN derivative for use in stereoselective reductions. Potassium 9-(2,3-dimethyl-2-butoxy)-9-boratobicyclo[3.3.1]nonane achieves stereoselectivities which are comparable to L-Selectride [37]. Brown, Cha, Nazer, Kim, Krishnamurthy, and Brown also studied the use of potassium triisopropoxyborohydride in selective reductions [38]. The reagent can be used to reduce aldehydes, ketones, and disulfides [39] in the presence of almost all functional groups. Singaram, Cole, and Brown found that lithium monoorganylborohydrides could be synthesized by treating boronic esters with lithium aluminum hydride [40]. They then extended the reaction to the syntheses of dialkyborohydrides [41]. The alkylborohydrides were found to be stable when stored under nitrogen; the reagents can be utilized to generate alkylborane derivatives.

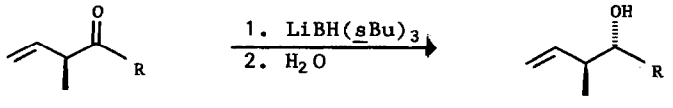
Brown, Mathew, Pyun, and Yoon prepared lithium 9-boratobicyclo-[3.3.1]nonane and examined its reactivity towards a number of functional groups [42]. The reagent is a mild reducing agent which will convert even hindered ketones to the corresponding alcohols; in addition, esters are readily reduced whereas carboxylic acids are not.



Trialkylborohydrides have continued to be valuable in organic reductions. Kabalka and Varma report that L-Selectride can be used to convert α,β-unsaturated nitroalkenes to the corresponding saturated nitro compounds [43].



Shimagaki, Maeda, Matsuzaki, Nakata, and Oishi used L-Selectride to stereoselectively reduce methylthioketones [44]. Suzuki, Katayama, and Tsuchihashi utilized the reagent to stereoselectively reduce α-methyl-β,γ-unsaturated ketones [45].



96%

Hutchins and Su used trialkyborohydrides to reduce benzhydrylimines to secondary amines [46].

3. Mechanism and Theory

a. Theory

Frenking performed ab initio calculations on boriryne [47].

He determined that, at 3-21G, boriryne is not a minimum on the potential energy hypersurface. A quadratic force field for methyldiborane was determined by Keeports and Eggers from ab initio calculations using a 4-21 basis set [48]. A preliminary matching of published IR and Raman experimental frequencies to calculated frequencies was made after the application of scale factors to the initial ab initio force constants. Additional least-squares refinement of force constants provided a fit of calculated frequencies to 35 experimental frequencies. A threefold barrier of 7.37 kJ/mol was calculated for the methyl torsion in methyldiborane.

Koga and Kobayashi applied the recently proposed method of momentum density to the problem of molecular geometry [49]. BH^{+2} and BH^{-2} were studied. Using a Hartree-Fock momentum density, the total molecular energy was partitioned into orbital components and a geometry correlation diagram was derived.

Garcia-Leigh and Murrell carried out ab-initio SCF-MO calculations on the adducts of borane and boron trifluoride. The calculations correctly predicted that BH_3 forms stronger complexes that BF_3 and that CO forms stronger complexes than N_2. These trends can be understood from the energies and wave functions of the HOMO and LUMO orbitals of the components [50].

A MO model supported by energy-optimized MNDO calculations was reported by Schoeller for the substituent effects on the rates of 1,5-sigmatropic rearrangement of a BR_2 unit over a cyclopentadiene system [51]. The degenerate rearrangement is retarded by electron-donating groups on the boron and/or electron-withdrawing substituents on the cyclopentadiene unit. In the transition-state geometry, inversion is favored over retention at the boron atom.

Kruger, Sopchick, and Kingsbury analyzed asymmetric induction in organometallic reagent additions to carbonyl group analogs [52]. Some of the additions obey the Cram rules for asymmetric induction but require that approach of the organometallic reagent occur over the large group in the ground-state conformation. They feel that this indicates that the ground-state conformation is not relevant, in agreement with the Curtin-Hammet principle. In other cases, little asymmetric induction was observed. A third type of behavior concerns opposite modes of

addition. The variability of the data was discussed in terms of the validity of rules for asymmetric induction. Secondary isotope effects were also explored in an attempt to resolve the dichotomy between additions to cyclic versus noncyclic ketones.

Houk, Rondan, Wu, Metz, and Paddon-Row performed ab initio calculations of transition states and a molecular mechanics treatment of the hydroboration of ab initio optimized alkene structures. The calculations lead to a rationalization of conformational, steric, and electronic effects on the stereochemistry and asymmetric inductions observed in these reactions [53].

b. Kinetics

Brown, Chandrasekharan, and Nelson studied the kinetics of hydroboration of representative alkenes with borinane dimer at 0° in heptane [54]. With many alkenes the reaction shows 3/2-order rate behaviour, indicating a fast dissociation of the dimer, followed by the rate-limiting step involving the monomer and the alkene. With a few alkenes, the reaction was too fast for accurate rate measurements. The rate data indicate a possible generalization of the earlier conclusion for the mechanism of hydroboration of alkenes by 9-BBN dimer. The relative rate calculated from the rate constants agree well with those determined competitively. A comparison of the reactivity of borinane toward various classes of alkenes with those of other hydroborating agents such as disiamylborane, dibromoborane, and thexylchloroborane, shows that borinane is similar to 9-BBN in its selectivity and differs markedly from that of disiamylborane, dibromoborane, and thexylchloroboranes.

Brown and Chadrasekharan also studied the hydroboration characteristics of representative borane-Lewis base complexes which indicate that the mechanism of hydroboration of such complexes involves prior dissociation. Thus, the rate of hydroboration of 1-octene with $BH_3 \cdot NRR_1R_2$ varies inversely and remarkably with the stability of the adduct [55]. The rate of hydroboration of alkenes with BH_3-Lewis base complexes is retarded by excess complexing agent. A study of the kinetics of hydroboration of 2,3-dimethyl-2-butene with BH_3- dimethylsulfide complex in toluene at 0 degrees also supports the dissociation mechanism. These results render questionable the generality of the recent conclusion based on ab initio calculations that hydroboration proceeds via a direct attack of alkene on borane complexes.

Kayser and McMahon investigated the reaction of borohydride ion with formaldehyde in the gas phase using ion cyclotron resonance spectroscopy [56]. Interestingly, no hydride transfer from borohydride to the carbonyl group is observed under the conditions utilized but a novel reaction between enolate ions and diborane was observed.

c. Spectroscopy

Mancini, Bougeard, Burns, Mlekuz, Sayer, Thompson, and McGlinchey carried out a multinuclear magnetic resonance investigation on a cyclo-

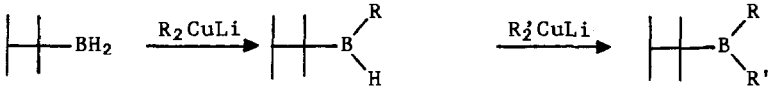
pentadienyl scandium borohydride compound which they synthesized [57]. They found no exchange between borohydride and ring hydrogens even at elevated temperatures. The borohydride apparently is triply bridged in the compound. The structures of the known main-group and transition-metal borohydrides are rationalized in terms of a correlation between the number of bridging hydrogen atoms and the number of vacant metal orbitals of suitable energy and symmetry.

Duncan and Harper determined 12 ground-state spectroscopic rotational constants for isotopic diboranes and a realistic harmonic potential function which enabled the ground state, substitution, and structure parameters to be calculated for diborane [58].

Idelmann, Mueller, Scheidt, Schuessler, Seevogel, and Koester determined the crystal structure of the product obtained when 9-BBN is solvolized with pivalic acid [59].

4. Synthesis of Organoboranes

Not all organoboranes (methyl, phenyl, etc.) are readily available via the hydroboration reaction. Transmetallation reactions are normally utilized in the syntheses of these organoboranes. Pickles, Spencer, Thorpe, Chopa, and Podesta treated tetraaryltin and triphenyltin halide reagents with borane [60]. The products were mixtures of mono- and diaryl boron reagents which could be oxidized to the corresponding phenols or hydrolized to mixtures of boronic and borinic acids. Whiteley reacted thexylborane with halomagnesium dialkylcuprates or lithium dialkyl cuprates to afford the corresponding totally mixed thexyldialkyorganoboranes [61].



Arase, Hoshi, and Masuda synthesized internal alkenyldialkylborane reagents by reacting 1-halo-1-alkenyldialkylborane with Grignard reagents [62]. The alkyl transfer product was formed as an impurity.

Hoshi, Masuda, Nunokawa, and Arase also prepared internal vinylboranes by reacting γ-iodovinylboranes with Grignard reagents [63].

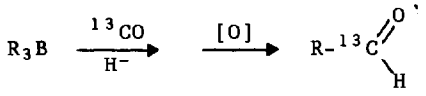
Ishikura, Mano, and Terashima treated 3- and 4- lithiopyridines with methylboronates to produce the corresponding dialkylpyridylboranes [64]. Kalbarczyk and Pasynkiewicz reported the synthesis of a new series of lithium tetraalkylborates [65]. Whiteleyand Zwane reacted vinylcuprates with 9-BBN to prepare vinyl 9-BBN derivatives which could be oxidized to aldehydes or converted to ketones by treatment with various nucleophiles [66].

C. CARBON-CARBON BOND FORMATION

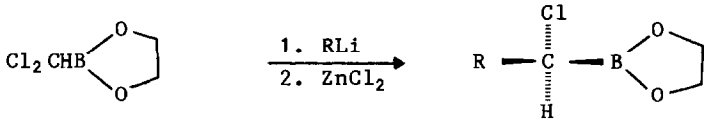
1. Homologation

One of the oldest organoborane homologation reactions is the carbonylation reaction in which an organoborane reacts with carbon monoxide in the presence of a hydride donor. Hubbard and Smith report that the hydride induced carbonylation of organoboranes proceeds via alkali metal trialkylborohydride intermediates regardless of the complex metal hydride used [67]. Apparent variations in alkyl group migratory aptitudes observed previously evidently arise from selective formation of products that are difficult to oxidize. For example, carbonylation of dicyclohexyl-n-octylborane at 25° in the presence of lithium tri-t-butoxyaluminum hydride gave 98% of cyclohexylcarboxaldehyde and 2% nonanal whereas nearly equal mixtures of the two aldehydes were obtained when the carbonylation was run at -25°.

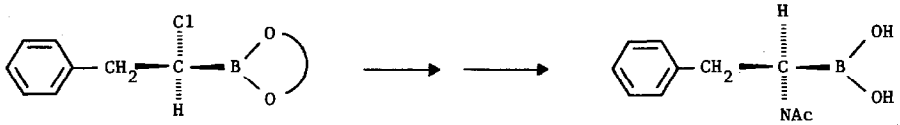
Kabalka, Delgado, Kunda, and Kunda utilized the hydride-induced carbonylation reaction to synthesize a series of carbon-13 labeled aldehydes, carboxylic acids, and alcohols [68].



Sadhu, Matteson, Hurst, and Kurosky report that (R,R)-2,3-butanediol is a convenient chiral directing group in the synthesis of (s)-α-chloro boronic esters [69]. The diasterioselectivity of the reaction approaches 96% and the method provides a convenient route for adding a chiral carbon to lithium or Grignard reagents.

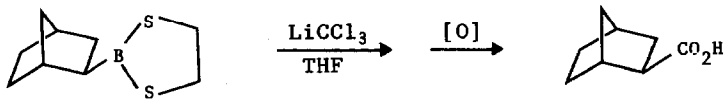


Matteson and Sadhu utilized an optically active chloroboronic ester to synthesize 1-amino-2-phenylethane-1-boronic acid derivatives which are analogs of N-acetylphenylalanine [70].



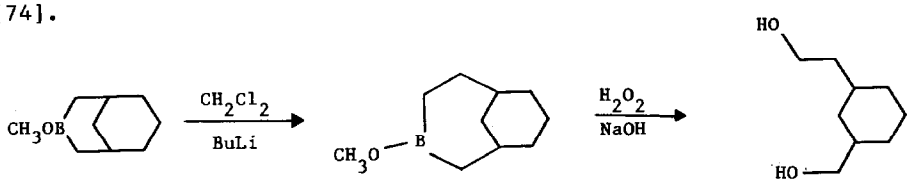
Matteson, Jesthi, and Sadhu applied the methodology to the syntheses of a series of α-amido boronic esters [71].

Brown and Imai developed a homologation sequence in which alkylthio-boronic esters are reacted with trichloromethyllithium to produce carboxylic acids [72]. The reaction takes advantage of the regiochem-

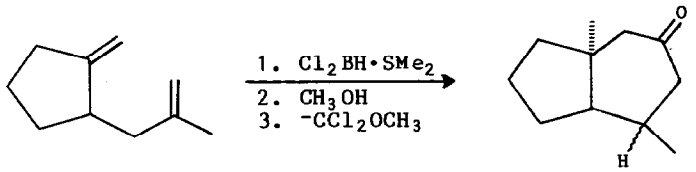


istry and stereochemistry of the hydroboration reaction and efficiently utilizes the organic group on the borane molecule. Brown, Jadhav, and Desai synthesized chiral acyclic ketones via the carbenoidation of chiral borinic acids [73].

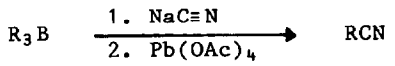
Gurskii, Baranin, and Mikhailov reacted a borabicylononane with dihalomethane in the presence of butyl lithium to produce the ring expanded product which could then be converted to all cis cycloalkanes [74].



Stevenson and Bryson used the dichloromethyl ether reaction to synthesize hydroazulenones which are prototypes of pseudoguanianolides [75].



Masuda, Hoshi, Yamada, and Arase developed a novel synthesis of alkyl cyanides by the reaction of trialkylcyanoborates with sodium acetate with sodium cyanide and lead(IV) acetate [76].



Shlegel and Schaefer subjected organoboranes to anodic oxidation and obtained dimeric products [77]. The yields exceeded those obtained by Kolbe electrolysis and were comparable to those obtained using a silver nitrate oxidation. Oxidation of mixed boranes gave a statistical distribution of the coupled products.

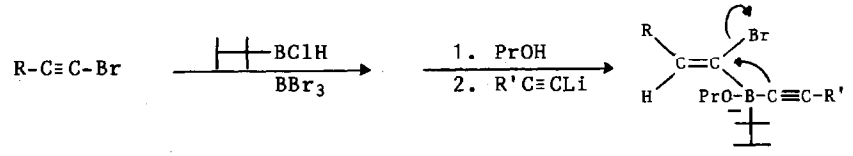
Calhoun and Schuster irradiated tri-1-naphthylboron in cyclohexene and found that low yields of 1,1'-binaphthyl were obtained [78].

2. Alkenyl- and Arylborates

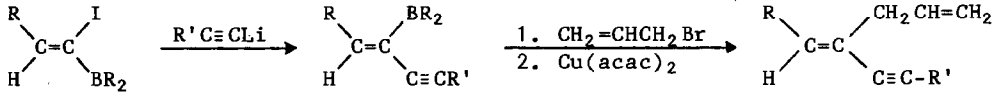
Halovinylboranes readily undergo a variety of rearrangement reactions in which an alkyl, vinyl, or alkynyl group migrates from an electron rich boron site to the neighboring electron deficient vinyl carbon. The electron deficiency can be induced by an electrophilic

attack on the vinyl group or by the presence of an electron withdrawing group such as a halogen. Torregrosa, Baboulene, Speziale, and Lattes report that the hydroboration and subsequent iodination of acetylenic amines produces the corresponding alkylated alkenyl amines [79].

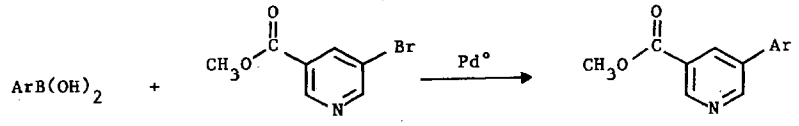
Brown, Bhat, and Bassavaiah synthesized (E)-1,3-alkenynes [80]. In this sequence the intermediate 1-bromo-1-boroalkene is reacted with an alkynyl lithium. The alkynyl group then displaces the bromine resulting in a vinylborane in which the alkene and alkyne groups are conjugated.



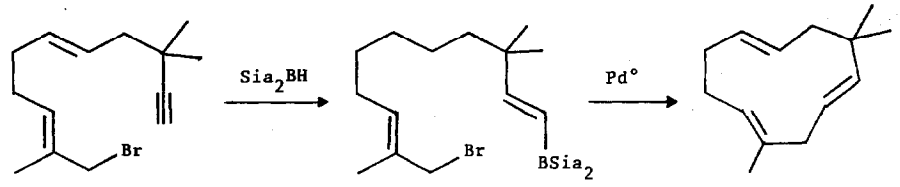
Vinyl and arylboranes readily undergo a variety of coupling reactions via the intermediacy of unstable organometallic reagents. Arase, Hoshi, and Masuda developed a regio- and stereospecific synthesis of unsaturated hydrocarbons from internal enynyldialkylboranes using a copper catalyst [81]. Ishikura, Kamada, Ohta, and Terashima



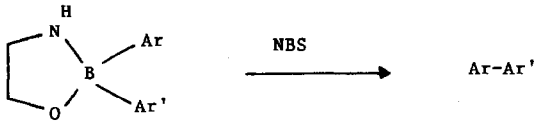
used a palladium cross-coupling reaction to synthesize vinylpyridines [82]. Thompson and Gaudino also used a palladium cross-coupling reaction to synthesize a series of 5-arylnicotinates [83].



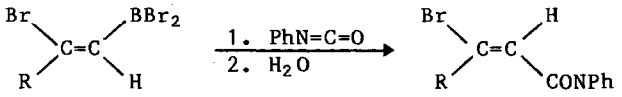
Miyaura, Suginome, and Suzuki used a palladium catalyzed cyclization reaction to prepare humulene from a haloalkenylborane [84].



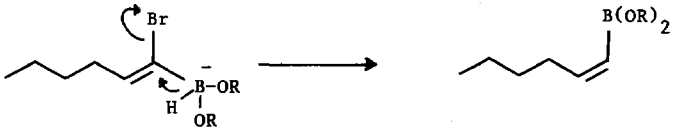
Carbon-carbon bond formation can also be achieved via the reaction of unsaturated boranes with electrophiles. Pelter, Williamson, and Davies used N-bromosuccinimide to couple furyl and thienyl residues to each other [85].



Satoh, Serizawa, Hara, and Suzuki prepared N-phenyl-β-bromo-α,β-unsaturated amides via treatment of a bromovinylboranes with phenyl isocyanate [86].

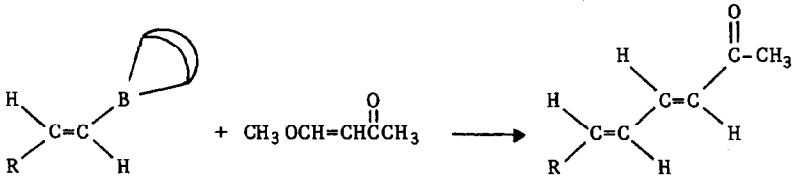


Brown and Imai used the rearrangement of a hydrido derivative of an α-bromovinylborate in an elegant synthesis of difficult to obtain (Z)-1-alkenylboronic esters [87].



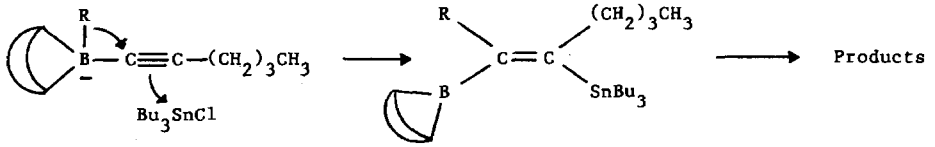
Koshino, Sugarawa, and Suzuki synthesized a series of 1-alken-3-ynes via the rearrangement of 1-methoxy-1,2,3,-butatrienyltrialkylborates [88].

Molander, Singaram, and Brown utilized a similar reaction to prepare conjugated dienones [89]. In their reaction sequence, an appropriately substituted enone serves as both a complexing ligand and an electrophile.



3. Alkynylborates

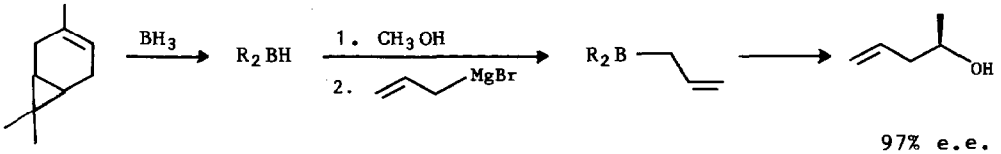
Alkynylborates are also subject to electrophilic attack and yield rearranged products Wang and Chu prepared a series of (Z)-alkenes, ketones and alkynes via the trialkyltin chloride induced intramolecular reaction of alkynyltrialkylborates [89]. They found that primary alkyl groups selectively migrated from the boron atom to the adjacent acetylenic carbon.



Wrackmeyer reported that an attempted synthesis of a β-stannyl vinylborane via the reaction of organoboranes with alkynylstannanes resulted in the synthesis of a 2,5-distannyl-3-borolene [91].

4.Allyl- and Propargylboranes

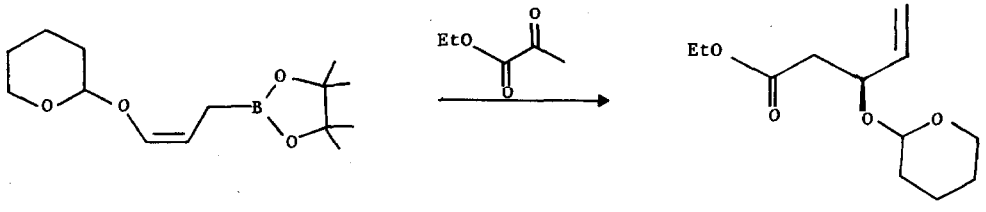
Brown and Jadhav prepared several chiral allyldialkylboranes and condensed them with acetaldehydes to produce optically active alcohols [92]. They successfully utilized the unique Grignard-like rections of the allylboranes in this approach to optical induction. They report that β-allyl-diisocaranylborane is the most effective chiral allylborating agent of the series investigated. Brown, Jadhav, and Perumal also



97% e.e.

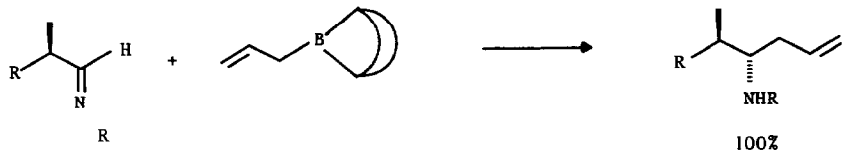
reported that methyllyldiisopinocamphenylborane and (3,3-dimethylallyldiisopinooampheylborane) would undergo methallylboration reactions with prochiral aldehydes [93,94].

Metternich and Hoffman reported that chiral tetrahydropyranyloxy groups in allylboronates could induce asymmetric induction in reactions of the allyl group [95].



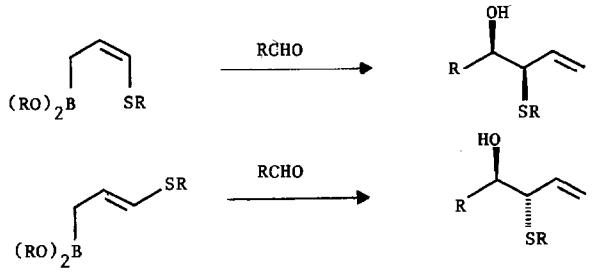
Hoffmann and Landmann also demonstrated chirality transfer from chiral α-chloroallylboronic acid esters to aldehydes [96].

Yamamoto, Komatsu, and Maruyama studied the reaction of allyl-9-BBN with imines [97]. They found that the stereoselectivity of the allyl reagent is greatly enhanced in the reaction with imines as compared to the corresponding free aldehydes. The enhancement can be explained by postulating a rigid six-membered chair transition state.

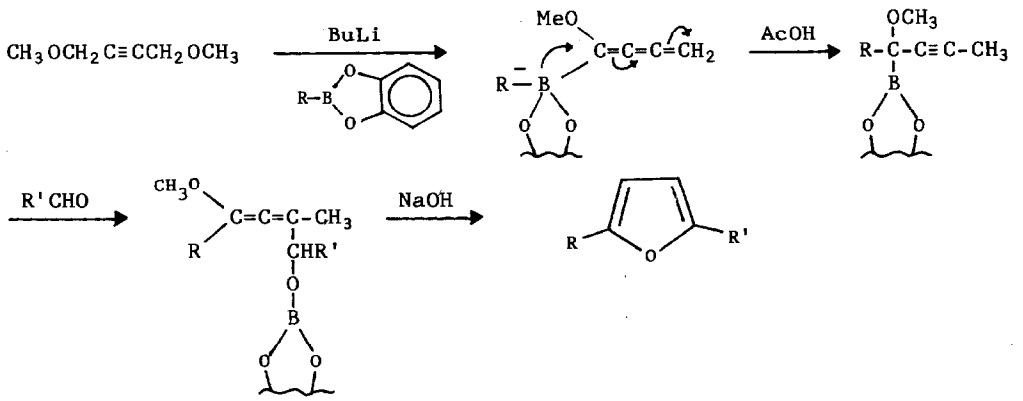


Yamamoto, Yatagi, and Saito also reported that the regiochemistry in reactions of heterosubstituted allylic carbanions is highly controlled via aluminum of boron complexes [97].

Hoffman and Kemper reported the stereoselective synthesis of alcohols via the addition of γ-(alkylthio)allylboronates to aldehydes [99].



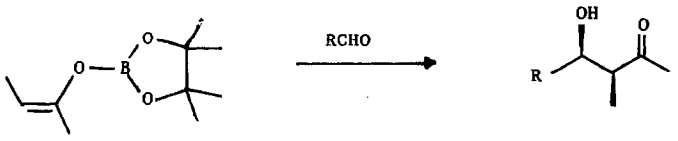
Koshino, Sugawara, and Suzuki synthesized furans via the reaction of 1-methoxy-1,2,3-butatrienylborate with acetic acid and then aldehydes [100].



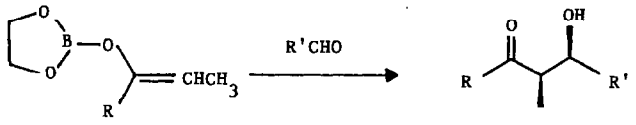
Furuta, Ishiguro, Haruta, Ikeda, and Yamamoto investigated the reactions of propargylboranes with aldehydes [101].

5. Boron Enolates

Brown enolates have been used in a number of stereoselective syntheses. Hoffman and Ditrich report that both Z- and E-enolborates underwent a stereoconvergent addition to aldehydes to produce the corresponding β-hydroxyketones with a syn/anti ratio exceeding 9:1 [102].

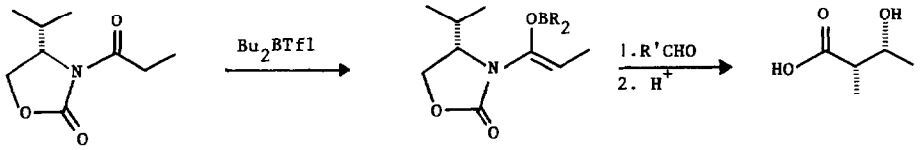


Gennari, Colombo, and Poli reported the synthesis of a series of enolboronates via the reaction of ethylenechloroboronate with carbonyl compounds [103]. Gennari and his coworkers utilized the reagent in stereoselective aldol condensations [104] in which the results were in agreement with observations made by Hoffmann.



Gennari, Colombo, Scolastico, and Todeschinin carried out a mechanistic and stereochemical investigation of alkenyloxydialkoxyboranes in aldol condensations [105].

Meyers and Yamamoto reported the use of chiral oxazoline derivatives in boron azaenolates from chiral oxazolines and various boron triflates and found that their reaction with aldehydes gives good erythro selectivity (>97%) and moderate enantiomeric purities (>50%).

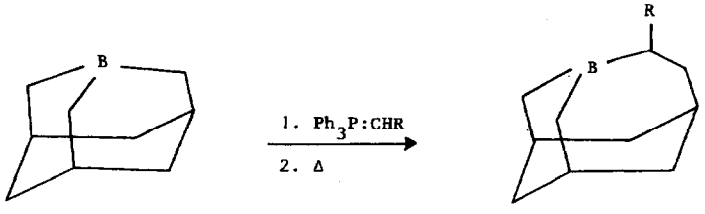


Gennari, Cardani, and Scolasstico studied the stereoselective condensations of boron enolates from thioesters [107]. Tamaru, Hioki, and Yoshida investigated the condensations of boron enolates from thioamides [108].

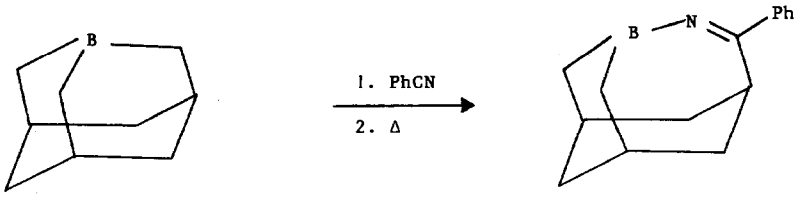
6. Adamantylboranes

Mikhailov and his coworkers continue to explore the chemistry of the boraadamantanes. He reviewed the chemistry of the polyhedralboranes in the Russian literature [109].

Gurskii, Pershin, and Mikhailov report that 1-boraadamantane reacts with phosphorus ylides to form stable adducts which rearrange to 4-alkyl-3-borahomoadamantane products [110].



Mikhailov and Baryshnikova reacted 1-boraadamantane with benzonitrile which formed a complex which was converted to a 3-bora-4-aza-1,1-bihomoadamant-4-ene upon heating [111].



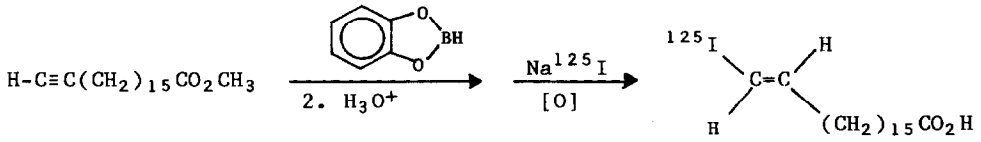
Mikhailov and Cherkasova prepared a 2-(2-thienyl)-1-boraadamantane complex via the reaction of 2-(2-propargyl)thiophene with triallylborane [112]. Mikhailov and Etinger reported the synthesis of a silicon containing 1-boraadamantane from the reaction of triallylborane with trimethylsilylbut-1-yne [113].

D. CARBON-HETEROATOM BOND FORMATION

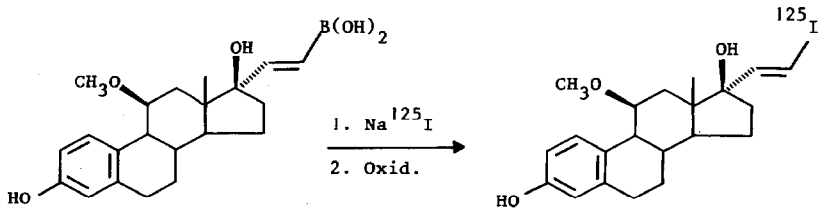
Reactions of organoboranes in which the boron atom is replaced by an atom other than carbon continue to play a major role in organic synthesis. One area in which these reactions become important is in the syntheses of isotopically labeled compounds. Kabalka reviewed the use of organoboranes in the synthesis of isotopically labeled agents [114].

1. Group VII

In recent years, the use of organoboranes for incorporating radioiodine atoms into physiologically active agents has increased dramatically because of the ability to produce functionally substituted iodinated products. Knapp, Kabalka, and their colleagues continued their development of a series of radioiodinated alkenyl fatty acids for use as myocardial imaging agents [115 and and 116].

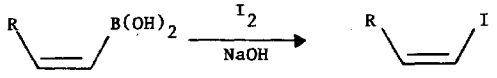


Eckelman and his collaborators reported the synthesis of an active estrogen-receptor, steroid which was prepared via the reaction of a vinylborane with sodium iodide [117].

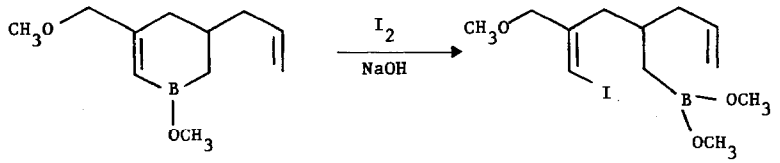


Srivastava and Knapp synthesized an alkenylphosphonium iodide utilizing a similar reaction sequence [118].

Brown and Somayaji reported that (Z)-1-iodo-1-alkenes could be prepared via reaction of the corresponding (Z)-vinylboronate esters with iodine [119]. A similar reaction sequence using bromine resulted in the (E)-bromoalkenes.



Mikhailov and Lavrinovich prepared 1-iodo-1,4-pentadienes via iodination of the corresponding 1-boro derivatives [120]. They also reported that reaction of 1-bora-2-cyclohexene compounds with iodine produces iodopentyenylboranes [121].



Hoshi, Masuda, and Arase found that trialkylboranes react with chlorinating agents such N-chlorosuccinimide and t-butyl hypochlorite under free radical conditions to produce the resulting alkyl chlorides in moderate yields [122].

$$R_3B \xrightarrow{NCS} RCl \quad (\sim 60\%)$$

2. Group V

Organoboranes react with N-chloroamine reagents to form amine derivatives. Kabalka, McCollum, and Sastry report that dialkylamines are readily prepared via the reaction of N-chloroalkylamines with trialkylboranes [123].

$$R_3B + ClNHR' \longrightarrow RR'NH$$

Masuda, Hoshi, and Arase synthesized azidoalkanes via the reaction of organoboranes with lead azide [124].

$$R_3B \xrightarrow[Me_3SiN_3]{Pb(OAc)_4} RN_3$$

3. Protonolysis

The protonolysis of boranes is an old but effective reaction. It is known that reagents which can coordinate with the boron atom, such as carboxylic acids, are most effective. Other reagents will react if

forced. Domaille, Druliner, Gosser, Read, Schmelzer, and Stevens studied the methanolysis of triphenylborane and they reported that the reaction is first order in triphenylborane and zero order in alcohol [125].

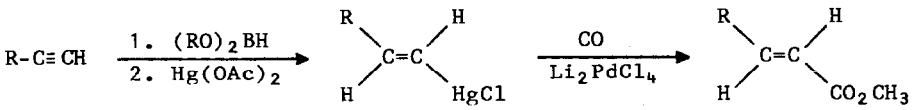
4. Metallation

The use of boranes as intermediates in the formation of other organometallics is also well known. Sastry, Varma, and Kabalka report that the reaction of organoboranes with mercuric acetate results in the formation of stable organomercuric acetates [126]. The reaction works equally well for alkyl, alkenyl, and phenyl derivatives.

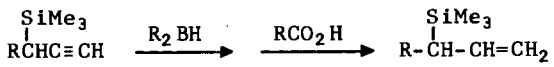
Kabalka and his coworkers then reported that vinylmercuric acetates reacted with vinylboronic acids [127] to produce divinylmercury derivatives [128].

$$RCH{=}CHHgOAc + RCH{=}CHB(OH)_2 \longrightarrow RCH{=}CHHgCH{=}CHR$$

Larock and Narayanan reported that vinylmercurials are readily prepared via the mercuration of B-vinyl catecholborane derivatives with mercuric chloride or acetate [129]. These mercurials could be readily carbonylated to yield unsaturated esters.

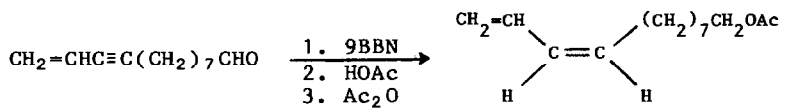


Wrackmeyer and Kershl report that bis(ethynyl)stannanes react with trialkylboranes to yield product mixtures which contain bis(alkenyl)-stannanes [130]. Rajagopalan and Zweifel prepared alkenylsilanes via the hydroboration-protonation of propargylic silanes [131].

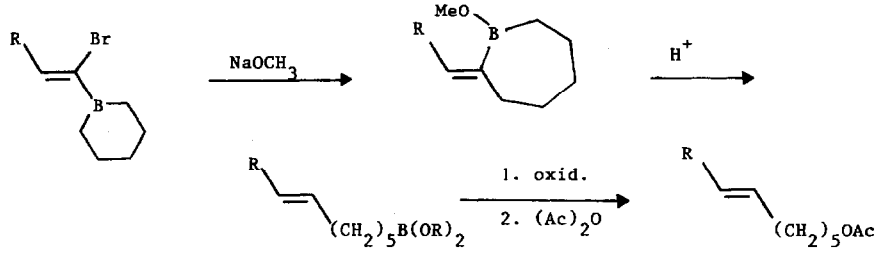


E. NATURAL PRODUCTS

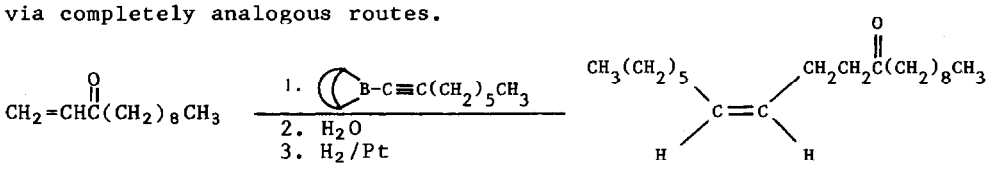
The use of organoborane reactions in the syntheses of natural products is becoming widespread due to the stereo- and regioselectivity of many of the organoborane reactions. Insect pheromone syntheses lend themselves to organoborane reactions due to the fact that the products often contain stereodefined sites of unsaturation. Balezina, Ishmuratov, Odinokov, Selimov, Dzhemilev, and Tolstikov utilized a straightforward, but selective, hydroboration-protonolysis sequence to prepare the sex pheromone of Diparopsis cactanea [132].



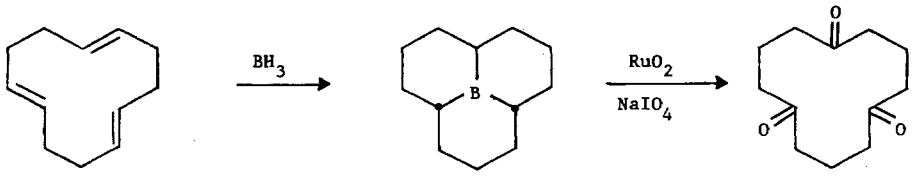
Brown, Basavaiah, and Singh utilized the intramolecular rearrangement of 1-bromo-1-boroalkenes in an elegant preparation of the sex pheromone of the mediterranean fruitfly [133].



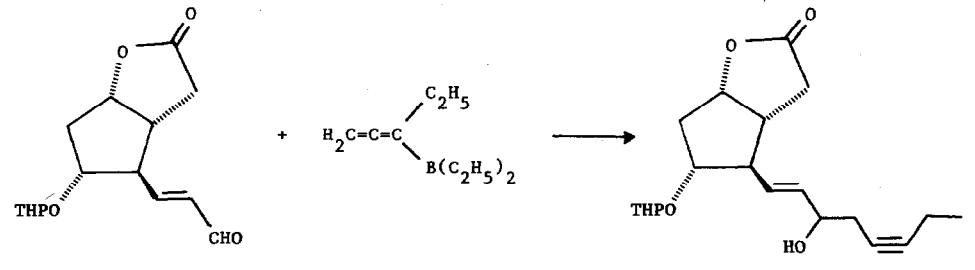
The well known conjugate addition reaction of alkynylboranes to α,β-unsaturated ketones was used by two groups in synthesizing pheromones. Brown, Racherla, and Basavaiah synthesized (Z)-5-undecene-2-one [134] whereas Kang and Cho synthesized (Z)-7-eicosene-11-one [135] via completely analogous routes.



Mueller, Thompson, and Dipardo synthesized hydropyrido[2,1,6-de]-quinolizine (a ladybug defensive alkaloid) via a symmetrical trione prepared using a hydroboration-oxidation sequence [136].



Torisawa, Okabe, and Shibasaki developed an improved route to isocarbacyclin via the hydroboration of the 9-methylene derivative [137]. Corey, Ohuchida, and Hahl reported the total synthesis of C22-prostanoids in the E and F series based on docosahexaenoic acid using an allenicborane addition to an aldehyde in a key step [138].



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