BORON: BORANES IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1980*

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*Previous survey, see J. Organometal Chem., 207 (1981) 13-65, this section 40-65.

A. INTRODUCTION

The leading contributor to this field has continued to be Professor Herbert C. Brown, whose 1979 Nobel Prize should still be fresh in everyone's memory. Many of other whose work is cited in this survey are former students of Professor Brown. However, an increasing number and diversity of organic chemists are beginning to discover the unique properties and synthetic utility of organoboron compounds. This field once consisted largely of hydroboration chemistry and transformations of the resulting trialkylboranes, but is rapidly expanding to include a more broadly based variety of organoboron compound and wider range of synthetic transformations.

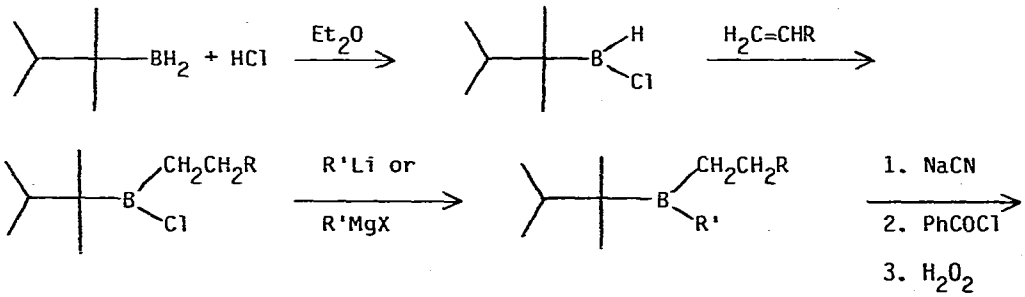
Reviews have not been grouped separately in this survey but are cited with the top to which they belong, with the most general reviews at the end of section B-1.

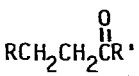
B. BORANE REAGENTS

1. Hydroborating Agents

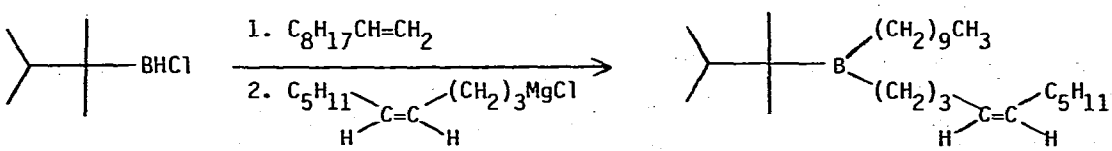
Hydroboration is such a useful reaction that considerable effort continues on the search for new, more selective hydroborating agents. Some are designed to accomplish highly specific objectives.

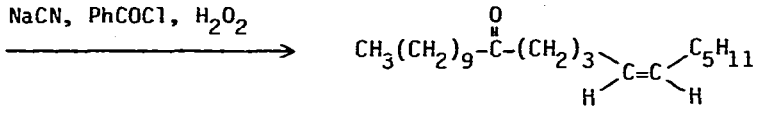
Zweifel and Pearson have reported the preparation of thexylchloroborane and its conversion to mixed thexyldiorganoboranes, which are useful intermediates in ketone syntheses [1].



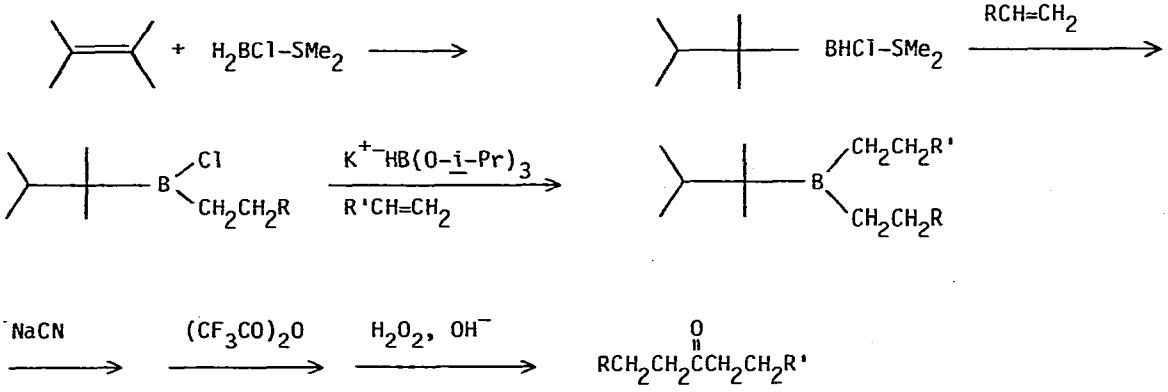


An illustrative application of this chemistry was the synthesis of the Douglas fir tussock moth sex pheromone.

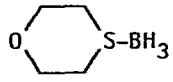




Brown and coworkers have prepared thexylchloroborane-methyl sulfide by hydroboration of tetramethylethylene with $H_2BCl-SMe_2$, and have found the reagent to be more regioselective than thexylborane for hydroboration of olefins [2]. Brown's group has also used thexylchloroborane in a synthesis of ketones [3]. Note that this differs from Zweifel's approach in the use of hydroboration to introduce the last alkyl group.



1,4-Oxathiane-borane is a new convenient hydroborating agent [4]. It is less odoriferous than dimethyl sulfide-borane.



The 1,4-oxathiane remaining after hydroborations with its borane complex can be selectively oxidized by hypochlorite to water soluble sulfoxide without affecting the trialkylborane product [5]. Conversely, the trialkylborane can be oxidized without oxidizing the sulfide if the medium is made sufficiently basic.

Brown and coworkers have reported that $HBCl_2-SMe_3$ hydroborates olefins relatively slowly, and requires an acid catalyst such as BCl_3 in order to complete the reaction within an hour. In contrast, $HBBr_2-SMe_2$ and HBI_2-SMe_2 react much more rapidly and hydroborate olefins such as 1-octene or cis-3-octene within a few hours in refluxing CH_2Cl_2 without any catalyst. The reagents are easily prepared by adding BX_3 to BH_3-SMe_2. The hydroboration products, RBX_2, form distillable complexes with dimethyl sulfide, from which the free RBX_2 may be obtained by treatment with BX_3 [6].

Reaction of $HBBr_2-SMe_2$ with alkynes yields alkenylboron dibromides, which may be hydrolyzed to boronic acids or coupled by the use of methylcopper to form symmetrical dienes [7].

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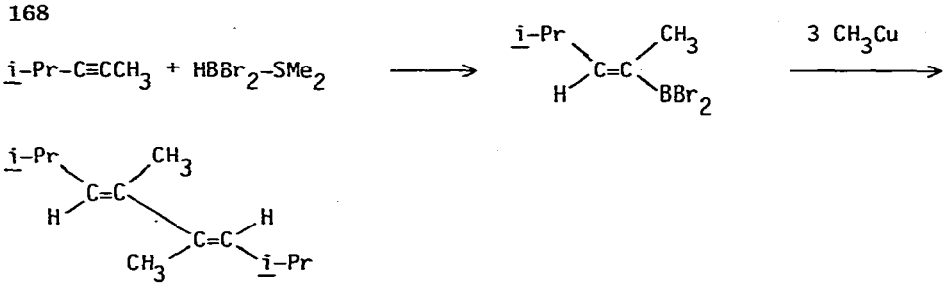


The useful hydroborating agent BH_2Cl-SMe_2 is produced in nearly quantitative yield by refluxing BH_3-SMe_2 with an equimolar amount of CCl_4 [8].

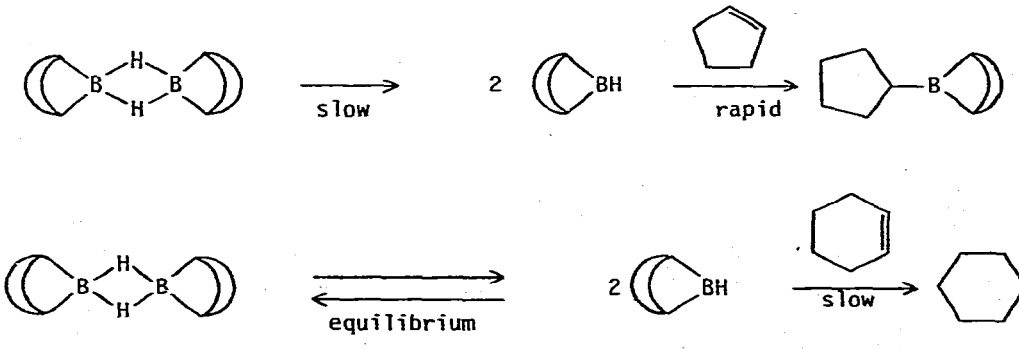
Dicyclopentadienyltitanium dichloride catalyzes the hydroboration of alkenes to lithium alkylborohydrides by $LiBH_4$ [9]. Hydroboration has been carried out with a mixture of $NaBH_4$ and $SnCl_4$ in THF [10]. Among the more exotic hydroborating agents is 6-SB_9H_{11}, which reacts with alkenes or acetylenes at 80°C to form 9-alkyl- or 9-alkenyl-6-SB_9H_{11} [11].

Brown's book, "Hydroboration," has been republished with his Nobel lecture added [12]. The chemistry of 9-BBN has been reviewed [13]. Odom has reviewed organoboron chemistry [14].

2. Mechanism and Theory

Significant additions to our knowledge of the mechanism of hydroboration from both experimental and theoretical points of view have been made during the past year. Structural characteristics of hydroborating agents are also included in this section.

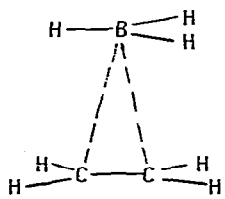
Wang and Brown have used infrared spectroscopy to follow the kinetics of hydroboration with 9-BBN in CCl_4 [15]. With reactive olefins such as cyclopentene, the rate-limiting step is the dissociation of $(9\text{-BBN})_2$ to 2 9-BBN, and subsequent hydroboration of the olefin is rapid, resulting in kinetics first-order in $(9\text{-BBN})_2$ and zero-order in olefin. With less reactive olefins, such as cyclohexene, the dissociation becomes reversible, resulting in kinetics half-order in $(9\text{-BBN})_2$ and first-order in olefin. Olefins giving intermediate kinetics were also found.



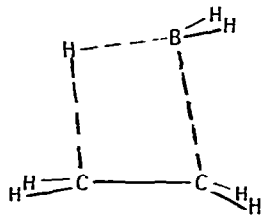
The kinetics of reaction of 9-BBN with 1-hexene, 2-methyl-pentene, 3,3-dimethyl-1-butene, and cyclopentene have been measured [16].

Relative rates of hydroboration of substituted styrenes by 9-BBN in THF have been measured by Vishwakarma and Fry [17]. A Hammett plot using σ^+ gave a value of $\rho = -0.49$, which corresponds to a slight buildup of positive charge on the β-carbon of the styrene, in accord with the idea that the addition is electrophilic. The products are more than 97% β-phenylethanols in all cases.

Calculations on the reaction of BH_3 with C_2H_4 have been carried out at the 4-31G level, which represents substantial improvement in accuracy over previous calculations [18]. The mechanism involves two steps, formation of a π-complex and its subsequent rearrangement to ethylborane. There is no activation energy for formation of the π-complex, which slightly exothermic, and a barrier of a few kcal/mol for rearrangement of this complex to ethylborane. It is expected that further refinement of the calculations will bring the estimated activation energy down to 4 kcal/mol, in good agreement with Fehlner's experimental estimate (JOM 41 (1972) 65-66). The transition state geometry is calculated to be a slightly distorted parallelogram.



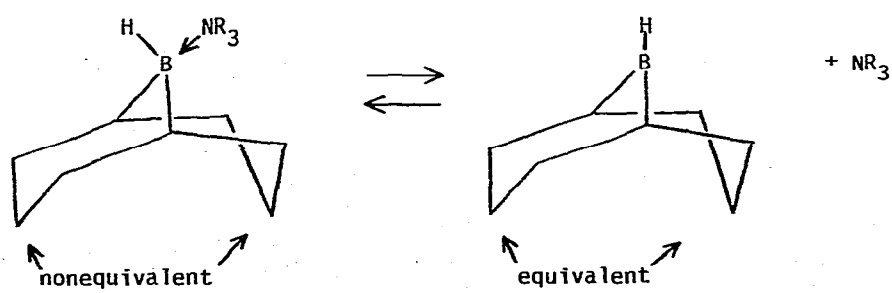
π-complex



transition state

A semiempirical MO study of the mechanism of hydroboration has been published [19]. Molecular orbital calculations on B_2H_6 have indicated that electron correlation is a major contributing factor to the dissociation energy [20].

Brown and Wang have studied the association of 9-BBN with a series of amines of differing steric requirements by the use of ^{13}C NMR [21]. The symmetry of the 9-BBN system is diminished by complexing, and systems were found in which the amine complexes either did not dissociate, dissociated rapidly and reversibly, were not favored at equilibrium, or were not formed detectably, depending on the steric bulk of the amine.



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9-Substituted-9-BBN derivatives typically show ^{13}C NMR spectra indicating that the 9-BBN group has the full symmetry expected [22]. The presence of a chiral substituent on the boron introduces corresponding diastereotopic nonequivalence in the 9-BBN ring carbons, and pyridine complexes of 9-R-9-BBN show nonequivalence between the two sides of the 9-BBN unit.

3. Trialkylborohydrides

Lithium triethylborohydride is an exceptionally powerful reducing agent, surpassing even lithium aluminum hydride in some respects. Brown, Kim, and Krishnamurthy have reported the use of $LiHBEt_3$ to reduce carbonyl compounds, acid anhydrides and chlorides, esters, lactones, epoxides, tertiary amides to alcohols, and various other functional groups [23]. Lithium triethylborohydride is a particularly effective reagent for reducing alkyl halides to alkanes [24]. Primary iodides are reduced quantitatively in minutes at 25°C, bromides in a few hours. Cyclohexyl iodide is 63% reduced in 24 hr.

Lithium trialkylborohydrides are readily formed by reaction of trialkylboranes with t-butyllithium as the hydride source [25].

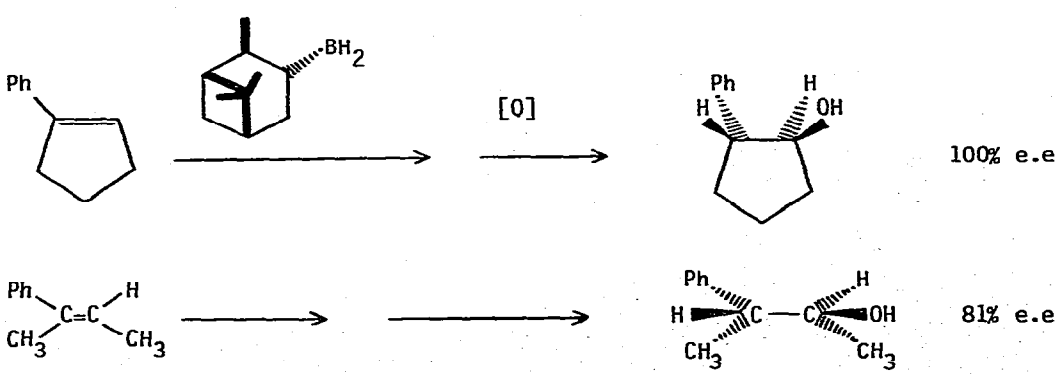
$$R_3B + (CH_3)_3CLi \longrightarrow R_3BH^- Li^+ + (CH_3)_2C{=}CH_2$$

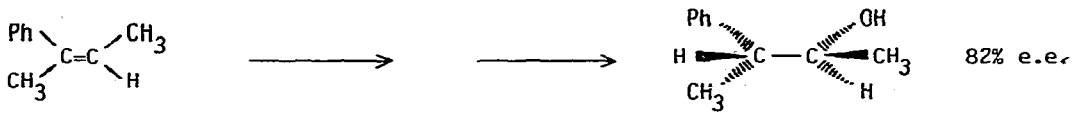
The reaction proved successful not only with the usual alkyl and cycloalkyl groups, but also with hindered boranes such as B-Me-9-BBN, B-isopinocampheyl-9-BBN, and thexyllimonylborane.

The crystal structure of $(NaHBEt_3)_4$-Et_2O has been determined [26]. The sodium and hydride hydrogen atoms occupy alternate corners of a distorted cube, with each hydride coordinated to one boron and three sodium atoms.

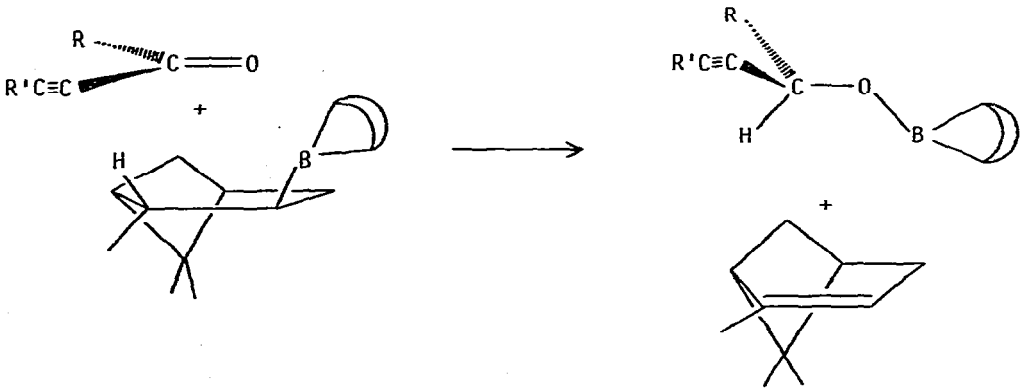
4. Asymmetric Hydroborations and Reductions

Monoisopinocampheylborane hydroborates phenyl-substituted tertiary olefins with a high degree of chiral specificity, yielding alcohols after oxidation having 81-100% enantiomeric excess (e.e.) [27].

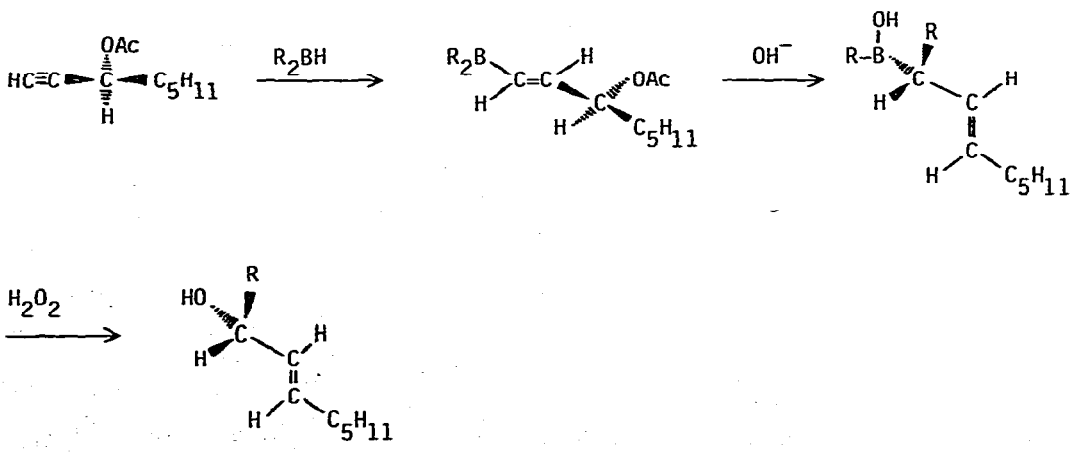




Midland and coworkers have reported that B-3-pinanyl-9-borabicyclo[3.3.1]nonane reduces α,β-acetylenic ketones to alcohols with high stereoselectivity [28]. Enantiomeric excesses were in the range 73-100%. The acetylenic group is the sterically smaller substituent in this series of reactions. This asymmetric reduction has also proved successful with the ketone group of $RCOC{\equiv}CCO_2R'$ [29].



Midland and Preston have hydroborated S-3-hydroxy-1-octynyl acetate, which is readily available by reduction of the corresponding ketone with dipinanylborane, with diethylborane or dicyclohexylborane, then rearranged the product by treatment with base and oxidized the borane to the allylic alcohol [30]. The product was all trans, and the predominant mode of alkyl migration was anti, yielding material having 50-74% enantiomeric excess.



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Factors involved in chiral selectivity in hydroboration and other reactions have been discussed [31].

Asymmetric reductions of ketones have been accomplished with reagents prepared from sodium borohydride, ketal derivatives of glucose, and carboxylic acids [32,33]. Stereoselectivities were in the range 12-64% e.e.

Directions for the hydroboration of α-pinene and cleavage of the resulting diisopinocampheylborane with hydroxylaminesulfonic acid to form 3-pinamine have been published in Organic Syntheses [34].

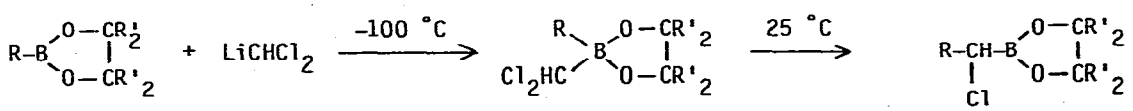
The preparation of asymmetric trialkylborohydrides has been cited in section B-3 [25]. Other types of asymmetric synthesis are included in sections C-1, C-4, and C-5, hydroboration of asymmetric natural products and control of relative chirality by hydroboration are covered in part D-1.

C. CARBON-CARBON BOND FORMATION

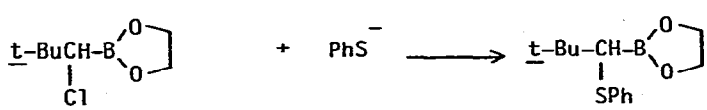
1. Homologation via Borate Complexes

This section includes formation of carbon-carbon bonds by rearrangement of alkyl(α-haloalkyl)borate complexes, carbonylations, and cyanidations. Examples of carbonylation and cyanidation in ketone syntheses have already been cited in section B-1 [1,3]. Oxidative rearrangements of alkyl(alkenyl)borate complexes, covered in sections C-2 and C-3, are mechanistically somewhat related. These types of reactions show great promise of synthetic utility, and together with allylboron and enol borinate condensations (sections C-4 and C-5) constitute the fastest-growing field of applications of organoborane chemistry to organic synthesis.

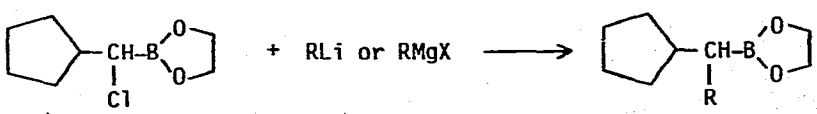
Matteson and Majumdar have reported the efficient homologation of boronic esters to α-chloro boronic esters with dichloromethyllithium [35]. The process involves the same type of borate intrmediate as the reaction of RLi with $Cl_2CHB(OR')_2$ to form $R\text{-}CHCl\text{-}B(OR')_2$, first reported by Rathke, Chao, and Wu [JOM 122 (1976) 145]. However, starting from $RB(OR')_2$ and Cl_2CHLi opens up a variety of new synthetic possibilities.



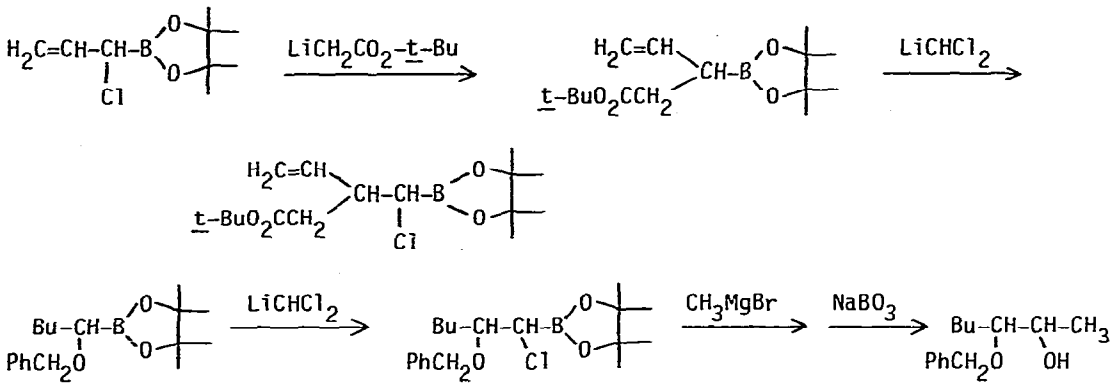
R = primary, secondary, tertiary alkyl, cycloalkyl, vinyl, allyl, benzyl; R' = H, CH_3



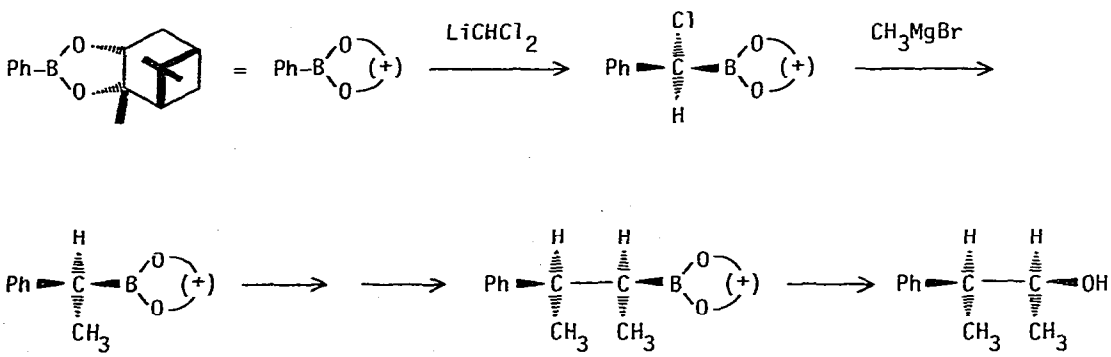
and similar displacements



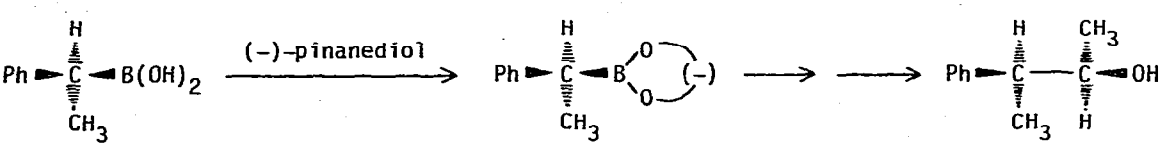
R = Ph, Bu, cyclohe



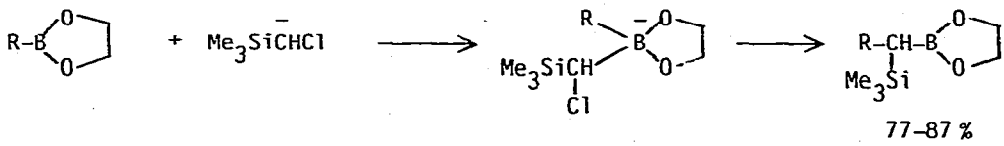
Extension of this chemistry to pinanediol esters by Matteson and Ray has led to a promising new type of directed chiral synthesis [36]. Homologation of (+)-pinanediol esters was found to give S-α-chloro boronic esters having high (83-97%) diastereoisomeric purity, except where the migrating group was methyl (74%). The potential utility of this approach was demonstrated by the synthesis of both separate diastereoisomers of 3-phenyl-2-butanol in high purity, chosen because they had already been thoroughly characterized by Cram for his classical studies of nonclassical ions.



1. BCl_3
2. H_2O

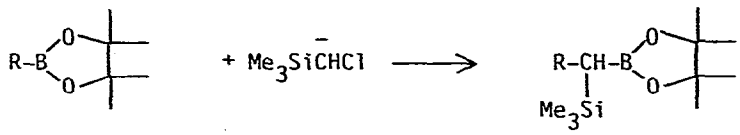


Boronic esters are homologated by $Me_3SiCHClLi$ to α-trimethylsilyl boronic esters in high yields [37].



77–87 %

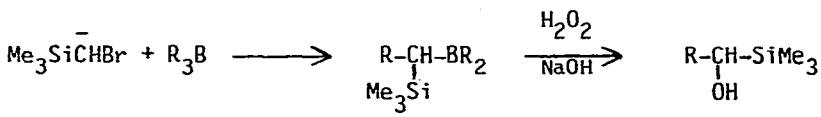
R = n-Bu, sec-Bu, cyclopentyl, cyclohexyl, $PhCH_2$, $PhSCH_2$

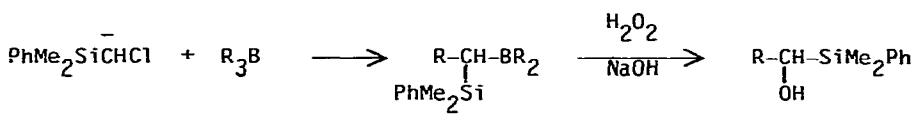


75–78 %

R = $CH_3CH{=}CH{-}$, $CH_2{=}CH{-}CH_2{-}$

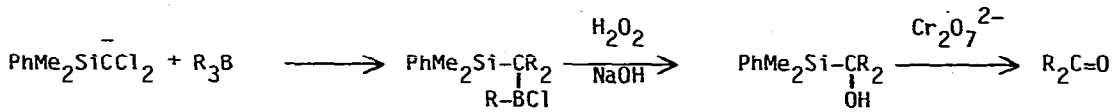
Larson and coworkers have found that trialkylboranes react with $Me_3SiCHBrLi$ or $PhMe_2SiCHClLi$ with homologation of one of the B-alkyl groups to form an α-silyl borane intermediate, which may be oxidized to the corresponding α-silyl alcohol [38].





R = primary, secondary, or cycloalkyl

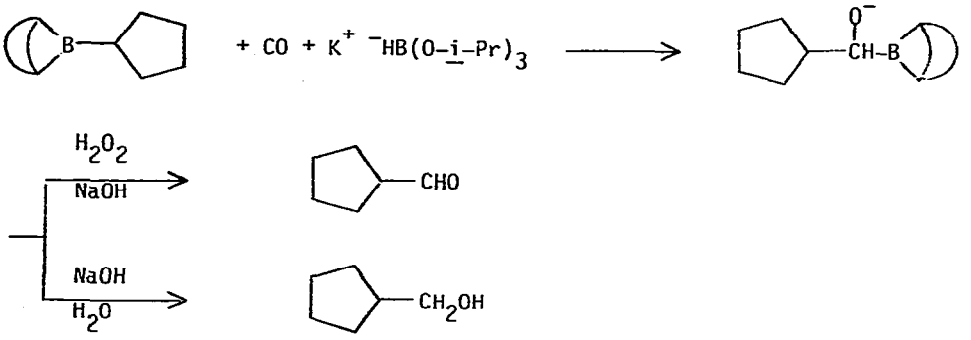
Two alkyl groups are transferred from R_3B in the reaction with $PhMe_2SiCCl_2Li$, leading to a synthesis of symmetrical silyldialkylcarbinols or ketones [39].



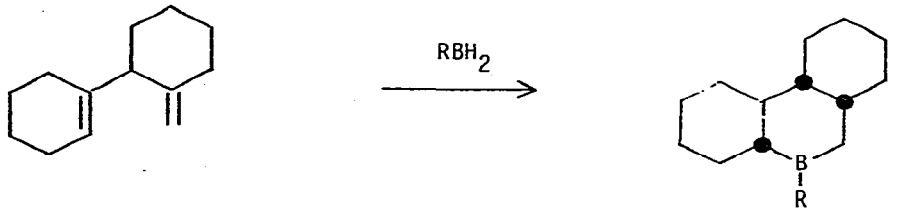
A simple homologation of 9-R-9-BBN to 9-RCH_2-9-BBN by way of carbonylation and reduction has been reported by Brown, Ford, and Hubbard [40].

R = n-octyl, cyclopentyl, cyclohexyl, cyclooctyl, exo-2-norbornyl, trans-2-methyl-cyclopentyl.

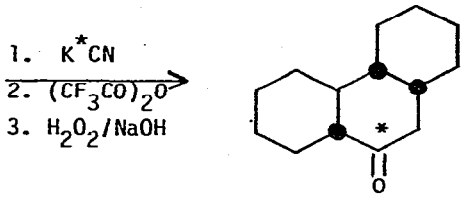
$KHB(O\text{-}\underline{i}\text{-}Pr)_3$ has been found to be a superior reagent for reductive carbonylation of trialkylboranes [41].



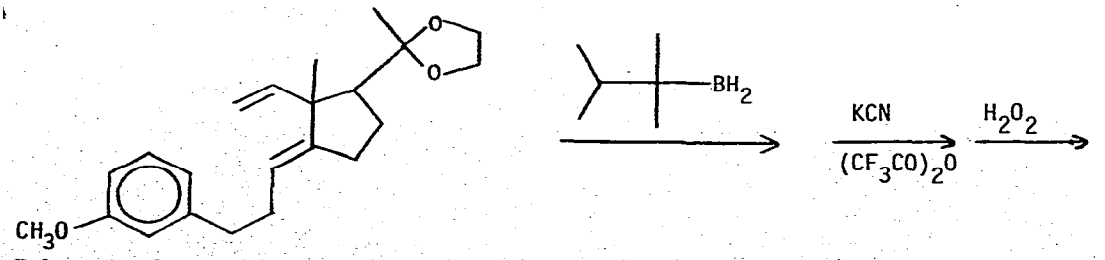
Kabalka has used the reaction of cyclic trialkylboranes with $KCN/(CF_3CO)_2O$ to introduce ^{13}C and ^{14}C labels into cyclic ketone carbonyl groups [42].



R = thexyl



Hydroboration–cyanidation has been used as a key step in a total synthesis of (±)-*estrone methyl ether* [43].



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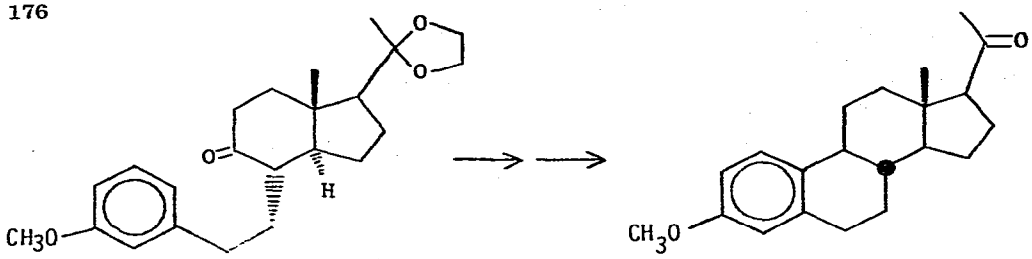
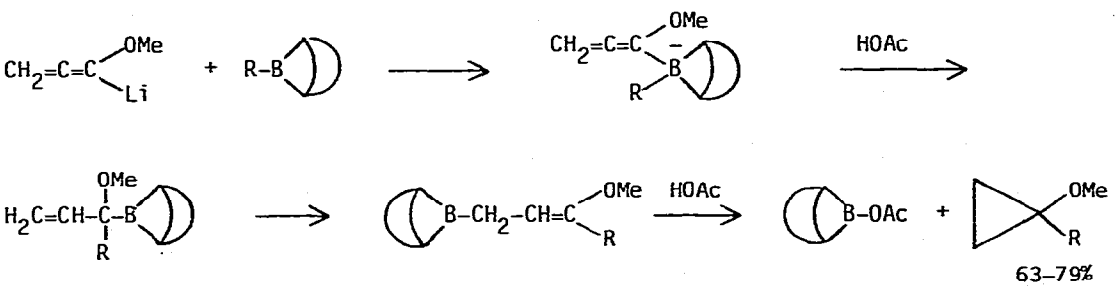


The conversion of 9-BBN to bicyclo[3.3.1]nonan-9-one by treatment with CH_3OCHCl_2 and Et_3COLi followed by oxidation has been described in detail in Organic Syntheses [44].

2. Alkenylborate Rearrangements

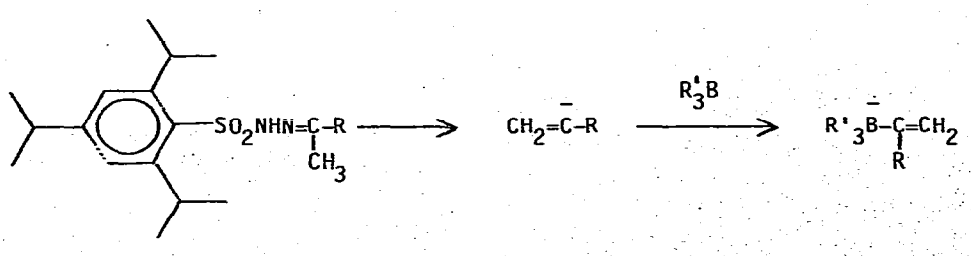
Alkyl(alkenyl)borates react with various electrophiles or oxidizing agents to join the alkyl and alkenyl groups, generally with a high degree of stereochemical control. This section first covers rearrangements initiated by protons, iodine, or other electrophiles, followed by rearrangements catalyzed by transition metals. Examples have already been cited in sections B-1 [7] and B-4 [30].

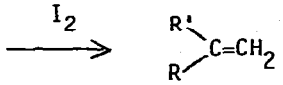
A group led by Suzuki has found that reaction of 9-alkyl-9-BBN's with 1-lithio-1-methoxyallene followed by rearrangement with acetic acid yields 1-alkyl-1-methoxy-cyclopropanes [45].



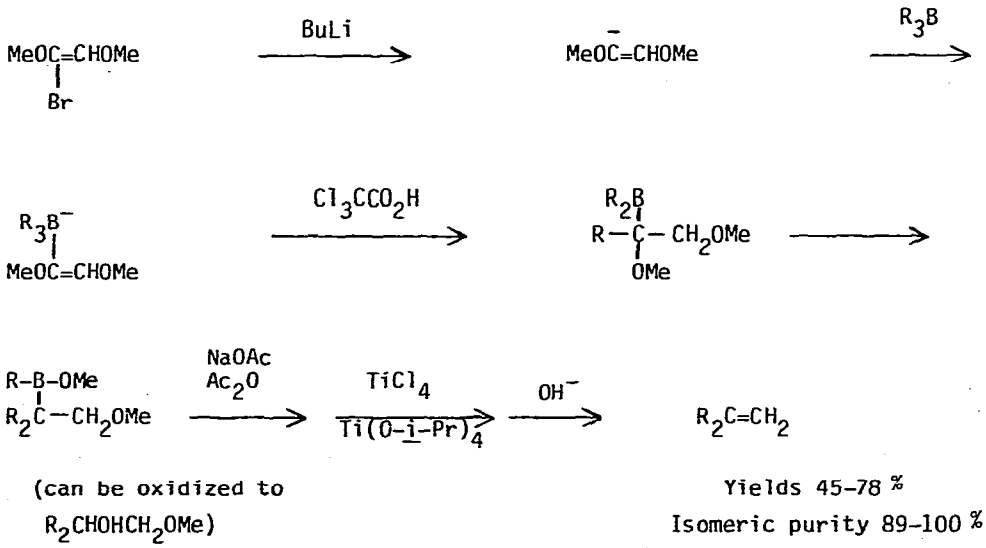
R = n-alkyl, cycloalkyl, exo-norbornyl, trans-2-trimethylsilyloxycyclohexyl

Reactions of anions from trisylhydrazones of methyl ketones with trialkylboranes has yielded vinyltrialkylborates, which rearrange on treatment with iodine to form 1,1-dialkylethenes [46].



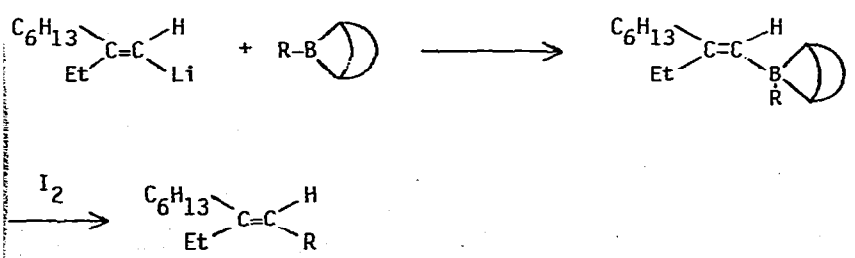


1,1-Dialkylethenes have been prepared from 1,2-dimethoxyethenyllithium and organoboranes by treatment with Cl_3CCO_2H followed by $NaOAc/Ac_2O$ and $TiCl_4/Ti(O\text{-}\underline{i}\text{-}Pr)_4$ [47].



R = <u>i</u>-Bu, <u>s</u>-Bu, <u>n</u>-pentyl, cyclopentyl, <u>n</u>-hexyl, cyclohexyl

Levy and coworkers have found that 9-alkyl-9-BBN reacts with alkenyllithiums followed by iodination to provide a stereocontrolled synthesis of trisubstituted olefins [48].



This stereochemical outcome is not what would have been expected on the basis of the behavior of <u>trans</u>-alkenylboranes toward I_2 and NaOH, but hydroxide is not present during the iodination in the present case.

Reactions of (1-halo-1-alkenyl)dialkylboranes with lead(IV) acetate or $(AcO)_2IPh$ have been studied by Suzuki's group [49].

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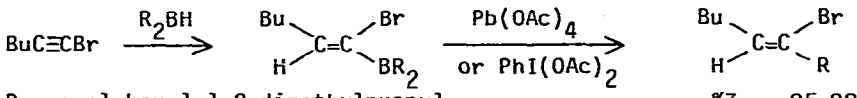
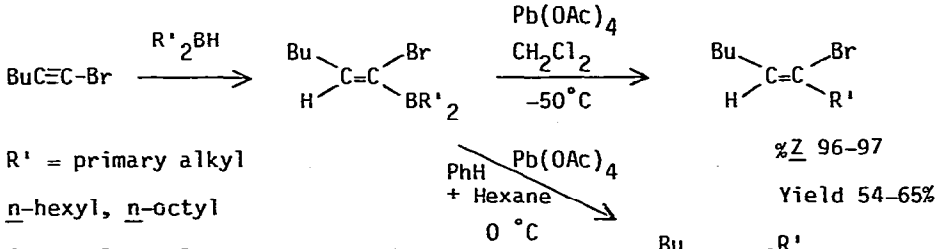


R = cyclohexyl, 1,2-dimethylpropyl

%Z 95-98

Yield 40-58%



R' = primary alkyl

n-hexyl, n-octyl

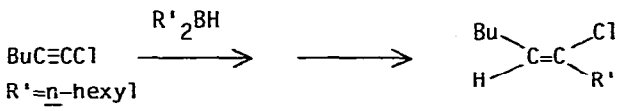
2-methylpentyl

%Z 96-97

Yield 54-65%

%E 90-96

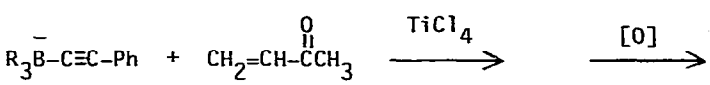
Yield 35-55 %

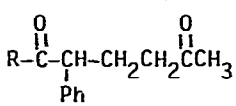


R'=n-hexyl

Z isomer, independent of conditions

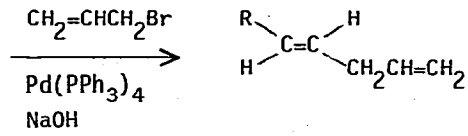
Lithium 1-alkynyltrialkylborates undergo rearrangement and Michael addition to methyl vinyl ketone in the presence of titanium tetrachloride [50].



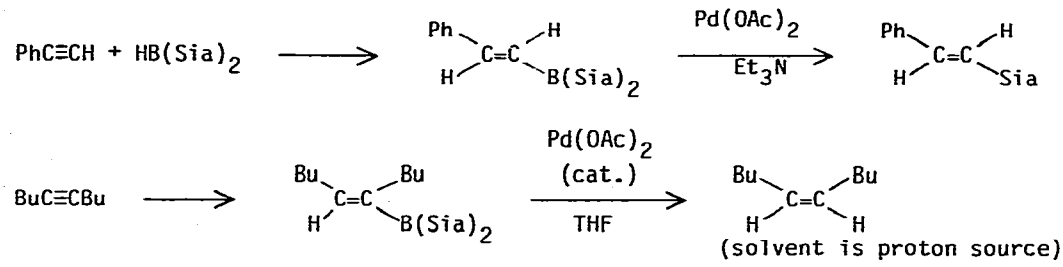


R = alkyl; similar results with $R_3B-C\equiv C(CH_2)_4CH_3$

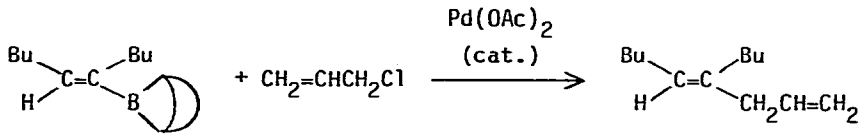
Alkenyldisiamylboranes and allyl or benzyl halides have been coupled with $Pd(PPh_3)_4$ to form alkenes [51].



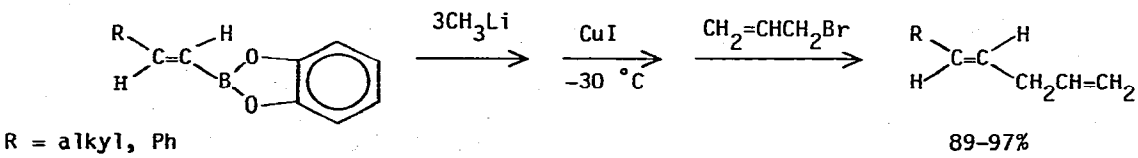
Alkenyldialkylboranes derived from terminal acetylenes are rearranged by an equimolar amount of palladium acetate and triethylamine to form E-olefins [52]. Alkenyldialkylboranes derived from internal acetylenes are cleaved by even a catalytic amount of palladium acetate to form Z-olefins.



If 9-BBN is used as the hydroborating agent, the internal alkenylborane can be cross coupled with allyl chloride.



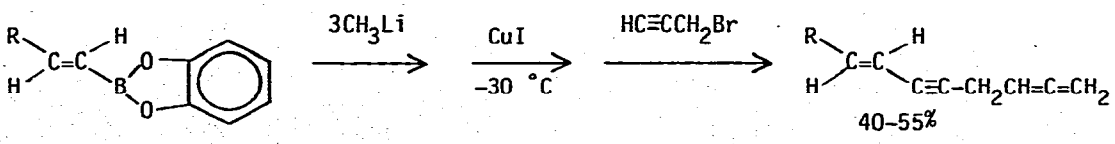
Catechol alkeneboronic esters have been treated with methyllithium and cross coupled with allylic bromides in the presence of CuI (53].



R = alkyl, Ph

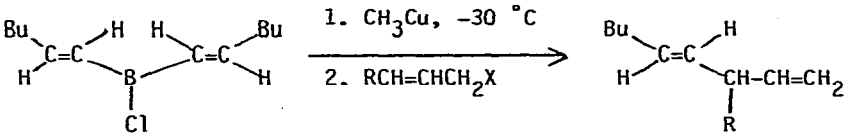
89-97%

Crotyl bromide gave a mixture of allylic isomers (46:52). Propargyl bromide gave more complex condensation products.



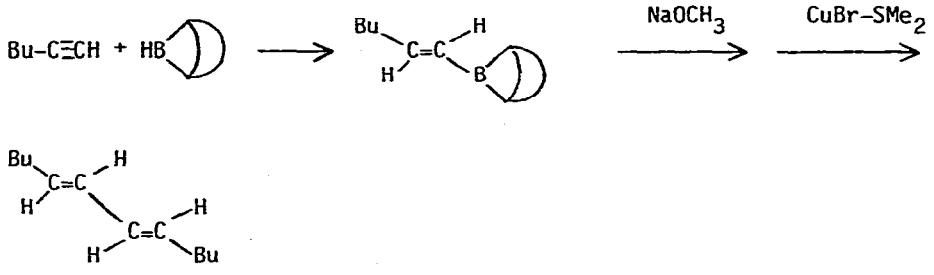
40-55%

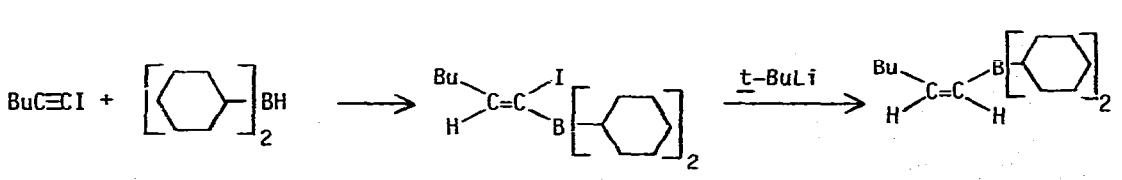
Yatagai has found that treatment of dialkenylchloroboranes with 3 mols of methylcopper at -40 to -30 °C followed by allylic halides yields 1,4-dienes [54]. The predominant product (73-86%) is that formed with allylic inversion. Alkenyl-9-BBN reacted similarly at 0 °C, with 87-92% allylic inversion. It was also found possible to couple butyl iodide with the organocopper intermediate in the presence of a nucleophilic cocatalyst such as $P(OEt)_3$ or PhSLi. Yields were generally 50-60%.

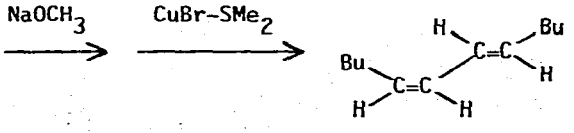


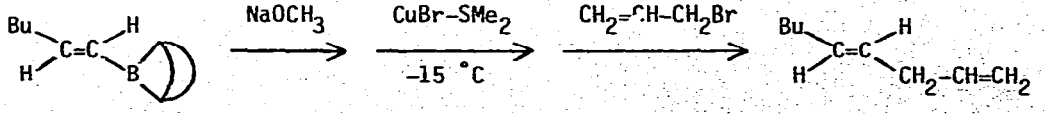
R = H, Ph, CH_3; X = Cl, Br (major isomer)

Hydroboration of acetylenes with 9-BBN followed by reaction of the resulting alkenylboranes with $NaOCH_3$ followed by $CuBr\text{-}SMe_2$ at 0 °C has been found by Campbell and Brown to yield symmetrical E,E-dienes [55]. A Z,Z-diene has been obtained by hydroborating 1-iodohexyne with dicyclohexylborane, reducing the iodide with t-butyllithium, and treating with $NaOCH_3$ followed by $CuBr\text{-}SMe_2$. By lowering the temperature to -15 °C, the organocopper intermediate can be stabilized and captured with allyl bromide to form 1,4-dienes in a stereospecific manner [56].

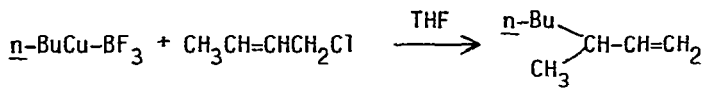


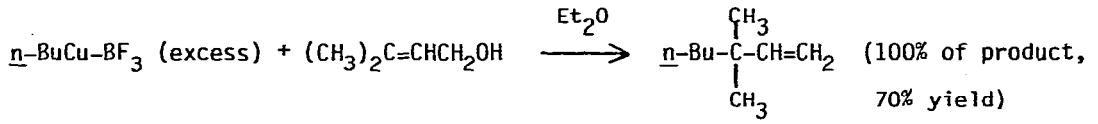




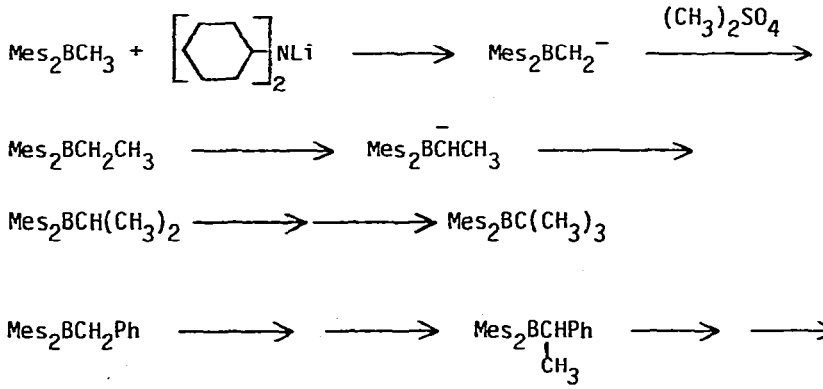


Yamamoto and coworkers have published a full account of the reactions of $RCu\text{-}BF_3$ reagents with allylic halides, acetates, and alcohols, which generally give high ratios of α-attack of R on the allylic group, regardless of the substituent pattern [57] (see JOM, 180 (1979) 48). Similarity to the behavior of $RCH{=}CHBR'^-_3Cu^+$ was noted, and it was suggested that the reaction may involve $RBF^-_3Cu^+$ as an intermediate.



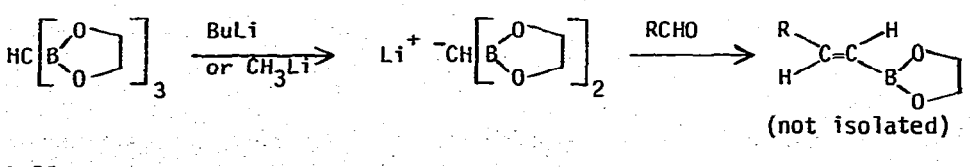


Dimesitylalkylboranes are deprotonated by lithium dicyclohexylamide in THF and the resulting anions have been methylated with dimethyl sulfate [58].



Mes = 2,4,6-trimethylphenyl

An efficient homologation of aldehydes, RCHO to RCH_2CHO, or of ketones to aldehydes, R_2CO to R_2CHCHO, utilizes $LiCH(BO_2C_2H_4)_2$ [59].



$NaBO_3$, pH 9–11 → RCH_2CHO

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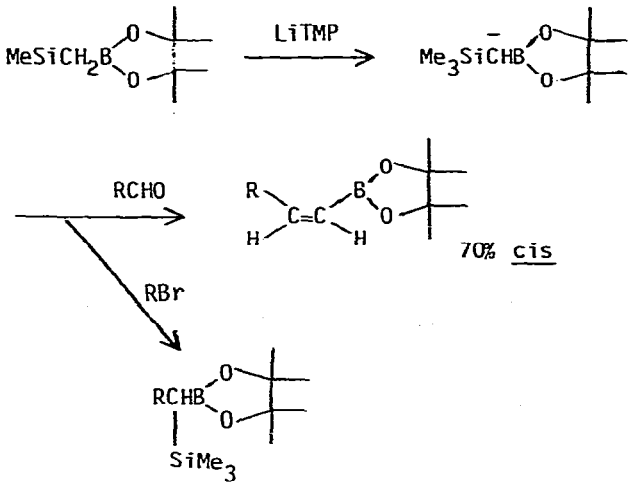
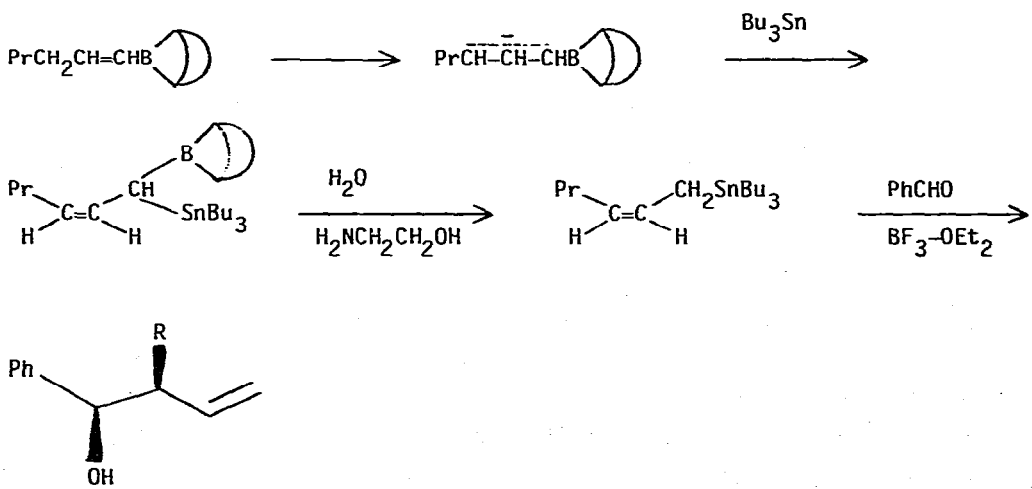
Deprotonation of pinacol trimethylsilylmethaneboronate has been accomplished with lithium 2,2,6,6-tetramethylpiperidide and the resulting anion has been alkylated with alkyl halides or condensed with aldehydes to yield predominantly Z-alkeneboronic esters [60].



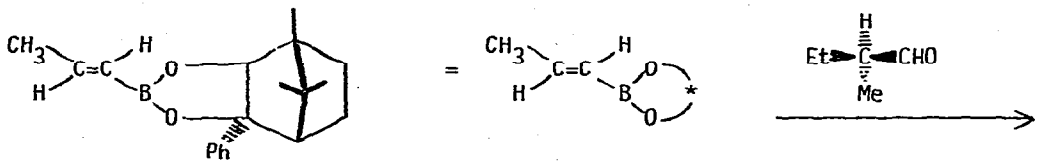
Allylic anions derived from 1- or 2-alkenyl-9-BBN react with Me_3SiCl or Bu_3SnCl at the 1-position to form almost exclusively Z-allylmetal derivatives, which are useful in erythro-selective coupling with aldehydes [61].



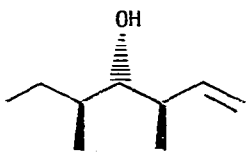
4. Allylboron compounds

The use of allylboronic esters in stereocontrolled synthesis has been developed by R. W. Hoffmann and coworkers. Related chemistry has just been cited in the preceding section [61].

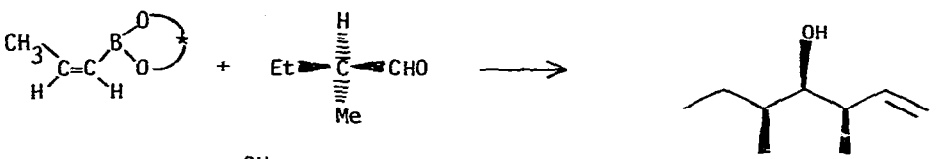
Hoffmann and Zeiss have been used the allylboronic ester reaction with aldehydes to achieve chiral synthesis of alcohols useful in natural products synthesis [62].



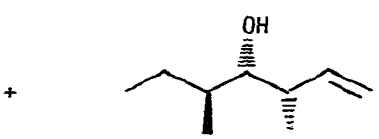
92% of product



8% of product

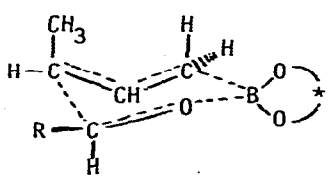


56% of product



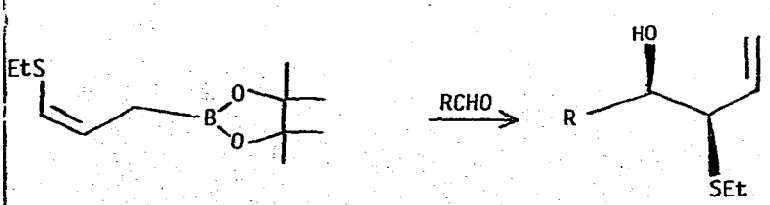
44% of product

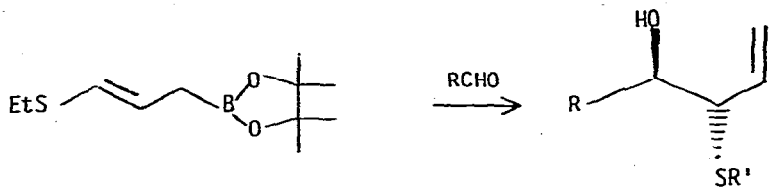
Transition state:



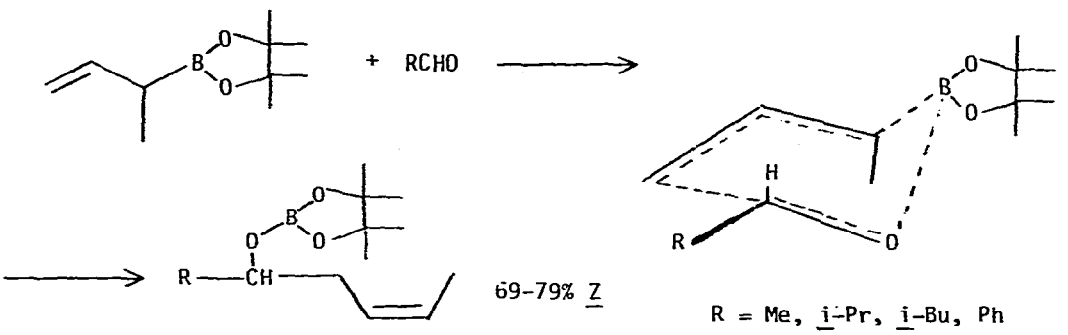
(derived from cis boronic ester)

Z and E-γ-alkylthioallylboronic esters react highly diastereoselectively with aldehydes [63].

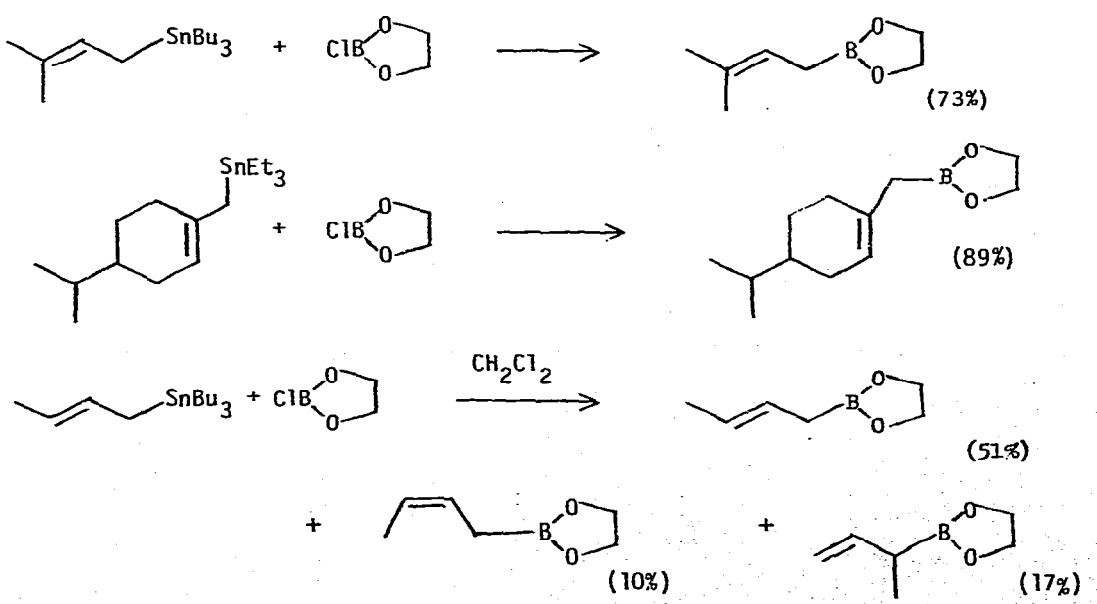




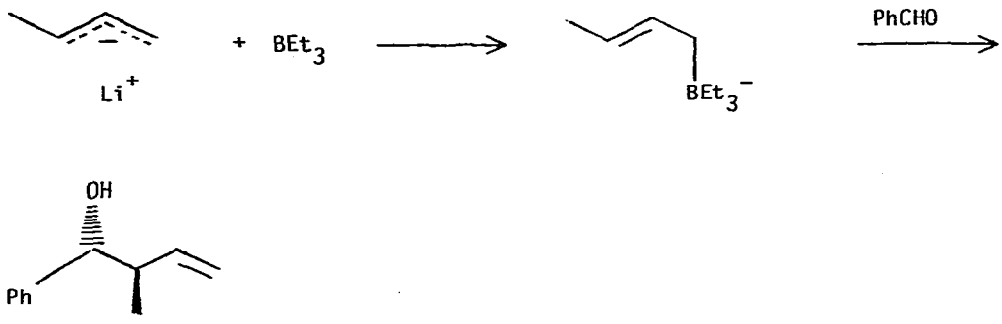
Reaction of 1-butene-3-boronic esters with aldehydes yields mixtures of E-and Z-homoallylic alcohols [64]. The Z-isomer predominates if sterically hindered boronic esters such as the pinacol ester are used. Interference by the pinacol group forces the α-methyl substituent into an axial conformation in the transition state.



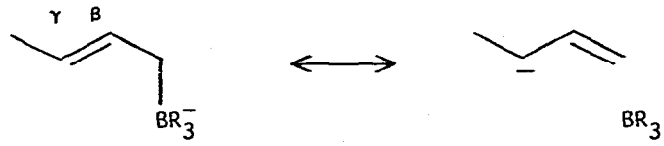
Allyltrialkyltin compounds react with 2-chloro-1,3,2-dioxaborolane to form allylboronic esters [65].



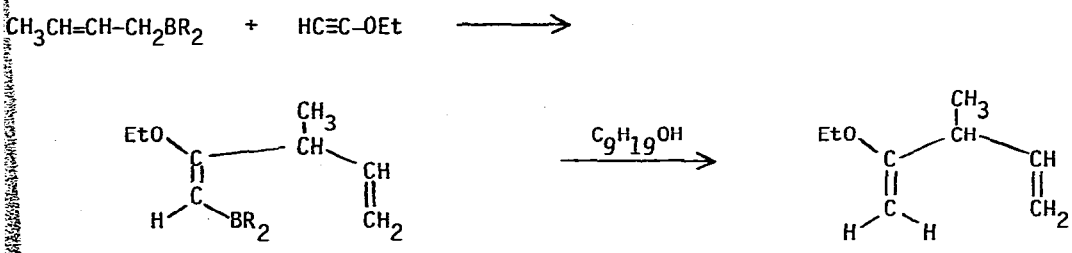
Reaction of crotyllithium with triethylborane or tributylborane to form the borate complex followed by reaction with an aldehyde results in a highly threo- selective condensation [66].



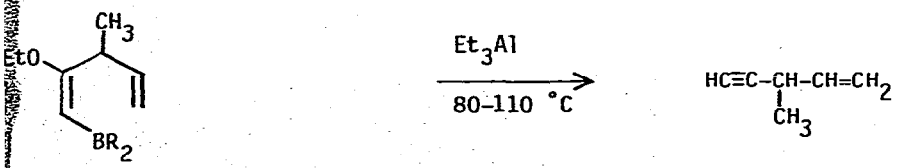
Carbon-13 NMR spectra of allyltrialkylborate complexes show shielding of the allylic γ-carbons and deshielding of the β-carbons, an effect consistent with C-B bond hyperconjugation with the allylic system [67].



Allyldialkylboranes add to ethoxyacetylene [68].



The trialkylborane-ethoxyacetylene adducts can be converted to allylacetylenes [69].



Further examples of related allylborane chemistry are included in section C-6 on boraadamantane chemistry.

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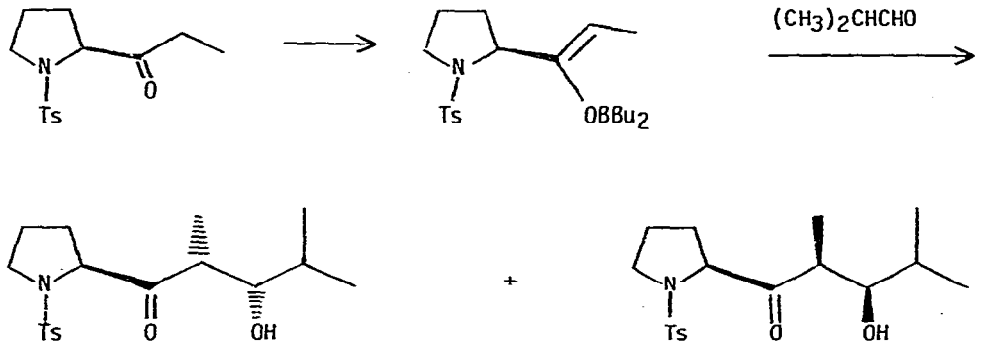
5. Enol Borinates

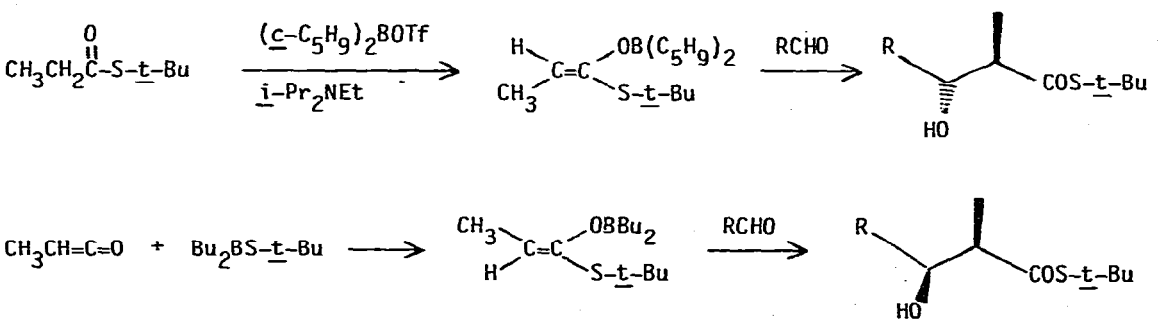
Boronic esters of enols or dialkyl(alkenoxy)boranes are rapidly becoming recognized as being among the most useful of intermediates for stereodirected aldol condensations, which are useful in syntheses of macrolide antibiotics.

Evans and Taber have reported the use of chiral boron enolates in directed chiral synthesis [70]. The most favorable case is illustrated. Other examples ranged from 45-83% content of the isomer corresponding to the one illustrated as the major isomer.



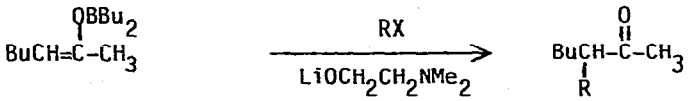
Major isomer (> 97%) Minor isomer (< 3%)

Hirama and Masamune have described the stereoselective enolate condensation of aldehydes with the E-and Z-dialkylboron enolates of CH_3CH_2COS-t-Bu [71].



The preparation of dibutylboron triflate and 9-BBN triflate has been described [72]. These reagents react with enolizable ketones in the presence of tertiary amines to generate one regioisomer of the enolate selectively, and the enolates condense with aldehydes with high regio and stereoselectivity.

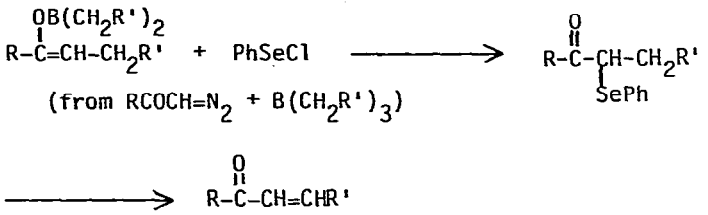
Hooz and Oudenes have found that addition of $LiOCH_2CH_2NMe_2$ to enol borinates permits alkylation [73]. Both the reaction used to form the enol borinate and the alkylation are regiospecific.



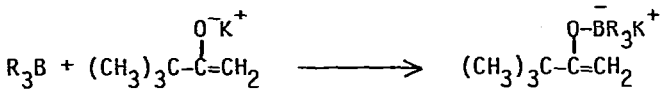
(from $N_2CHCOCH_3$ and BBu_3)

R = CH_3, $PhCH_2$, $CH_2{=}CHCH_2$, C_2H_5

Enol borinates react with PhSeCl at -78 °C to form α-phenylselenyl ketones, which are readily converted to α,β-unsaturated ketones [74]. The over-all synthesis is regiospecific.



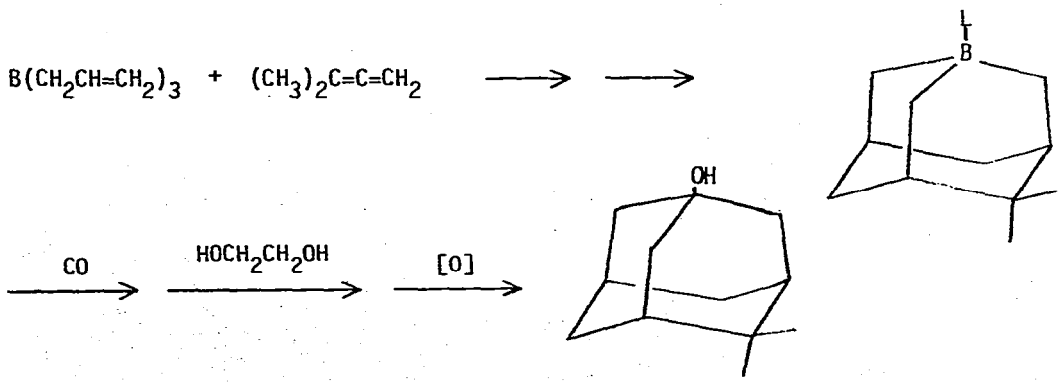
Lithium enolates from ketones fail to react with trialkylboranes, but the potassium enolates readily form borate complexes [75].



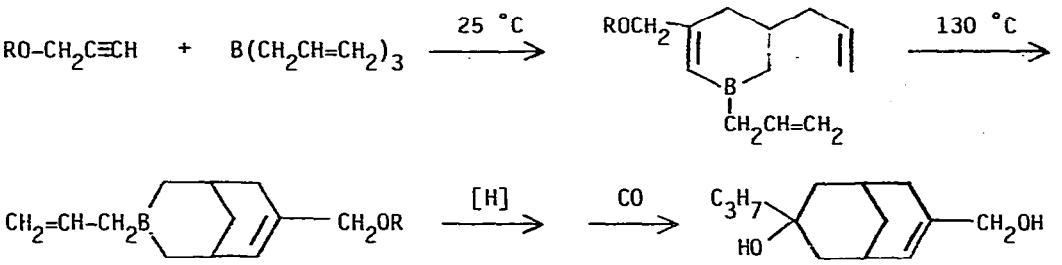
6. Boraadamantanes

This field has been created by Mikhailov and coworkers, who discovered that trialkylboranes can be elaborated with allenic or acetylenic reagents to form adamantane-like structures having a tetracoordinate boron at one apex. The applicability of this organoborane chemistry to synthesis is not as general as most of the other topics discussed in this review, but it does provide a novel route to adamantane derivatives by borane carbonylation, as well as other cyclic compounds. Mikhailov has reviewed his work in this field recently in English [76].

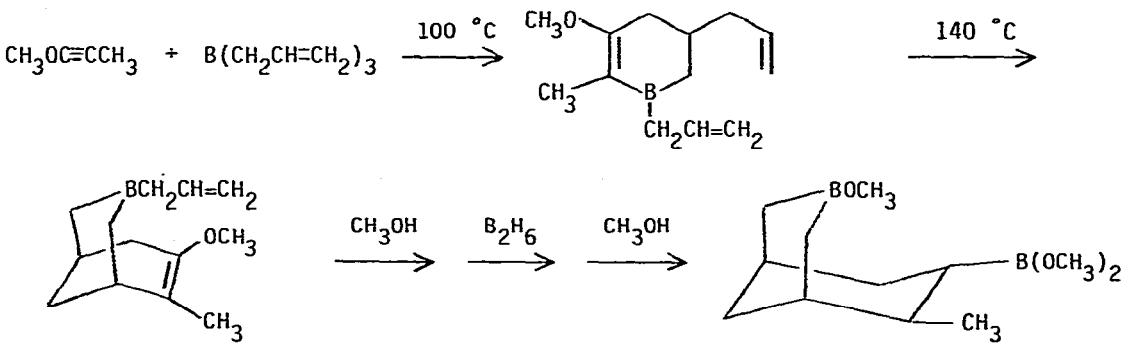
A boraadamantane has been synthesized from triallylborane and 1,1-dimethylallene [77]. Carbonylation and oxidation has yielded the corresponding 1-hydroxyadamantane.



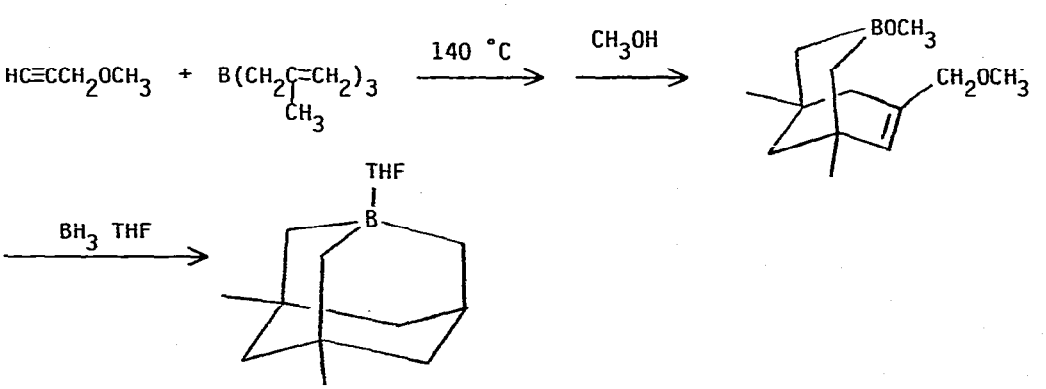
Triallylborane condenses with propargyl ethers [78, 79].



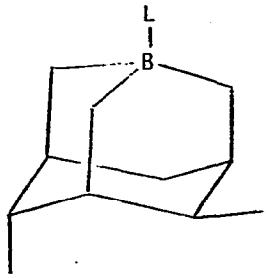
Triallylborane undergoes cyclization with 1-methoxypropyne [80].



Tris(2-methylallyl)borane shows similar behavior to triallylborane toward methyl propargyl ether [81].



More details of boraadamantane synthesis have appeared [82]. The dimethylated boraadamantane derived from tricrotylborane and $MeOCH_2C{\equiv}CH$ has been synthesized as the THF and pyridine complexes [83].



L = THF or pyridine

Treatment of lithium 1-alkyl-1-boraadamantanates with acetyl chloride results in elimination with cage opening [84]. Bromination of 1-boraadamantane opens the ring to form a bromomethyl compound, which can be hydrolyzed with base to form a ring-expanded B-O derivative [85]. Several reactions of boraadamantane have been reported, including carbonylation and oxidation to form 1-adamantanol [86].

D. HYDROBORATION-OXIDATION

1. Natural Products

Hydroboration-oxidation has become a standard procedure for synthesizing alcohols. This section covers the use of this process in syntheses and transformations of natural products. Other hydroboration chemistry related to natural products has been cited in previous sections, such as the conversion of α-pinene to the corresponding amine in section B-4 [34] and carbonylation of boranes to make an insect pheromone in B-1 [1] or a steroid in C-1 [43].

Rearrangement of a trialkylborane has been used in a synthesis of triacontanol, which is a naturally occuring plant growth regulator [87].

$$CH_3(CH_2)_{13}CH{=}CH_2 \xrightarrow[CH_3CN,\ Bu_4Sn]{WCl_6,\ Cl_2C{=}CHCl} CH_3(CH_2)_{13}CH{=}CH(CH_2)_{13}CH_3 \xrightarrow{BH_3\text{-}THF}$$

$$\xrightarrow[\text{diglyme}]{\text{heat}} \xrightarrow[OH^-]{H_2O_2} CH_3(CH_2)_{28}CH_2OH$$

Hydroboration-oxidation of various steroids, for example, 5α-cholesta-8,14-dien-3β-ol to 5α-cholest-8-ene-3β,15α-diol, has been reported [88]. Hydroboration-oxidation has been used in a steroid synthesis [89]. Hydroboration-oxidation of the indole alkaloid tabersonine has been reported [90]. Further study of hydroboration of coumarins has been reported [91].

Still and Darst have studied hydroboration of nonconjugate dienes with thexylborane as a means of controlling stereochemical relationships between separated chiral centers [92]. High stereoselectivities (80-95%) result from the geometric requirements of transition states leading to cyclic organoboranes. The utility of these reactions was demonstrated in syntheses of dihydromyoporone and the vitamin E side chain.

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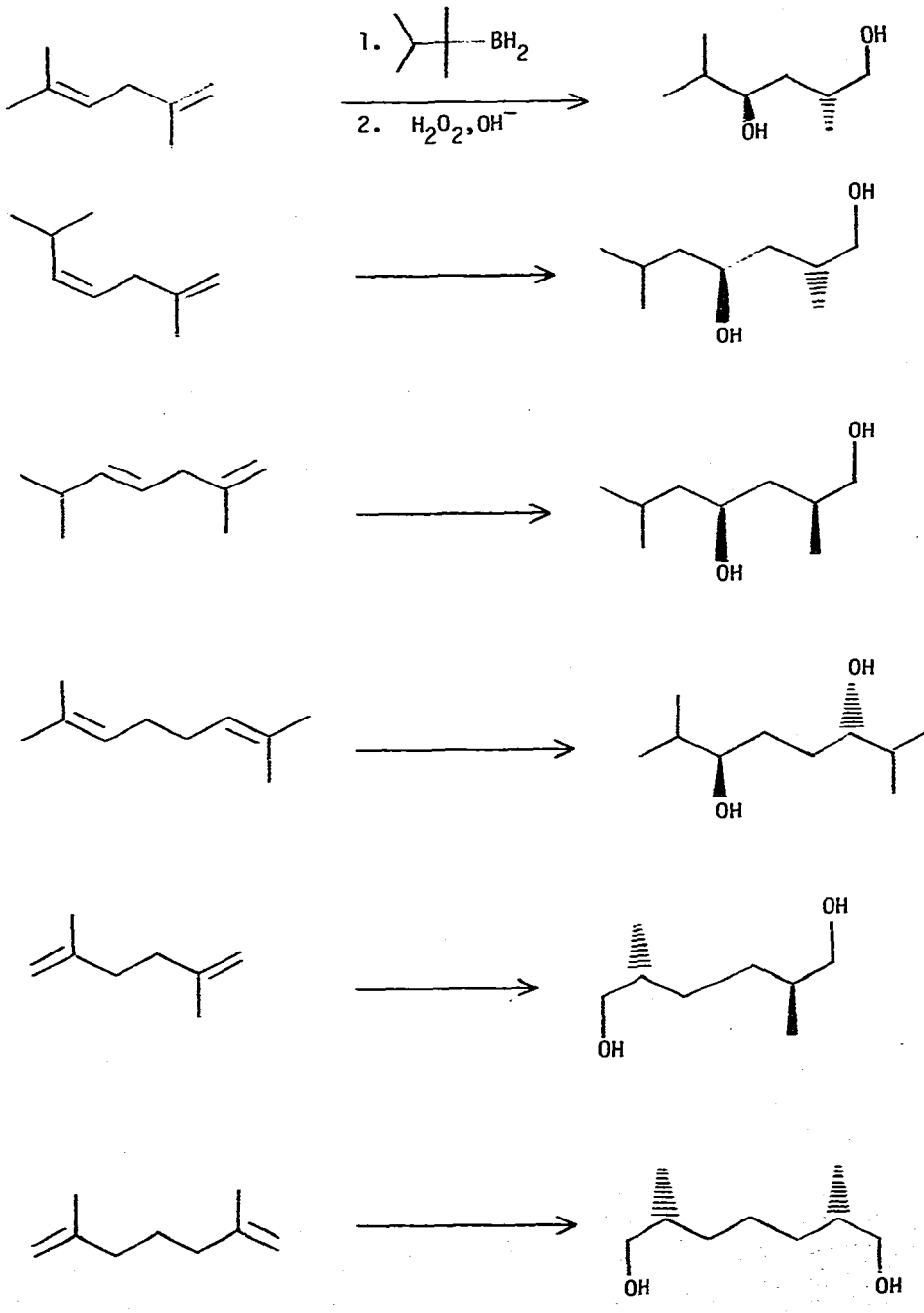
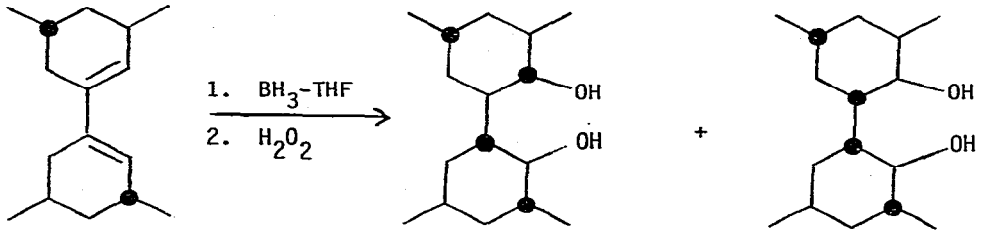


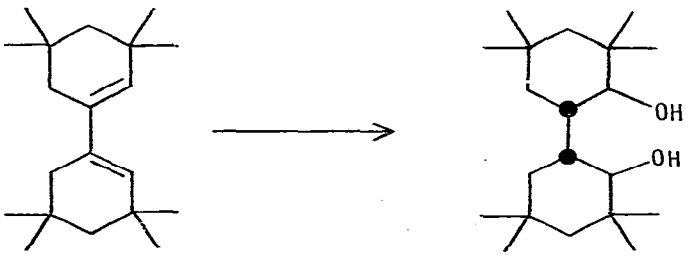
2. General Synthetic Applications

A variety of synthetic applications and general studies of the hydroboration process are summarized in this section.

Hydroboration-oxidation of bicyclohexenyls has been studies as a route to chiral 1,4-diols [93].

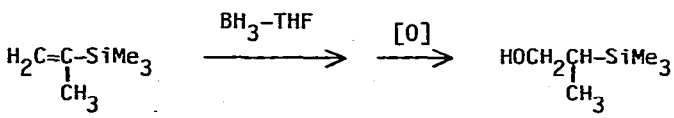


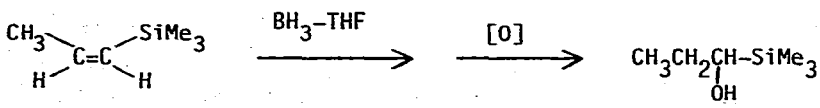
(21%) (51%)



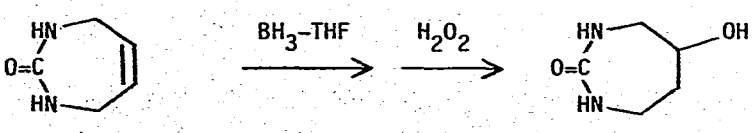
meso only

Soderquist and Brown have reported a detailed study of the hydroboration of vinyl-, propenyl-, allyl-, and 3-buten-1-yltrimethylsilane with BH_3-THF and 9-BBN [94]. Vinyltrimethylsilane yields mixtures of α and β-boryl derivatives with BH_3-THF, but 9-BBN yields mainly β-boryl isomer. 2-Propenyltrimethylsilane yields 91% β-boryl derivative even with BH_3-THF, and cis-1-propenyltrimethylsilane yields 95% α-boryl derivative with BH_3-THF. More remote olefinic functions follow the usual stereochemical rules for hydroboration.





Hydroboration-oxidation has been used in the synthesis of a 1,3-diazepinone derivative of interest as a possible cytidine deaminase inhibitor [95].



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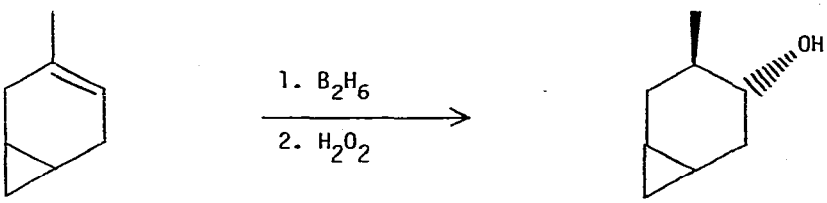
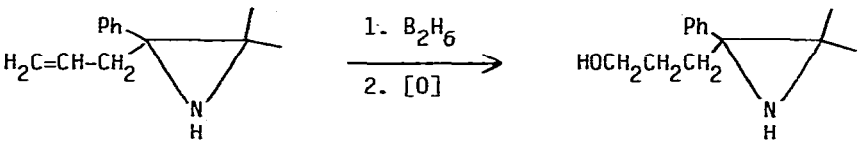
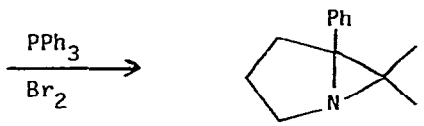
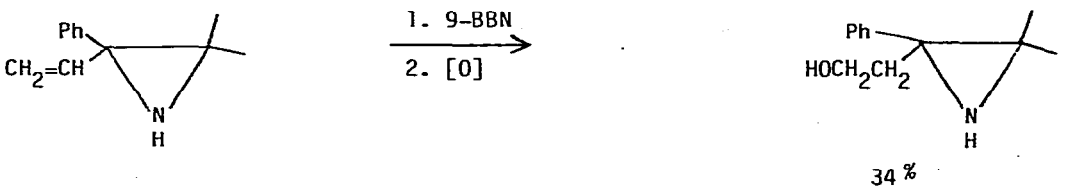
Hydroboration-oxidation of benzocycloalkenes with diborane and thexylborane has been studied [96]. Hydroboration-oxidation of a bicyclo[4.1.0]heptene has been reported [97].



Hydroboration of allylaziridines and vinylaziridines has been reported in a synthetic study [98].







Hydroboration of cyclopentene and norbornene to the RBH_2 and R_2BH stages has been studied [99]. Hydroboration with BH_2Cl followed by oxidation converts cyclopentadiene to 3-cyclopenten-1-ol, norbornadiene to exo-dehydronorborneol, 1,3-cyclohexadiene to 3-cyclohexen-1-ol, and limonene to 1-p-menthen-9-ol [100]. Hydroboration of $CH_3C{\equiv}C\text{-}CH_2CH(CH_3)_2$ with various R_2BH gives a very slightly higher proportion of attack of boron at the 3-position (to yield $CH_3CH_2COCH_2CH(CH_3)_2$) than does similar hydroboration of the unbranched alkyne, $CH_3C{\equiv}C\text{-}CH_2CH_2CH_3$ [101].

Lithiation of alkynes followed by hydroboration-oxidation provides a synthesis of 1,3-diols [102].

$$R\text{-}CH_2\text{-}C{\equiv}CH \xrightarrow[2.\ BH_3\text{-}THF \\ 3.\ NaOH\text{-}H_2O_2]{1.\ BuLi} R\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2CH_2OH$$

Hydroboration of alkenylphosphonates has been reported [103].

$$CH_2{=}\underset{\underset{R}{|}}{C}\text{-}\overset{\overset{O}{\|}}{P}(OMe)_2 \xrightarrow[2.\ [O]]{1.\ B_2H_6} HOCH_2\underset{\underset{R}{|}}{CH}\overset{\overset{O}{\|}}{P}(OMe)_2$$

Hydroxymethyl crown ethers and cryptands have been prepared by hydroboration-oxidation of a $C{=}CH_2$ group to $CHCH_2OH$ [104, 105].

Although diborane normally opens epoxides without carbon-boron bond formation, epoxides from trisubstituted olefins such as 1- and 2-methylindene evolve hydrogen on treatment with diborane, and oxidation yields diol products [106]. Halogenation of R_3B to R_2BX and reduction to R_2BH with $LiAlH_4$ has been reported [107].

3. Studies of Oxidative Processes

This section includes several more or less mechanistic investigations, most of them directed toward achieving more efficient synthetic applications.

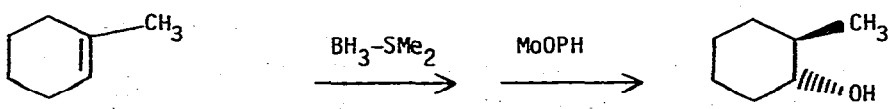
Davies has reviewed his work on autoxidation of organometallic compounds, including trialkylboranes and benzylic boronic acids, to form peroxides [108]. Related radical reactions are also reviewed.

Disiamylborane hydroboration followed by pyridinium chlorochromate oxidation converts terminal olefins into aldehydes [109].

$$R\text{-}CH{=}CH_2 + (Sia)_2BH \rightarrow RCH_2CH_2B(Sia)_2 \xrightarrow{CrO_3\text{-}HCl\text{-}py} RCH_2CHO$$

The reaction of Pr_3B with t-Bu-OOH has shown evidence of a radical mechanism in a CIDNP study [111]. Oddly enough, the same research group does not appear to have considered a radical mechanism in their kinetic study of the rapid reaction of t-Bu-OOH with R_2B-O-n-Bu (R = n-pentyl) in octane [112]. Pentane was said to be a major product (by GLC), together with RB(OBu)(-O-O-t-Bu), RB(OBu)OR, and t-BuOH, though this reviewer would not care to wager too many rubles on it.

To end with a couple of definitive results, Midland and Preston have shown that the reagent MoO_5-pyridine-HMPA (MoOPH) oxidizes organoboranes to alcohols with complete retention of configuration [113].



The use of ICl and NaOAc to convert trialkylboranes to alkyl iodides has been described by Kabalka and Gooch [114]. Two of the three alkyl groups can be cleaved

highly efficiently. Hydroboration of cis-2-butene with diisopinocampheylborane from 92% e.e. (-)-α-pinene followed by the ICl treatment yielded R-(-)-2-iodobutane having 87% e.e., which corresponds to displacement with inversion.

$$R\text{-}CH{=}CH_2 \xrightarrow{BH_3\text{-}THF} (RCH_2CH_2)_3B \xrightarrow{ICl,\ NaOAc} 2\ RCH_2CH_2I + RCH_2CH_2B(OH)_2$$

REFERENCES

1. G. Zweifel and N. R. Pearson, J. Am. Chem. Soc., 102 (1980) 5919-5920
2. H. C. Brown, J. A. Sikorski, S. U. Kulkarni, and H. D. Lee, J. org. Chem., 45 (1980) 4540-4542
3. S. U. Kulkarni, H. D. Lee, and H. C. Brown, J. Org. Chem., 45 (1980) 4542-4543
4. H. C. Brown and A. K. Mandal, Synthesis, (1980) 153-155
5. H. C. Brown and A. K. Mandal, J. Org. Chem., 45 (1980) 916-917
6. H. C. Brown, N. Ravindran, and S. U. Kulkarni, J. Org. Chem., 45 (1980) 384-389
7. H. C. Brown and J. B. Campbell, Jr., J. Org. Chem., 45 (1980) 389-395
8. W. E. Paget and K. Smith, J. Chem. Soc., Chem. Commun., (1980) 1169-1170
9. K. Isagawa, H. Sano, M. Hattori, and Y. Otsuji, Chem. Lett., (1979) 1069-1072
10. S. Kano, Y. Yuasa, and S. Shibuya, J. Chem. Soc., Chem. Commun., (1979) 796
11. B. J. Meneghelli, M. Bower, N. Canter, and R. W. Rudolph, J. Am. Chem. Soc., 102 (1980) 4355-4360
12. H. C. Brown, "Hydroboration. With Supplement Nobel Lecture, Dec. 8, 1979," Benjamin/Cummings Publishing Co., Inc., Reading, Mass., 1980
13. V. V. R. Rao, I. Mehrotra, and D. Devaprabhakara, J. Sci. Ind. Res., 38 (1979) 368-379
14. J. D. Odom, Organomet. Chem., 8 (1980) 34-59
15. K. K. Wang and H. C. Brown, J. Org. Chem., 45 (1980) 5303-5306
16. H. C. Brown, K. K. Wang, and C. G. Scouten, Proc. Natl. Acad. Sci. U. S. A., 77 (1980) 698-702
17. L. C. Vishwakarma and A. Fry, J. Org. Chem., 45 (1980) 5306-5308
18. S. Nagase, N. K. Ray, and K. Morokuma, J. Am. Chem. Soc., 102 (1980) 4536-4537
19. M. K. Datta, S. Dasgupta, and R. Datta, Indian J. Chem., Sect. A, 19A (1980) 611-614
20. T. E. Taylor and M. B. Hall, J. Am. Chem. Soc., 102 (1980) 6136-6142
21. H. C. Brown and K. K. Wang, J. Org. Chem., 45 (1980) 1748-1753
22. H. C. Brown and J. A. Soderquist, J. Org. Chem., 45 (1980) 846-849
23. H. C. Brown, S. C. Kim, and S. Krishnamurthy, J. Org. Chem., 45 (1980) 1-12
24. S. Krishnamurthy and H. C. Brown, J. Org. Chem., 45 (1980) 849-856
25. H. C. Brown, G. W. Kramer, J. L. Hubbard, and S. Krishnamurthy, J. Organometal. Chem., 188 (1980) 1-10
26. N. A. Bell, H. M. M. Shearer, and C. B. Spencer, J. Chem. Soc., Chem. Commun., (1980) 711-712

27. A. K. Mandal, P. K. Jadhav, and H. C. Brown, J. Am. Chem. Soc., 45 (1980) 3543-3544
28. M. M. Midland, D. C. McDowell, R. L. Hatch, and A. Tramontano, J. Am. Chem. Soc., 102 (1980) 867-869
29. M. M. Midland and A. Tramontano, Tetrahedron Lett., 21 (1980) 3549-3552
30. M. M. Midland and S. B. Preston, J. Org. Chem., 45 (1980) 747-748
31. P. Pino, A. Stefani, and G. Consiglio, Jerusalem Symp. Quantum Chem. Biochem., 12 (1979) 347-354; Chem. Abstr. 92 (1980) 163314u
32. J. D. Morrison, E. R. Grandbois, and S. I. Howard, J. Org. Chem., 45 (1980) 4229-4231
33. A. Hirao, S. Nakahama, H. Mochizuki, S. Itsuno, and N. Yamazaki, J. Org. Chem., 45 (1980) 4231-4233
34. M. W. Rathke and A. A. Millard, Org. Synth., 58 (1978) 32-36
35. D. S. Matteson and D. Majumdar, J. Am. Chem. Soc., 102 (1980) 7588-7590
36. D. S. Matteson and R. Ray, J. Am. Chem. Soc., 102 (1980) 7590-7591
37. D. S. Matteson and D. Majumdar, J. Organometal. Chem., 184 (1980) C41-C43
38. G. L. Larson, R. Argüelles, O. Rosario, and S. Sandoval, J. Organometal. Chem., 198 (1980) 15-23
39. O. Rosario, S. Sandoval, and G. L. Larson, Synth. Commun., 10 (1980) 813-819
40. H. C. Brown, T. M. Ford, and J. L. Hubbard, J. Org. Chem., 45 (1980) 4067-4068
41. H. C. Brown, J. L. Hubbard, and K. Smith, Synthesis, (1979) 701-702
42. G. W. Kabalka, Synthetic Commun., 10 (1980) 93-97
43. T. A. Bryson and C. J. Reichel, Tetrahedron Lett., 21 (1980) 2381-2384
44. B. A. Carlson and H. C. Brown, Org. Synth., 58 (1978) 24-31
45. N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, Tetrahedron Lett., 21 (1980) 537-540
46. K. Avasthi, T. Baba, and A. Suzuki, Tetrahedron Lett. 21 (1980) 945-946
47. T. Yogo and A. Suzuki, Chem. Lett., (1980) 591-594
48. A. B. Levy, R. Angelastro, and E. R. Marinelli, Synthesis, (1980) 945-947
49. Y. Masuda, A. Arase, and A. Suzuki, Bull. Chem. Soc. Jpn., 53 (1980) 1652-1655
50. S. Hara, K. Kishimura, and A. Suzuki, Chem. Lett., (1980) 221-222
51. N. Miyaura, T. Yano, and A. Suzuki, Tetrahedron Lett., 21 (1980) 2865-2868
52. H. Yatagai, Bull. Chem. Soc. Jpn., 53 (1980) 1670-1676
53. N. Miyaura, T. Yano, and A. Suzuki, Bull. Chem. Soc. Jpn., 53 (1980) 1471-1472
54. H. Yatagai, J. Org. Chem., 45 (1980) 1640-1644
55. J. B. Campbell, Jr., and H. C. Brown, J. Org. Chem., 45 (1980) 549-550
56. H. C. Brown and J. B. Campbell, Jr., J. Org. Chem., 45 (1980) 550-552
57. Y. Yamamoto, S. Yamamoto, H. Yatagai, and K. Maruyama, J. Am. Chem. Soc., 102 (1980) 2318-2325
58. J. W. Wilson, J. Organometal. Chem., 186 (1980) 297-300
59. D. S. Matteson and R. J. Moody, J. Org. Chem., 45 (1980) 1091-1095
60. D. S. Matteson and D. Majumdar, J. Chem. Soc., Chem. Commun., (1980) 39-40
61. H. Yatagai, Y. Yamamoto, and K. Maruyama, J. Am. Chem. Soc., 102 (1980) 4548-4550

62. R. W. Hoffmann and H.-J. Zeiss, Angew. Chem., 92 (1980) 218-223; Angew. Chem. Internat. Ed. Engl. 19 (1980) 218-219
63. R. W. Hoffmann and B. Kemper, Tetrahedron Lett., 21 (1980) 4883-4886
64. R. W. Hoffmann and U. Weidmann, J. Organometal. Chem., 195 (1980) 137-146
65. R. W. Hoffmann, G. Feussner, H.-J. Zeiss, and S. Schulz, J. Organometal. Chem., 187 (1980) 321-329
66. Y. Yamamoto, H. Yatagai, and K. Maruyama, J. Chem. Soc., Chem. Commun.,(1980) 1072-1073
67. Y. Yamamoto, H. Yatagi, Y. Naruta, K. Maruyama, and T. Okamoto, Tetrahedron Lett., 21 (1980) 3599-3602
68. Yu. N. Bubnov, M. Sh. Grigorian, A. V. Tsyban', and B. M. Mikhailov, Synthesis, (1980) 902-904
69. Yu. N. Bubnov, A. V. Tsyban', and B. M. Mikhailov, Synthesis, (1980) 904-905
70. D. A. Evans and T. R. Taber, Tetrahedron Lett., 21 (1980) 4675-4678
71. M. Hirama and S. Masamune, Tetrahedron Lett., (1979) 2225-2228
72. T. Inoue and T. Mukaiyama, Bull. Chem. Soc. Jpn., 53 (1980) 174-178
73. J. Hooz and J. Oudenes, Synthetic Commun., 10 (1980) 139-145
74. J. Hooz and J. Oudenes, Synthetic Commun., 10 (1980) 667-674
75. M. J. Idacavage, E. Negishi, and C. A. Brown, J. Organometal. Chem., 186 (1980) C55-C57
76. B. M. Mikhailov, Pure Appl. Chem., 52 (1980) 691-704
77. B. M. Mikhailov, V. N. Smirnova, O. D. Smirnov, E. P. Prokof'ev, and A. S. Shashkov, Izv. Akad. Nauk SSSR., Ser. Khim., (1979) 2340-2346
78. B. M. Mikhailov and T. K. Baryshnikova, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2541-2544
79. B. M. Mikhailov and K. L. Cherkasova, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2729-2734
80. B. M. Mikhailov and M. E. Gurskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2335-2339
81. B. M. Mikhailov, T. V. Potapova, and A. S. Shashkov, Izv. Ikad. Nauk SSSR, Ser. Khim., (1979) 2724-2728
82. B. M. Mikhailov, T. K. Baryshnikova, V. G. Kiselev, and A. S. Shashkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2544-2551
83. B. M. Mikhailov, M. E. Gurskii, and A. S. Shashkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2551-2556
84. B. M. Mikhailov, M. E. Gursky, T. V. Potapova, and A. S. Shashkov, J. Organometal. Chem., 201 (1980) 81-88
85. B. M. Mikhailov, L. S. Vasil'ev, and V. V. Veselovskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 1106-1113
86. B. M. Mikhailov, N. N. Govorov, Ya. A. Angelyuk, V. G. Kiselev, and M. I. Struchkova, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 1621-1626
87. K. Maruyama, K. Terada, and Y. Yamamoto, J. Org. Chem., 45 (1980) 737-738
88. E. J. Parish and G. J. Schroepfer, Jr., Chem. Phys. Lipids, 25 (1979) 381-394

89. B. Dayal, G. S. Tint, and G. Salen, Steroids, 34 (1979) 581-588
90. C. Caron-Sigaut, L. Le Men-Olivier, G. Hugel, J. Levy, and J. Le Men, Tetrahedron, 35 (1979) 957-960
91. S. Kirkiacharian, J. D. Brion, and P. Reynaud, C. R. Hebd. Seances Acad. Sci., Ser. C., 289 (1979) 227-229
92. W. C. Still and K. P. Darst, J. Am. Chem. Soc., 102 (1980) 7385-7387
93. T. W. Bell, Tetrahedron Lett., 21 (1980) 3443-3446
94. J. A. Soderquist and H. C. Brown, J. Org. Chem., 45 (1980) 3571-3578
95. V. E. Marquez, P. S. Liu, J. A. Kelley, and J. S. Driscoll, J. Org. Chem., 45 (1980) 485-489
96. P. A. Marshall and R. H. Prager, Aust. J. Chem., 32 (1979) 1251-1260
97. E. Kh. Kazakova, Z. G. Isaeva, and Sh. S. Bikeev, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2330-2334
98. R. Chaabouni, A. Laurent, and B. Marquet, Tetrahedron, 36 (1980) 877-885
99. H. Taniguchi, Bull. Chem. Soc. Jpn., 52 (1979) 2946-2949
100. I. Uzarewicz and A. Uzarewicz, Pol. J. Chem., 53 (1979) 1989-1994
101. S. W. Slayden, J. Org. Chem., 45 (1980) 2908-2910
102. A. Medlik-Balan and J. Klein, Tetrahedron, 36 (1980) 299-304
103. M. Yamashita, M. Kojima, H. Yoshida, T. Ogata, and S. Inokawa, Bull. Chem. Soc. Jpn., 53 (1980) 1625-1628
104. H. Kakiuchi, M. Tomoi, O. Abe, and K. Kihara, Jpn. Kokai Tokkyo Koho, 80 19,222, Feb. 9, 1980; Chem Abstr., 93 (1980) 204707r
105. H. Kakiuchi, M. Tomoi, O. Abe, and K. Kihara, Jpn. Kokai Tokkyo Koho 80 19,220, Feb. 09, 1980; Chem. Abstr., 93 (1980) 114579w
106. P. A. Marshall and R. H. Prager, Aust. J. Chem., 32 (1979) 1261-1271
107. A. R. Qureshi, M. Y. Qureshi, Badar-ud-Din, and Riazur-Rehman, Pak. J. Sci., 29, (1977) 129-132
108. A. G. Davies, J. Organometal. Chem., 200 (1980) 87-99
109. H. C. Brown, S. U. Kulkarni, and C. G. Rao, Synthesis, (1980) 151-153
110. H. C. Brown, S. U. Kulkarni, and C. G. Rao, Synthesis, (1979) 702-704
111. Yu. A. Kurskii, V. N. Alyasov, V. P. Maslennikov, N. M. Lapshin, and Yu. A. Aleksandrov, Zh. Obshch. Khim., 49 (1979) 2123-2126
112. V. N. Alyasov, V. P. Maslennikov, and Yu. A. Aleksandrov, Zh. Obshch. Khim., 50 (1980) 362-368; J. Gen. Chem. USSR (Engl. Transl.), 50 (1980) 295-301
113. M. M. Midland and S. B. Preston, J. Org. Chem., 45 (1980) 4514-4515
114. G. W. Kabalka and E. E. Gooch III, J. Org. Chem., 45 (1980) 3578-3580