BORON: BORANES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1985

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CONTENTS

A. INTRODUCTION

A variety of new synthetic methods involving organoborane transformations were developed this year. A number of groups focused on the synthesis of chiral molecules via appropriate organoborane precursors while others attempted to develop new borane agents in which the organic moieties were utilized more efficiently. Many individuals contributed to the advances reported in this review but, not suprisingly, Professor H. C. Brown continued to lead the way [1].

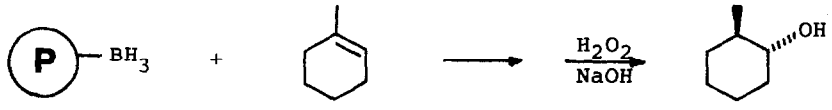
The format of this year's review remains unchanged. In some instances, the placement of the research summary is somewhat arbitrary but, hopefully, logical. For example, haloborations involving iodo-9-BBN are found in Section B.1.c. along with hydroborations involving 9-borobicyclo[3.3.1]nonane (9-BBN).

B. BORANE REAGENTS

1. Hydroborating Agents

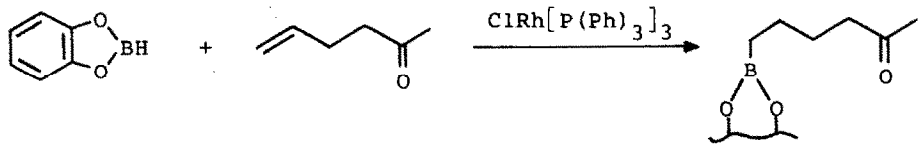
a. BH_3

The hydroboration reaction is the foundation upon which most of the new organoborane methodology rests. It provides for the ready availability of a variety of interesting and useful borane intermediates. Not suprisingly, the hydroboration reaction is itself subject to intensive scrutiny and a number of modified methods have been reported over the years. This year is no exception. Domb and Avny reported that borane and haloborane complexes can be prepared using poly(propylene sulfide) grafted onto polystyrene [2]. They found that these graft polymers can be used to hydroborate alkenes (and reduce carbonyl compounds) with good regioselectivity.

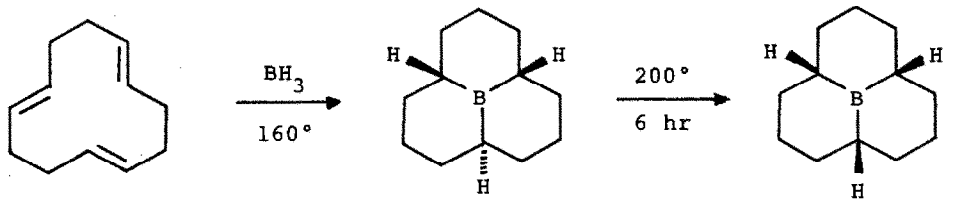


Narayana and Periasamy report that functionally substituted alkenes such as methyl 10-undecenoate can be conveniently hydroborated

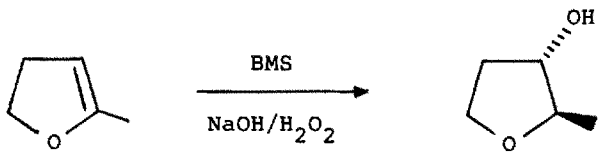
via an in situ hydroboration involving the addition of acetic acid to the alkene dissolved in a suspension of sodium borohydride in THF [3]. Noeth and Maennig found that hydroborations involving catecholborane are catalyzed by rhodium complexes [4]. Interestingly, they were able to hydroborate alkenes bonds in the presence of keto groups.



Brown, Negishi, and Dickason reexamined the stereochemsitry of the perhydro-9b-boraphenalenes obtained via the hydroboration of a series of isomeric trienes using triethylamine-borane as well as borane-THF [5]. They found that the thermodynamically stable products were not formed initially but formed readily after thermal treatment.

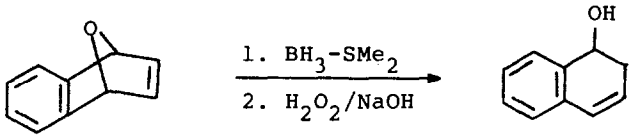


Brown, Prasad, Vara, and Zee examined the hydroboration of a series of heterocyclic olefins using borane-methyl sulfide and a number of other hydroboration agents [6]. The desired trialkylboranes were



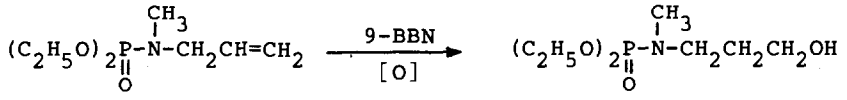
formed when stoichiometric quantities of the reactants were used; however they discovered that reductive ring opening occurred in the presence of excess borane-methyl sulfide. Clean hydroborations could be obtained if the stoichiometry of the reaction was carefully

controlled. Brown, Prasad, and Vara also observed ring opening when 1,4-epoxy-1,4-dihydronaphthalene was hydroborated with borane-methyl sulfide or 9-BBN [7]. Interestingly, the use of dicyclohexylborane or



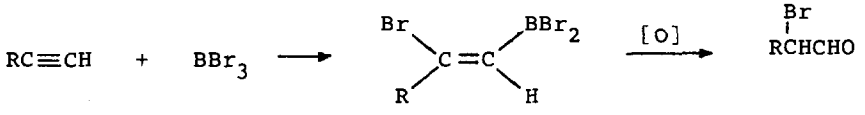
disiamylborane obviated the ring opening reactions.

Benmaarouf-Khallaayoun and Baboulene used a phosphorylation technique to protect the amino group during the hydroboration of unsaturated amines [8]. The method appears to be a general one.



Kafka, Ferles, and Richter used borane-triethylamine to hydroborate 1-allyl-1,2,3,4-tetrahydroquinoline [9]. Noeth and his coworkers used borane itself to protect a nitrogen function during hydroboration [10].

Suzuki and his coworkers continued their investigation of the bromoboration reaction [11]. The bromoboration of alkynes lead to



the expected vinylic intermediate but normal oxidation methodology was not applicable because the required strong base lead to extensive beta elimination. They overcame the problem through the use of buffers.

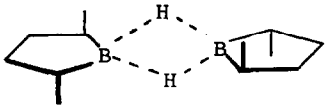
b. RBH_2

Shiner, Garner, and Haltiwanger reported an improved preparation of BH_2Cl (a RBH_2 analog) and utilized it to prepare an optically active alkylchloroborane monomer [12]. They also reported the crystal struc-

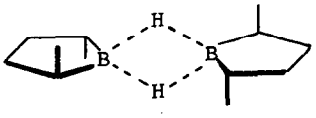
ture of the monomer which they feel is the first complete x-ray analysis of a monoborane-ether complex.

c. R_2BH

Masamune, Kim, Peresen, Sato, Veenestra, and Imai synthesized a pair of totally new asymmetric hydroborating agents, (R,R)- and (S,S)-2,5-dimethylborolane [13]. The reagents are somewhat difficult to



(R,R)

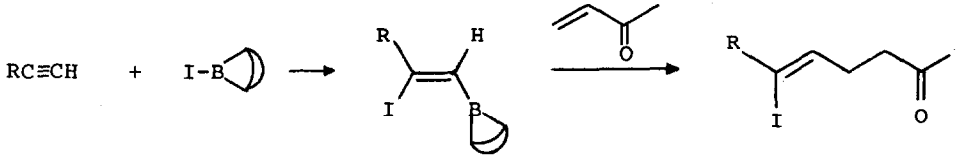


(S,S)

synthesize but are very effective chiral hydroboration agents. The authors report that the new agents surpass the more traditional agents (dipinanylborane, etc.) in terms of chiral induction during the hydroboration of achiral alkenes. Partridge, Chadha, and Uskokovic used di-3-pinanylborane to achieve the asymmetric hydroboration of a series of 5-substituted cyclopentadienes [14].

Brown and Racherla used ultrasound to enhance the rate of hydroboration reactions involving dibromoborane-methyl sulfide [15]. As an example, 1-methylcyclopentene can be hydroborated in one hour using ultrasonic acceleration as compared to a 5 hour reaction time under normal conditions.

Suzuki and his coworkers utilized haloboration to prepare a series of iodoalkenyl-9-BBN derivatives which were used in Michael addition reactions to prepare unsaturated ketones [16].



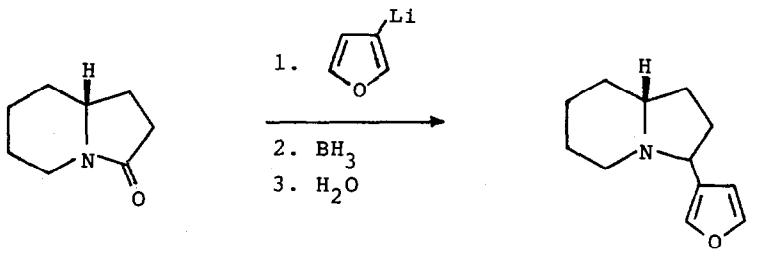
2. Reducing Agents

a. BH_3

Domb and Avny synthesized a cross-linked poly(4-vinyl-pyridine)borane and utilized it to reduce aldehydes and ketones to the

corresponding alcohols [17]. The reductions were carried out at a pH of 1 due to the relatively high hydrolytic stability of the borane bound polymer. Only two-thirds of the borane hydrides are available for reduction.

Hwang, Chu, and Fowler report that <u>in situ</u> generated borane ($NaBH_4/CF_3CO_2H$) can be used to prepare α-substituted amines from amides via reaction of the amide with organolithium reagents followed by borane reduction [18]. Imamoto, Kusumoto, Suzuki, and Sato described

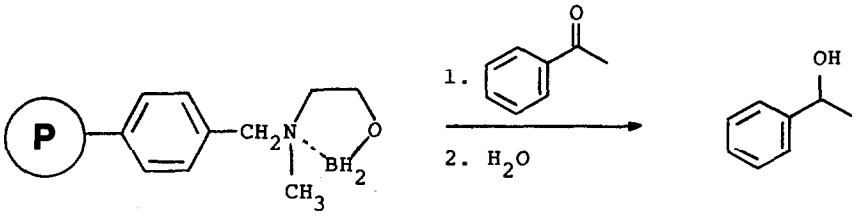


a method to prepare phosphine-borane complexes from phosphine oxides using lithium aluminum hydride-sodium borohydride-cerium(III) chloride [19].

Jalass and Haller used chiral amines complexed with borane to reduce ketones [20]. The optical yields approached 50%.

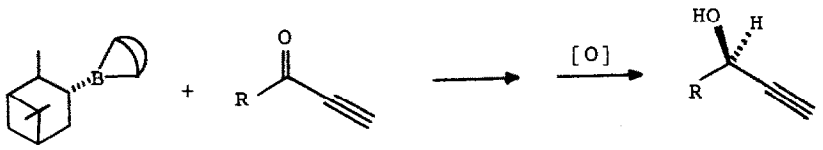
b. RBH_2

Itsuno, Wakasugi, Ito, Hirao, and Nakahama utlized a new reagent prepared by reaction of amino alcohols with borane [21]. The reagents are chemoselective. Ketones can be reduced in the presence of esters, oxime ethers, tertiary amides, nitriles, halides, and acyl chlorides. Interestingly, amino alcohols attached to polymeric materials can also be utilized.



c. R_3B

Midland and Graham utilized B-(3-pinanyl)-9BBN to reduce α,β-acetylenic ketones [22]. The chiral materials were formed in



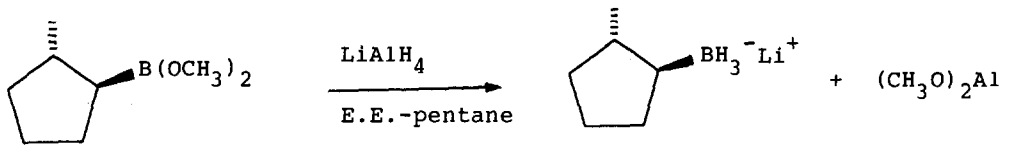
86% enantiomeric excess. Midland and Lee also examined the reduction of acyl cyanides using the reagent [23]. They again achieved chiral products which were formed in approximately 80% enantiomeric excess.

Brown and Pai examined the reduction of a series of prochiral ketones utilizing B-(3-pinanyl)-9-BBN [24]. Among the carbonyl compounds reduced were alkyl, α,β-unsaturated, and haloalkyl ketones. All underwent rapid reduction to produce chiral alcohols in excellent enantiomeric excess.

Chandrasekharan, Ramachandran, and Brown reported that a new agent, diisopinocampheylchloroborane, is a remarkably efficient chiral reducing agent for aromatic prochiral ketones [25]. Enantiomeric excesses approaching 98% were obtained as long as the alkyl group was not branched near the carbonyl site.

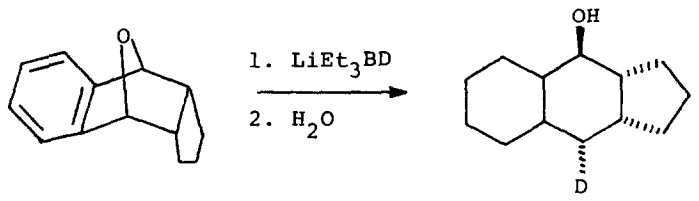
d. RBH_4

The use of borohydride reagents in organic synthesis is extensive. The reactions noted in this review appear to be novel ones. Brown, Singaram, and Cole reported an efficient synthesis of monoalkyl and dialkylborohydride reagents [26]. They found that boronic esters react readily with lithium aluminum hydride in diethyl ether-pentane to form the corresponding lithium monoalkylborohydrides and dialkoxyalanes (which precipitate quantitatively). A parallel synthesis can be

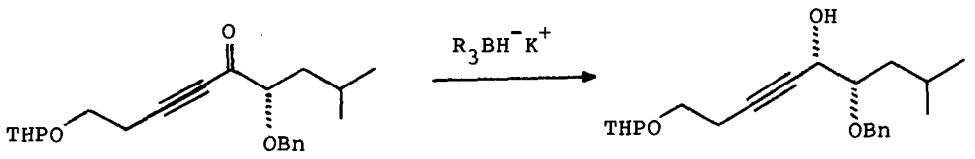


achieved using borinic esters to produce dialkylborohydrides.

Moss and Rickborn prepared triethylborodeuteride in situ and utilized it to investigate the stereochemistry of the reductive cleavage of two 7-oxabicyclo[2.2.1]heptanes [27].

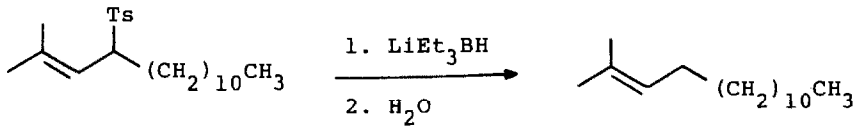


Takahashi, Miyazawa, and Tsuji reported that potassium tri-sec-butylborohydride produces the threo alcohol predominantly when acetylenic ketones are reduced [28]. This is in contrast to the results obtained when zinc borohydride is used as the reducing agent.



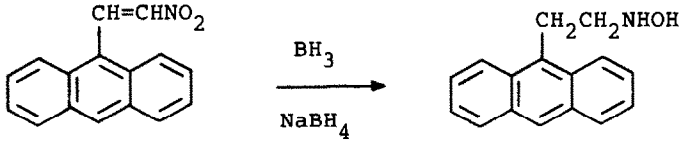
Jeyaraj and Porter report that S,S- and R,R-warfarin alcohols can be prepared in 99% diastereomeric excess through the use of the appropriate Alpine-Hydride agent [29].

Mohri, Kinoshita, Inomata, and Kotake found that allyl p-tolyl sulfones are easily desulfonylated without rearrangement to the corresponding alkenes by superhydride in the presence of a catalytic amount of a palladium catalyst [30].



Kim and Yi used tri-sec-butylborohydride to reduce alkyl halides to the corresponding alkanes [31]. Steliou, Slama, and Corriveau used triethylborohydride to prepare very reactive lithium sulfide for use in the synthesis of thiacycloalkanes [32].

Mourad, Varma and Kabalka utilized a sodium borohydride catalyzed borane reduction scheme to prepare a series of N-substituted hydroxyl amines from the corresponding α,β-unsaturated nitroalkenes [33].



3. Mechanism and Theory

a. Theory

Ip and Li used MNDO calculations to investigate the dimerization of BH_3 [34]. Three pathways were studied by imposing different symmetry restrictions: C2h, least-motion, and none. The activation energies of the 3 pathways are 3.8, 31.5, and 2.7 kcal/mol, respectively. They conclude that the dimerization of BH_3 has either no, or a very small, energy barrier.

The low-lying excited states of HCB (no pun intended!) and HBC were examined using ab initio MO theory at the MP4/6-311G**//HF/6-31G** + ZPE level by Luke, Pople, and Schleyer [35]. Linear triplet structures were found to have the lowest energy. The singlet triple-bond structures are much less favorable. For HCB, the $3.\pi$- state is 12.7 kcal/mol more stable than the $3.\sigma$-state, while for CBC the $3.\sigma$-state is more stable than the $3.\pi$-state by 9.4 kcal/mol. The energy difference between the lowest energy structures of HCB and HBC is only 3.9 kcal/mol, with the $3.\pi$-state of HCB being the most stable. The barrier

to conversion of HBC into HCB is 23.7 kcal/mol, suggesting that both triplet species might exist independently.

Budzelaar, Kos, Clark, and Schleyer also investigated the effects of boron substitutients in borirenes, boriranes, and boranes [36]. Boron bonds to electronegative groups are considerably stronger than the corresponding bonds of the same groups to carbon due to both sigma and pi effects. The borirane system has a high strain energy, approximately 16 kcal/mol higher than that of cyclopropanes; this is probably a major contributor to the difficulties encountered in preparing compounds of this type. Borirene shows a large resonance energy of approximately 47 kcal/mol. This compensates for the strain of the small ring system, and substituted borirenes should be chemically more stable than the corresponding boriranes.

Godik, Rodionov, and Shigorin calculated the electronic structure of triphenylborane in the ground and excited states using the CNDO/S CI method. The electron densities, first ionization potential, dipole moment, and oscillator strengths were calculated. Carmichael used UHF/STO-3G calculations to characterize the combined effect of methyl rotation and pyrimidal inversion in the trimethyl borane radical anion and its third row counterparts [38]. Energy barriers and structures were quantified by employing a split-valence F/3-21G procedure. For the trimethylborane species, the predicted barriers to both inversion and concerted methyl rotation make these motions thermally unfeasible at room temperature.

Delbecq, Ilavsky, Nguyen, and Lefour reported a theoretical study of regioselectivity in radical additions to vinylborane [39]. Using UHF 3-21G + CIPSI calculations, with all important structures fully optimized by a gradient procedure, they studied the addition of a hydrogen atom to vinylborane. Entropies, Arrhenius parameters A and Ea, and rate constants were calculated.

Hoffman, Ditrich, Forech, and Cremer carried out MO calculations and NOE experiments to study the effect of conformation on stereoselec-

tivity of the aldol addition reaction involving enol borates [40]. STO-3G calculations on MNDO optimized geometries of E-enol borates indicated both extended and U conformations. Thus aldol additions of E-enolates are not stereoselective. On the other hand, Z-enol borates exist exclusively in the extended conformation, which is maintained in a chair transition state, resulting in stereospecific additions.

b. Kinetics

Chandrasekharan and Brown reinvestigated the kinetics of hydroboration of representative alkenes with disiamylborane dimer [41]. With many alkenes the reaction exhibits 3/2 order kinetics, indicating that the reaction involves a prior dissociation of the dimer. This contrasts earlier results which supported a bimolecular reaction of the alkene with the disiamylborane dimer. Brown and his coworkers also investigated the relative rates of hydroboration of representative heterocyclic olefins with 9-BBN [42]. 2,3-Dihydrofuran is hydroborated 106 times faster than cyclopentene whereas dihydropyran and tetrahydrooxepin react at rates that are 6.4 and 0.034 times as fast as those of their corresponding carbocyclic analogs.

Gaines, Heppert, and Kunz report that B_2H_6 undergoes H isotope exchange with deuterated aromatic hydrocarbons in the presence of Lewis acids catalysts [43]. They postulate that diborane participates in a reversible hydroboration of the aromatic ring.

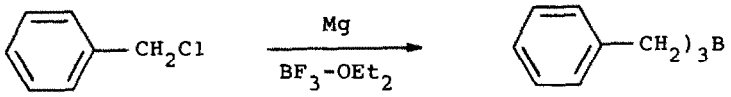
c. Spectroscopy

Spectroscopic data were presented in the experimental sections of many of the reports highlighted in this review and it would be impossible to tabulate them in this summary. Kalbarczyk and Pasynkiewicz did report detailed studies of the ^{1}H, ^{13}C, and ^{11}B NMR as well as the IR of a series of organoborate species [44].

4. Synthesis of Organoboranes

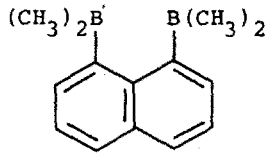
Brown and Racherla reported that ultrasound increases the rate of formation of trialkylboranes from Grignard reagents generated in situ

[45]. The desired organic halide is simply mixed with magnesium metal and boron trifluoride and the mixture sonicated.

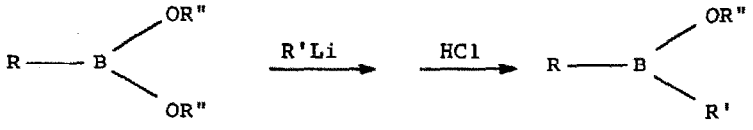


Brown and Cole utilized the classical reaction of a preformed Grignard reagent with boron esters to form simple methylborane derivatives [46].

Organolithium reagents were utilized extensively to prepare organoboranes. Katz reported the synthesis of 1,8-naphthylenediylbis-(dimethylborane) which he calls a Hydride Sponge [47,48].

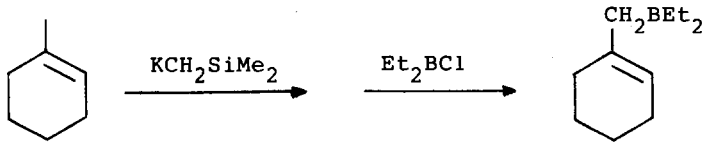


Brown, Cole, and Srebnik reacted organolithium reagents with selected boronic esters in a simple route to borinic esters [49].



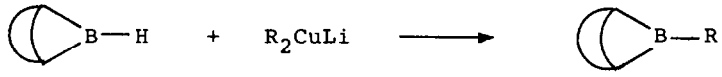
Danheiser and Savoca utilized the reaction of cyclopropyllithium reagents with boranes to prepare cyclopropylborate intermediates which were then oxidized to the corresponding cyclopropanols [50].

Zaidlewicz prepared allylic boranes via the reaction of allylic organopotasssium compounds with B-chloro reagents [51].

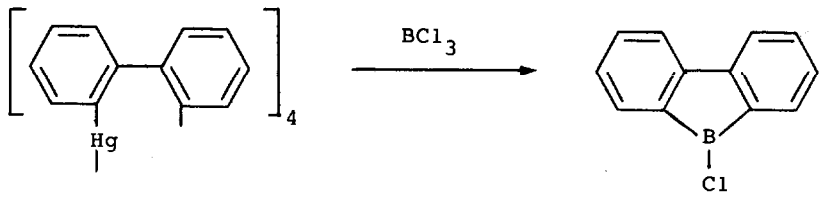


Liou, Yang, and Lin report that ultrasonic irradiation is effective in the formation of triethylborane from ethylaluminum sesquihalide and triethylborate [52]. Synoradzki, Boleslawski, and Lewinski prepared mixed trialkylaluminum reagents in a similar fashion utilizing the reaction of diethylborinic acid with trialkylaluminum reagents [53].

Whitely used a direct reaction of 9-BBN with organocuprates to prepare a series of alkyl 9-BBN reagents [54]. He reported that no selectivity was observed in the transfer reaction when mixed cuprates containing both alkyl and alkynyl groups were used in the reaction.



Narula and Noeth formed borafluorenes via a transmetallation reaction of the appropriate mercury reagent [55].



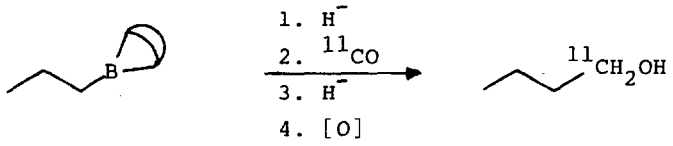
C. CARBON-CARBON BOND FORMATION

1. Homologation

The formation of carbon-carbon bonds via organoborane intermediates was reviewed by Negishi in "Organic Reactions" [56]. The article contains a wealth of information on these reactions as well as on the use of organoboranes to form carbon-heteroatome bonds.

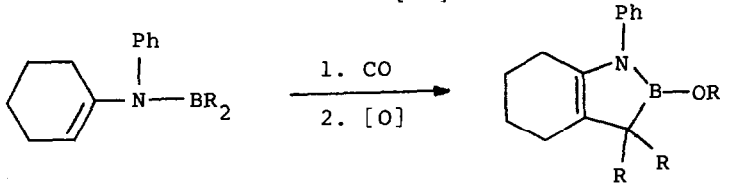
Kabalka, Finn and coworkers utilized the carbonylation

reaction (one of the fundamental homologation reactions) to prepare carbon-11 labeled butanol [57].

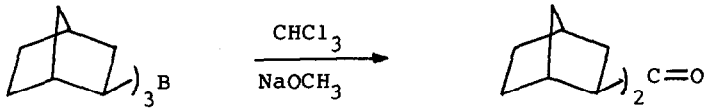


The carbonylation reaction was also used by Kabalka, Finn, Mohammadi, and Sastry to synthesize carbon-13 labeled alcohols and ketones [58]. It is clear that the carbonylation reaction is one of the most cost effective methods for incorporating carbon isotopes.

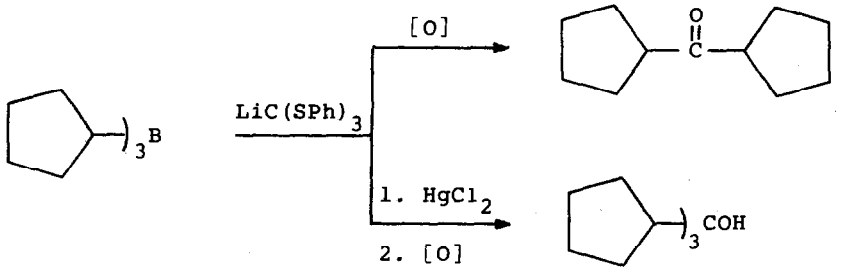
Dorokhov and Cherkasova carbonylated enaminoboranes in a synthetic route to azaborolines [59].



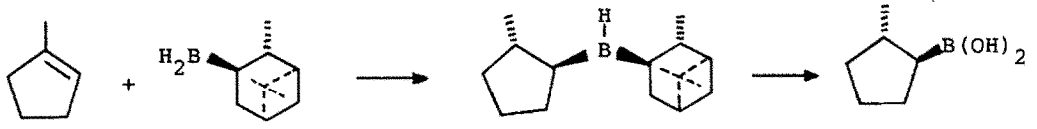
Narayana and Periasamy synthesized dialkyl ketones using a one-carbon homologation reaction which employs chloroform in the presence o a strong base [60].



Pelter and Rao preferred to use lithium tris(phenylthio)methane for homologating trialkylboranes to the corresponding ketones and trialkylcarbinols [61].

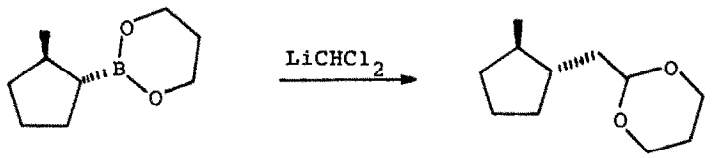


Brown, Imai, Desai and Singaram used a related thio precursor to prepare a series of chiral boronic esters in essentially quantitative enantiomeric excess [62]. The necessary precursor borinates were prepared via an asymmetric hydroboration of the readily available prochiral olefins with subsequent removal of the chiral auxilary.



Matteson reviewed the homologation reactions of chiral boronic esters using dichloromethyllithium [63]. Sadhu and Matteson also reported an efficient method for generating chloromethyllithium and reacting it with borate esters in a simple route to (chloromethyl)-boronate [64].

Brown, Singaram, and their coworkers also investigated the homologation of boronic esters using dichloromethyllithium [65,67]. They report that it is now possible to synthesize a variety of optically active boronic ester, not available by direct asymmetric hydroboration, in essentially 100% enantiomeric excess [67].

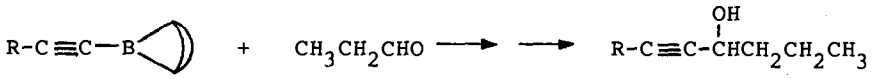


Matteson and Wilson report that α-lithio boronic esters can also be formed from their trimethylstannylboronic esters by reaction with methyllithium [68].

Pelter, Buss, and Pitchford reported a unique variant of the boron-Wittig reaction in which alkyldimesitylborane anions react with aldehydes to yield erythro 1,2-diols [69]. The Pelter group also

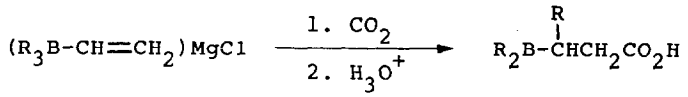
found that the reagent reacts readily with oxiranes to yield the corresponding 1,3-diols [70].

Brown, Molander, Singh, and Racherla note that B-1-alkynyl-9BBN reagents readily undergo addition to aldehydes and ketones to afford the corresponding propargylic alcohols [71]. The borane reagents may contain a variety of functionality and can distinguish between unhindered aldehydes in the presence of ketones.

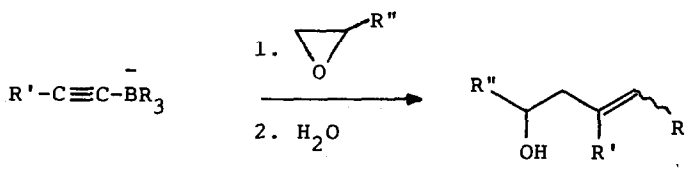


2. Alkenyl- and Alkynylborate Rearrangements

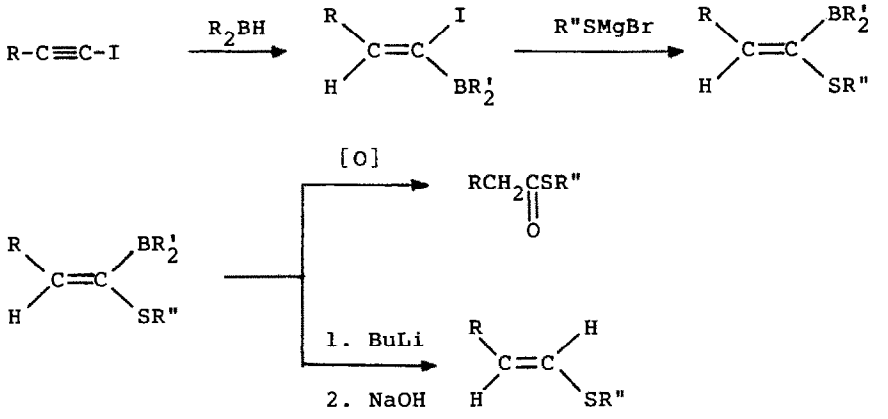
Vinyl- and alkynylborates undergo a wide variety of addition-rearrangement reactions which produce a number of useful synthetic intermediates. For example Deng, Lu, and Xu reports that trialkyl vinylborates react with carbon dioxide to generate carboxylic acid products [72,73].



Mas, Malacria, and Gore report that trialkyborates react with epoxides to yield the corresponding alkenyl alcohols [74].

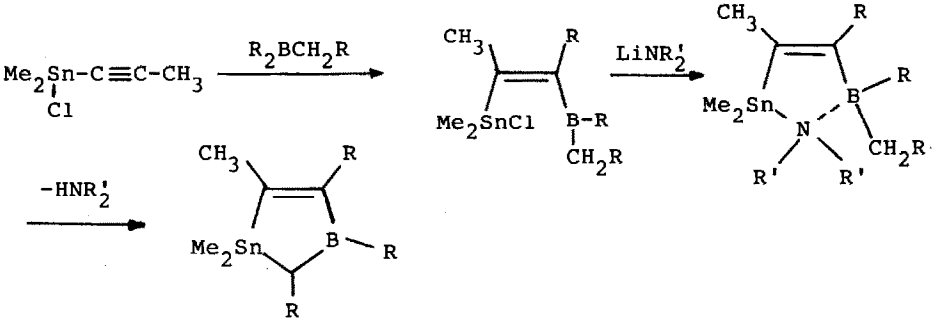


Hoshi, Masayuki, and Arase report that 1-halo-1-alkenyldialkylboranes can be used to prepare both S-alkylthioates [75] and vinyl sulfides [76]. They also reported that conjugated enynes can be

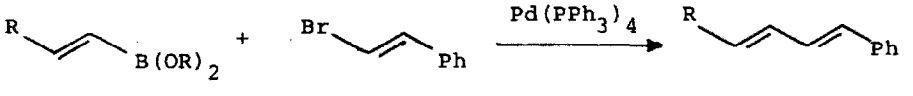


prepared using the same iodoalkenyl starting reagents [77].

Wrackmeyer and Kerschl prepared 2,5-dihydro1-2,5-azoniastannaboratoles [78] and 2,5-dihydro-1,3-stannaboroles via organoboration of functionally substituted alkynylstannane derivatives [79].



Miyaura, Yamada, Suginome, and Suzuki reported a novel and convenient method for the stereo- and regiospecific synthesis of conjugated alkadienes and alkenynes via the palladium-catalyzed cross coupling reaction of vinylboranes with bromoalkenes and bromoalkynes [80].



Bumagin, Ponomarev, and Beletskaya report the cross- and homo-coupling of arylboronates using palladium catalysts [81].

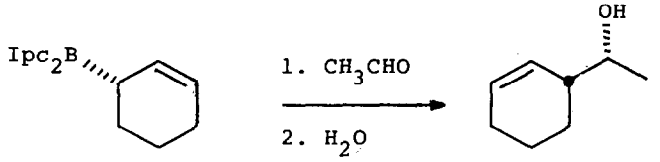
3. Allyl- and Propargylboranes

Rousch, Walts, and Hoong prepared tartrate based allylboronate esters which appear to be the most highly enantioselective allylboronates reported to date [82]. The reagents react with achiral aldehydes to yield homoallylic alcohols in 71-91% enantiomeric excess. Rousch and his coworkers also investigated the stereochemistry of pinacol allylboronates [83] and croytylboronates [84] additions to α, β-dialkoxyaldehydes.

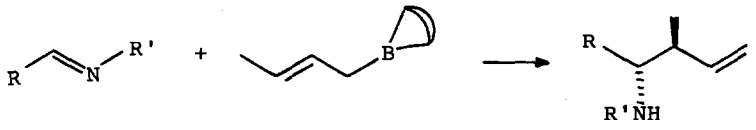
Jadhav, Bhat, Perumal, and Brown found that allyldiisopinocampheylborane reacted smoothly with aldehydes, transferring the allyl group to the carbonyl carbon with high enantioselectivity [85]. The enantioselectivity in the reaction varies with the reaction temperature, increasing considerably with decreasing temperature.

Hoffman and Weidman investigated the stereoselectivity of the addition of (E)-crotylboronates to aldehydes containing an α-methyl branch. The expected Cram products are formed predominently. On the other hand (Z)-crotylboronates produce the anti-Cram products on reaction with the same aldehydes [86]. The sense of 1,2-asymmetrical induction thus depends on the nature of the achiral reagents. Hoffman, Kemper, Metternich, and Lehmeier also investigated the stereoselective reaction of γ-alkoxyallylboronates to aldehydes [87,88].

Brown, Jadhav, and Bhat synthesized a stereochemicaly stable allylic borane, B-2-cyclohexen-1-yldiisopinocampheylborane, which reacted readily with aldehydes to provide 1-(2-cyclohexen)-1-alkanols with 100% erythro selectivity and 94% enantiomeric excess [89].

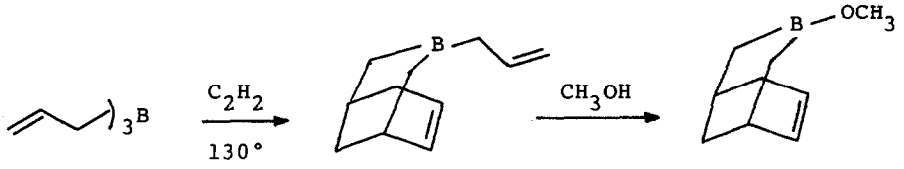


Yamamoto, Komatsu, and Maruyama report that the Cram/anti-Cram selectivity in the reactions of allylmetals with aldehydes and the erythro/threo selectivity in the reaction of substituted allylic organometallic compounds with aldehydes can be controlled by the metal [90]. The group also studied the reaction of simple imines with a variety of allyl metals. The reaction produces the erythro isomer, predominantly, regardless of the metal used [91].



Yamamoto, Ito and Maruyama also prepared a series of amino acid esters with very high enantio- and diasteroselectivity by reaction of 9-allyl-9-BBN compounds with imino esters [92].

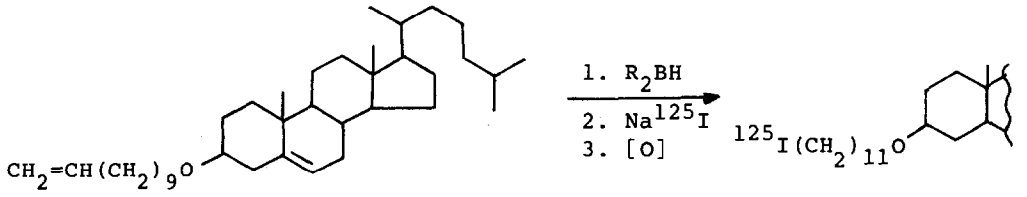
Finally, Bubnov, Grandberg, Grigorian, Kiselev, Struchkova, and Mikhailov reported an allylborane/acetylene condensation followed by a carbonylation/oxidation reaction which lead to interesting bicyclononane derivatives [93].



D. CARBON-HETEROATOM BOND FORMATION

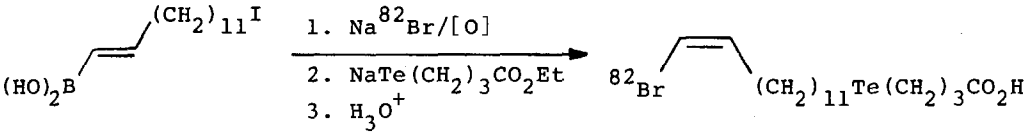
1. Group VII

Kabalka and his coworkers have developed a variety of halogenation methods involving organoboranes which are of utility for radiolabeling organic molecules. The radioiodination reactions were recently reviewed [94]. As an example of the utility of the organoboranes, Kabalka and his coworkers reported the synthesis of γ-[^{125}I]iodoundecyl cholesteryl ether [95].



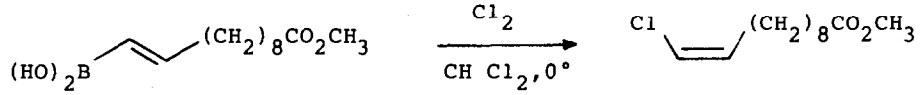
Srivastava, Hay, and Knapp also utilized the iodination method to synthesize radioiodinated iodovinyl phosphonium, arsonium, and ammonium cations for possible use as myocardial imaging agents [96].

Kabalka, Knapp and their coworkers then developed a series of new myocardial agents containing bromine-82 labeled (E)-vinyl bromides as potential myocardial agents [97].



Mikhailov, Schegoleva, Sashkova, and Kiselev investigated the bromination of isopropylboracyclononane under photolytic conditions [98]. They found that the reaction involves either radical substitution at the alpha hydrogen of the isopropyl group or electrophilic cleavage of the B-isopropyl bond depending on the reaction conditions.

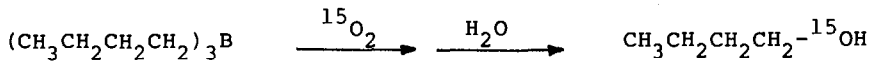
Kabalka and his coworkers also examined the chlorination of organoborane reagents [99]. Vinyl chlorides can be formed stereospecifically and in high yields from the corresponding vinylborane derivatives.



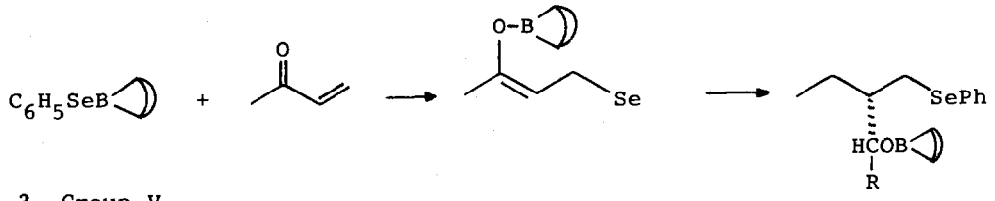
2. Group VI

Kabalka, Lambrecht and their associates used the direct reaction of organoboranes with molecular oxygen to prepare the first example of

an oxygen-15 labeled alcohol as a potential blood flow agent for use in nuclear medical imaging [100].

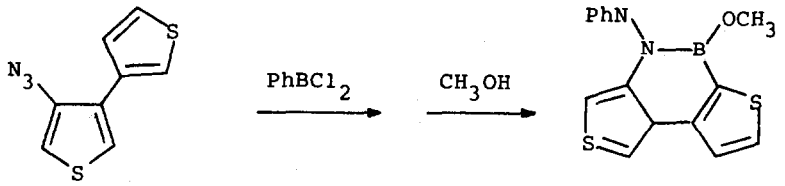


Leonard and Livinghouse reported a novel 1,4-addition of phenylselenoborinates to α,β-unsaturated ketones to produce the corresponding β-selenoboron enolates which could be utilized in aldol condensation reactions [101].



3. Group V

Zanirato found that the reaction between α,β-unsaturated-o-thienyl azides and phenyldichloroborane gave 1,2-dihydro-1-phenyl-2-chloro-thien-[b]-, or -thieno[c][1,2]azaborines in very good yield [102].



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