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Boron: boranes in organic synthesis. Annual survey covering the year 1990 *

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Contents

1. Introduction

Boron hydrides and boranes are being utilized extensively in all aspects of organic chemistry. In the not too distant future, they may be considered to be ubiquitous. Obviously, it has become impossible to report on each instance in which boron was used in organic chemistry. As in the past, we have attempted to identify research that the reader might find both novel and potentially useful. It is exciting to observe the ever expanding list of investigators who are developing new chemoselective and stereoselective borane reagents. One can only anticipate the exciting new discoveries which lie ahead.

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* No reprints available. For previous Annual survey see *J. Organomet. Chem.*, 457 (1993) 1.

2. Borane reagents

2.1. Hydroborating agents

Boron hydride reagents such as the borane complexes with tetrahydrofuran and dimethyl sulfide are now utilized in commercial quantities. Nevertheless, new applications of these versatile reagents continue to appear in the literature.

2.1.1. BH_3

In an interesting application, Al-Takrity *et al.* used the hydroboration reaction to prepare symmetrical α,ω-difunctional polymers [1]. Anionic polymerization of methyl methacrylate initiated by allyllithium and terminated by allyl iodide affords polymer molecules with allyl units at both ends. The allyl-terminated polymers can undergo hydroboration and oxidation to give hydroxy end groups, which can then be esterified.

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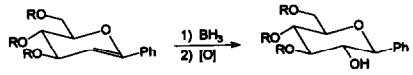
Friesen and Daljeet hydroborated C-arylglucals and synthesized the β-C-arylglucoside nucleus of chaetiacandin [2].



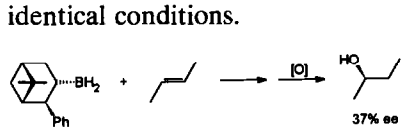
Baboulene *et al.* synthesized alkyl(dialkoxyphosphinyl)aminopropanal *via* the hydroboration/oxidation of N-protected amines [3]. Chmielowiec *et al.* synthesized alcohols by hydroborating 1-amino-3-cycloalkenes [4]. Akers and Bryson reported that tin affects the hydroboration of hindered olefins [5]. Intramolecular hydroboration using hindered allylic tin substrates is inefficient, presumably because of the steric bulk of the trialkylstannane group.

A convenient method for isomerization of α-pinene to β-pinene was reported by Zhang. α-Pinene was hydroborated and then isomerized to bis-10-pinanylborane upon heating. β-Pinene was then liberated on heating in the presence of dipentene [6].

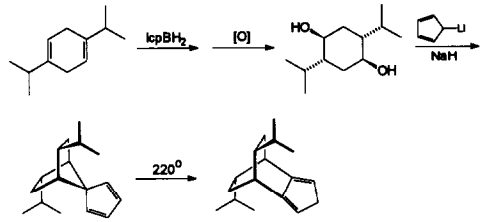
2.1.2. RBH_2

Srebnik *et al.* investigated the controlled and sequential hydroboration of simple representative alkenes with methylborane in tetrahydrofuran [7]. They examined the directive effects in the first and second stages of hydroboration and found that the reagent possesses extraordinary hydroborating characteristics.

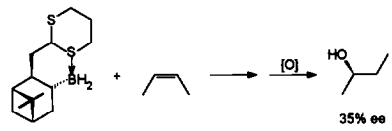
Brown *et al.* reported the synthesis and hydroboration of (−)-2-phenylapopinene and compared the resultant mono(2-phenylapoisopinocampheyl)borane with its 2-methyl and 2-ethyl analogs for the chiral hydroboration of representative alkenes [8]. Hydroboration of (−)-2-phenylapopinene with BMS (1.2:1 ratio) provides an equilibrium mixture of the mono(2-phenylapoisopinocampheyl)borane ($PapBH_2$) and the corresponding dialkylborane. Treatment of this mixture with tetramethylethylenediamine (TMEDA) precipitates crystalline $(PapBH_2)_2 \cdot TMEDA$. Liberation of the $PapBH_2$ using BF_3 provides the monoalkylborane in approximately 99% ee, thus providing the required reagent in significantly higher optical purity than the starting olefin. Unfortunately, hydroboration of a series of representative olefins, followed by oxidative workup, provided the respective chiral alcohols in unexpectedly lower enantiomeric purities than those obtained from the 2-methyl and 2-ethyl analogs under identical conditions.



Chen and Halterman detail the asymmetric synthesis of C2-symmetric annulated bicyclooctylcyclopentadienes [9]. The key step in the synthesis is an asymmetric dihydroboration of 1,4-dialkyl-1,4-cyclohexadienes using enantiomerically pure isopinocamphenylborane.



De Richter *et al.* reported that (+)- and (−)-[2-(1,3-dithianyl)]myrtanyl-borane are stable, solid monoalkylboranes for asymmetric hydroboration [10]. These new chiral reagents, when tested on representative classes of olefins, react similarly to isopinocampheylborane. Reduction of asymmetric prochiral ketones achieves high diastereoselectivity but low enantioselectivity. An intramolecular stabilization presumably accounts not only for the easy access to monoalkylboranes but also for its remarkable physical properties.

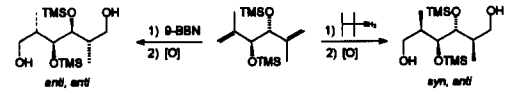


Bai *et al.* reported a facile one-pot synthesis of 2-alkyl-1,2-oxoborolanes in 50%–69% yields *via* the hydroboration of allyl borate esters using borane dimethylsulfide [11].

2.1.3. R_2BH

Ramakrishnan and Chung synthesized organoborane polymers which were then oxidized to polyalcohol derivatives. The unsaturated organoboranes were prepared *via* hydroboration of cyclooctadiene or norbornadiene with dialkylborane reagents [12,13]. For example, (5-cyclooctenyl)diethylborane was prepared and polymerized by ring-opening metathesis. The resultant polyborane gave poly(5-hydroxyoctenylene) upon oxidation. The hydroboration–oxidation reaction could be controlled to give polymers with varying amounts of hydroxyl groups on the backbone.

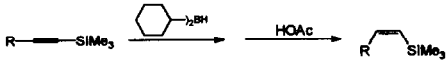
Harada *et al.* achieved stereocontrol of consecutive stereogenic centers by intramolecular hydroboration of dialkenyl carbinol derivatives by utilizing an intramolecular hydroboration. Thus, hydroboration of a (D,L)-silyl ether with 9-BBN followed by oxidation gave 90% of the *anti,anti*-isomer whereas the same procedure with thexylborane gave 62% *syn,anti*-isomer [14].



Sato *et al.* investigated the rhodium(I)-catalyzed asymmetric hydroboration of alkenes with 1,3,2-benzodioxaborole [15]. Several rhodium(I) complexes containing chiral phosphines were effective catalysts for the asymmetry hydroboration of prochiral alkenes with 1,3,2-benzodioxaborole to give optically active 2-alkyl-1,3,2-benzodioxaboroles.

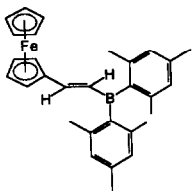
Hoshi *et al.* studied the hydroboration of (trimethylsilyl)ethyne with dialkylboranes and its application to the syntheses of (*E*)-1-(trimethylsilyl)alk-1-enes and 2-(trimethylsilyl)alk-1-enes [16]. Evans and Fu carried out a mechanistic investigation of the rhodium-catalyzed hydroboration of olefins [17]. Labeling studies carried out on the rhodium-catalyzed olefin hydroboration reaction reveal that the degree of reversibility of the elementary steps in the catalytic cycle is highly substrate dependent. For the reaction of 1-decene, both olefin binding and hydride migration are reversible. In contrast, hydroboration of styrene with deuterocatechol-borane provides no evidence of reversibility for these two processes. Other olefins show intermediate levels of reversibility. This divergent kinetic behavior manifests itself in different regioselectivity-determining steps for 1-decene and styrene. The implications of these observations for rationales of diastereoselective olefin addition reactions are discussed.

Soderquist and Santiago converted alkynylsilanes to *cis*-vinylsilanes *via* hydroboration [18]. Hydroboration of trialkysilylated alkynes with dialkylboranes, followed by non-oxidative work with acetic acid, gave (*Z*)-vinylsilanes.

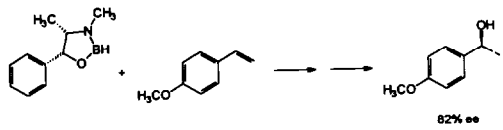


Boldrini *et al.* developed a new approach to (*Z*)-vinyloxyboranes *via* 1,4-hydroboration of (*E*)-α,β-unsaturated ketones [19]. (*Z*)-Vinyloxyboranes are obtained *via* 1,4-hydroboration of acyclic disubstituted (*E*)-α,β-unsaturated ketones with dicyclohexylborane or diisopinocampheylborane.

Yuan *et al.* found that hydroboration of π-donor substituted alkynes with dimesitylborane yields air-stable push–pull (*E*)-alkenes which possess large molecular hyperpolarizabilities [20].



Brown and Lloyd-Jones report that the cyclic secondary boranes derived from ephedrine and pseudoephedrine undergo rhodium complex-catalyzed hydroboration of styrene [21]. The regiochemistry and derived enantiomeric excess depend strongly on the structure of the catalyst with the ferrocenebiphosphine (4*R*,5*R*) complex.

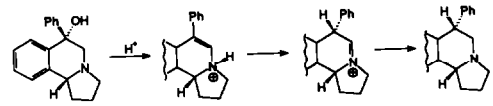


Knoerzer and Siebert carried out a double hydroboration of acetylene, 1-propyne, and tert-butylacetylene with $HBCl_2$ [22]. The reaction leads to 1,1-bis(dichloroboryl)alkanes. Ryu *et al.* used haloboranes to ring open silyl substituted cyclopropanes [23]. Thus the reactions of (silylmethyl)cyclopropanes with haloboranes, such as $BHBr_2$, result in desilylative ring opening to give homoallylboranes and boracyclopentanes, respectively. Coupled with a subsequent oxidation procedure, these reactions provide ready access to homoallylic alcohols and 1,4-diols by a one-pot procedure. Soundararajan and Matteson investigated hydroboration with boron halides and trialkylsilanes [24].

2.2. Reducing agents

2.2.1. BH_3

Sorgi *et al.* reported that the reductive deoxygenation of 6-hydroxy derivatives of *trans*-pyrrol[2,1-*a*]isoquinoline with borane–THF in trifluoroacetic acid yielded a product mixture in favor of the *trans* diastereomer [25]. The mechanism of this process was proved by NMR spectroscopy and deuterium-labeled reagents and substrates. The reaction proceeds *via* dehydration of the substrate to an enammonium salt comprised mainly of the *cis*-fused diastereomer, prototropic rearrangement to an iminium salt highly enriched in the *trans* isomer, and hydride transfer to the iminium carbon.



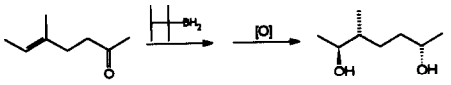
Chihara *et al.* developed a selective reduction of less reactive carbonyl groups in the presence of diborane and sodium bisulfite on silica gel [26]. The less reactive carbonyl group of a mixture of reducible groups of carbonyl compounds was reduced preferentially with diborane on silica gel by first forming an adduct of the more reactive carbonyl group with sodium bisulfite.

Trapani *et al.* found trimethylamine-borane to be a useful reagent in the one-pot preparation of carboxylic esters from carboxylic acids [27]. Kriz *et al.* also report that triethylamine borane is a stable, efficient and safe reductant for transforming carboxylic acids to primary alcohols [28].

Ketcha *et al.* developed a method for the reductive deoxygenation of 2- and 3-acyl-1-(phenylsulfonyl)pyrroles [29]. Thus the reductive deoxygenation of acyl-1-(phenylsulfonyl)pyrroles to the corresponding alkyl derivatives can be effected in moderate to high yields using the borane-tert-butylamine complex in the presence of aluminum chloride.

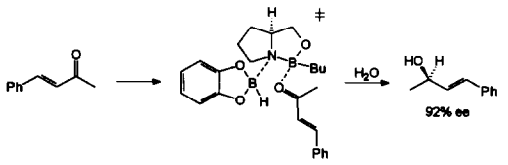
2.2.2. RBH_2

Harada *et al.* report that remote stereocontrol can be achieved by utilizing intramolecular carbonyl reduction with thexylborane [30].

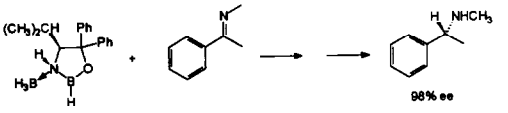


2.2.3. R_2BH

The Corey CBS reduction is difficult to categorize since both BH_3 and disubstituted boranes are utilized. Since the exciting aspects of the chemistry (its stereospecificity) are dependent on the disubstituted borane, it is included in this section. Corey and Bakshi report a new system for catalytic enantioselective reduction of achiral ketones to chiral alcohols [31]. The reduction of a variety of achiral ketones with catecholborane as the reducing agent in the presence of a stoichiometric reductant and 0.1 equivalent of oxazaborolidine. The reaction has exciting synthetic potential.

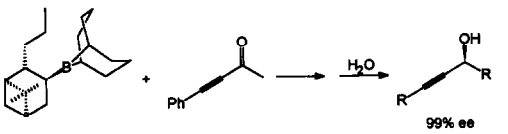


Rao *et al.* described the enantioselective reductions of ketones with borane and oxazaborolidines [32] derived from (*R*)- and (*S*)-α,α-diphenyl-2-piperidinemethanol. Cho and Chun report the asymmetric reduction of N-substituted ketimines with the reagent prepared from borane and (*S*)-(−)-2-amino-3-methyl-1,1-diphenylbutan-1-ol (Itsuno's reagent). The sequence constitutes an enantioselective synthesis of optically active secondary amines [33].

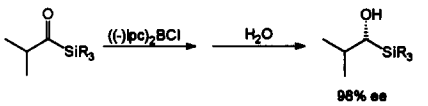


2.2.4. R_3B

Brown *et al.* studied the effect of the steric requirement at the 2-position of apopinene on chiral reductions. B-(iso-2-ethylapopinocampheyl)- and B-(iso-2-n-propylapopinocampheyl)-9-borabicyclo[3.3.1]nonanes were found to be improved reagents for the chiral reduction of α,β-acetylenic ketones and α-keto esters [34]. Both produce higher optical induction than does Alpine-Borane. 4-Phenyl-3-butyn-2-one was reduced to the corresponding propargylic alcohol in 89% ee and 96% ee by Eapine-Borane and Prapine-Borane, respectively, as compared to 82% ee with Alpine-Borane.



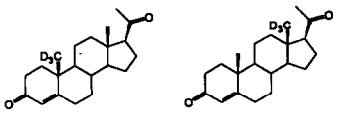
Soderquist *et al.* developed a synthesis of essentially homochiral 1-silyl alcohols from the reduction of aliphatic acylsilanes with chloro-diisopinocampheylborane [35]. The enantioselective reduction of aliphatic acylsilanes with (−)-B-chlorodiisopinocampheylborane provides (*R*)-1-silylated alcohols in high enantiomeric excess in good isolated yields.



2.2.5. R_4B^-

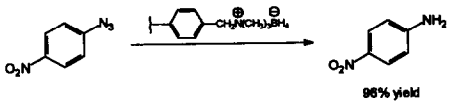
Ramachandran *et al.* report that lithium B-iso-2-ethylapopinocampheyl-9-borabicyclo[3.3.1]nonyl hydride is an improved reagent for asymmetric reduction of unhindered aliphatic ketones [36]. The study provides further evidence for the improved enantioselectivity in reductions by reagents containing increased steric requirements at the 2-position of apopine. Lithium B-iso-2-ethylapopinocampheyl-9-borabicyclo [3.3.1]nonyl hydride (Eapine-Hydride), was prepared by hydroborating 2-ethylapopinene with 9-borabicyclo [3.3.1]nonane, followed by treatment with tert-butyllithium.

Kirk *et al.* synthesized [19-^{2}H3]progesterone and [18-^{2}H3]progesterone by reducing 19-*p*-toluenesulfonate with lithium triethylborodeuteride (superdeuteride) followed by hydrolysis of the ethylenedioxy groups [37]. [18-^{2}H3]Progesterone was obtained from (20*R*)-3β-acetoxy-pregn-5-ene-20,18-lactone *via* conversion into methyl (20*R*)-3β-20-dihydroxypregn-5-en-18-oate; a two-stage introduction of three atoms of deuterium at C-18 *via* the tosylate of the derived [18-^{2}H2]-18-ol was successful but required unusual experimental conditions.



Cho prepared potassium 9-O-(1,2:5,6-di-O-cyclohexylidene-α-D-glucofuranosyl)-9-boratabicyclo[3.3.1]-nonane, which he reports to be useful as a new chiral reducing agent [38]. Treating acetophenone with the new agent gave 97% of the alcohol corresponding to the (*R*)-enantiomer in 77% ee.

Kabalka *et al.* developed a method for reducing azides which involves the the use of borohydride supported on an ion exchange resin [39]. They found that borohydride supported on an ion exchange resin in methanol reduced aryl and arylsulfonyl azides to the corresponding aromatic amines and aryl sulfonamides in excellent yields. The isolation of pure products by simple filtration and evaporation is an important feature of this method.



Kabalka *et al.* summarized their studies on the reduction of conjugated nitroalkenes using borohydride and borane derivatives [40]. The reduction of conjugated nitroalkenes with borane or borohydride reagents produces nitroalkanes, amines, *N*-hydroxylamines, or oximes depending on the reaction conditions and the nature of the borane agent.

2.3. Mechanism and theory

2.3.1. Theory

Wang *et al.* carried out calculations to locate the transition structures for hydroborations of alkenes, allenes, and alkynes by borane, diborane, methylborane, methylfluoroborane, and dimethylborane [41]. The transition structures were located with *ab initio* MO calculations and the 3-21G basis set. The parent reactions of borane with ethylene and acetylene have also been studied at higher theoretical levels. Substituent effects on the stabilities of complexes and on the activation energies are in accord with experimental data.

Rodger *et al.* found that the energetic results from MO calculations on fragments of boron hydrides and hydrocarbons illustrate the fundamental differences in bonding between these two types of compounds. Combining the results for boranes with an extension of the Lipscomb topological approach yields a procedure for constructing potentially stable boranes and understanding their bonding characteristics [42].

Alberts and Schaefer determined the structure of the organoboron anions using *ab initio* methods that include the effects of dynamic electron correlation. Optimized geometries, electronic dipole moments, and harmonic vibrational frequencies were presented and discussed the various levels of theory employed [43]. The dependence of these molecular properties on the inclusion of diffuse functions in the basis set was investigated. It may be argued that the prototypical HBCH anion contains a formal B–C triple bond, while the larger $HBCBH_2$ anion incorporates a weaker B–C triple bond and a very strong C–B single bond. Cioslowski and Hay investigated the electronic structures of borabenzene and its adducts with carbon monoxide and nitrogen utilizing HF/6-31G and MP2/6-31G MO calculations [44]. At the highest level of theory used (MP2/6-31G), the calculated heats of formation (relative to the isolated molecules) are −39.4 and −19.2 kcal mol^{-1} for the carbon monoxide and the nitrogen adducts, respectively.

Eisch *et al.* describe the thermal generation and transformation of the borepin ring system [45]. The borepin ring system results from the interaction of an alkyne with the highly reactive borole ring and the occurrence of an unusual sequence of skeletal rearrangements. In this manner, both heptaphenylborepin and 1-phenyl-2,3,4,5,6,7-hexa-*p*-tolylborepin were prepared. The isolation of these hydrocarbons was consistent with the cleavage of the C–B bonds of the borepins and the disrotatory electrocyclic ring closure of the resulting (*E,Z,E*)-1,3,5-hexatrienes. Further heating of these borepins leads to electronic and NMR spectral changes which show that all the six C-aryl substituents become non-equivalent and that an isomer of the borepin has now been formed. The overall conversion of borole to this isomer of borepin involves a remarkable sequence of pericyclic reactions: a Diels–Alder cycloaddition, 1,3-sigmatropic suprafacial rearrangements of the resulting 7-borabicyclo[2.2.1] heptadiene, a 1,6-disrotatory electrocyclic ring opening to the borepin, a 1,3-sigmatropic ring expansion to a boracyclononatetraene, and a final ring-closing ene reaction yielding the 5-bora-3a,4-dihydro-5*H*-benz[*e*]indene system. The role of the unoccupied $2p_z$ orbital on B in facilitating these rearrangements and in influencing the spectral properties of the unsaturated boracarbocycles involved is discussed in terms of HMO theory.

2.3.2. Kinetics

Sheikh *et al.* studied the thermal decomposition of substituted tetraphenylborates [46]. Combined TG/DTA and pyrolysis by a bench technique have been used to study alkylammonium, dialkylammonium, tri-

alkylammonium and tetraalkylammonium tetraphenylborates.

Schroedner *et al.* carried out an EPR investigation of gamma-irradiated triallyl compounds The structure and the reactions of allyl radicals produced by δ-irradiation at 77 K of triallyl borate, are reported [47]. By variation of temperature and microwave power it was shown that the EPR spectra consist of a quartet and a quintet feature which are both assigned to allylic radicals. One radical (the quintet) is identified as the allyl radical. It is suggested that it is formed by release from the radical anion or cation of the parent compounds. The other radical (the quartet) is formed by loss of an H atom from the precursors.

2.3.3. NMR / IR

Brown *et al.* carried out a high-field variable-temperature proton and boron-11 NMR study of the effects of solvent and structure on reactivity in allylboration [48]. The reactions of benzaldehyde with structurally representative allylboron reagents were examined under a variety of conditions by high-field variable-temperature ^{1}H and ^{11}B NMR spectroscopy. In general, polar solvents which are poorly coordinating enhance the rate of allylboration while solvents capable of relatively stronger coordination retard the rate. α-Trisubstituted aldehydes undergo allylboration relatively slowly compared to the less substituted aldehydes. Among cyclic allylboronates, the 1,3,2-dioxaborolane derivatives undergo allylboration more rapidly compared to the B-allyl-1,3,2-dioxaborinane. The B-allyl-1,3,2-dioxabenzoborole undergoes exceptionally rapid allylboration (100%, < 30 s, -50°C). While the reactivity of B-allyl-1,3,2-oxazaborolidines is comparable to that of B-allyl-1,3,2-dioxaborolane, the B-allyl-3-(*p*-tolylsulfonyl)-1,3,2-oxazaborolidine undergoes allylboration remarkably rapidly, even at -78°C. The acyclic allylboronates undergo, without exception, more rapid allylboration at 0°C compared to allyl-1,3,2-dioxaborinane. These individual variations in the rates of allylboration of the boronate derivatives can be rationalized essentially in terms of the relative availability of the lone pairs of electrons on the atoms attached to boron.

Fehlner *et al.* applied the Fenske–Hall molecular orbital method to the calculation of boron-11 NMR chemical shifts [49]. By utilizing Fenske–Hall wave functions and eigenvalues combined with the Ramsey sum over states (SOS) approximation, it was demonstrated that the sign and magnitude of the paramagnetic contribution correlate well with the observed ^{11}B chemical shifts. Johnson *et al.* used ESR spectroscopy to characterize reactions of the aminyl–borane radicals in solution [50].

Pombrik *et al.* reported a fluorine-19 NMR study of the transmissive ability of boron-containing bridged systems with three- and four-coordinated boron atoms [51].

Bendel *et al.* reported a method for imaging nuclei with short T2 relaxation and its application to boron-11 NMR imaging of a BNCT agent in an intact rat [52]. An NMR imaging method designed for nuclei with very short T2 relaxation times utilizing free induction decay (FID) was used to obtain ^{11}B images of aqueous boron phantoms and the boron distribution.

2.3.4. Structure

Eisch *et al.* utilized X-ray crystallography to remove uncertainties in the apparent C–C and B–C bond lengths of the borirene ring, as previously estimated from X-ray crystallography [53]. In this system the carbon–carbon triple bond showed no unusual lengthening and hence gave no indication of significant conjugation with the tricoordinate boron. When the tricoordinate boron of the borirene ring becomes tetracoordinate by ligation with an amine, such as pyridine, or a sterically suitable alcohol like methanol, the borirene ring is promptly ruptured and, in the presence of a proton source, irreversibly converted into an acyclic borinic ester. Such rupture of the borirene ring by pyridines can be monitored by electronic and multinuclear NMR spectroscopy. These observations corroborate the role of the available $2p_z$-orbital on sp^2-hybridized boron in stabilizing the borirene ring.

Yalpani *et al.* report that bis(9*H*-9-borabicyclo[3.3.1]nonane) reacts with pyrazole and its derivatives to give the 9-pyrazolyl-9-borabicyclo[3.3.1]nonanes [54]. The crystal structures were determined. Farfan *et al.* carried out NMR and X-ray diffraction studies of two bicyclic borates containing chiral boron and nitrogen atoms [55]. They found that ring closure between the N and B atoms during the synthesis of bicyclic organoboron compounds occurs with asymmetric induction.

Chapelle and Verchere studied the formation of 1:1 or 1:2 borate–sugar complexes by sugars having ribo configurations by ^{11}B- and ^{13}C-NMR spectroscopy [56]. Two 1:2 complexes can be formed, depending on whether the sugar is α or β. The main species involved *cis*-HO-1,2. D-Psicose formed a single complex at HO-2,3. A second species was formed by D-talose (10%), D-ribose (30%), and D-allose (30%), which involved *cis*-HO-2, 3 with HO-1,2 *trans*. The order of stabilities of the complexes was that D-psicose was more stable than D-ribose, which was more stable than D-talose, which was more stable than D-allose.

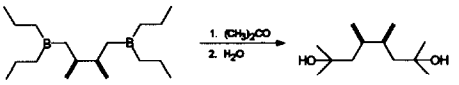
Koester *et al.* prepared and characterized 9-fluoro-9-borabicyclo[3.3.1]nonane in solution and in the solid state [57]. The compound was characterized by IR,

mass, and multinuclear NMR spectroscopy. Pure, in solution, the material has a small ^{11}B-NMR singlet signal. The X-ray structure has three differently bonded molecules in the cell and shows a monomer and a dimer with BFB coordination bond.

Grachek *et al.* reported the mass spectra of some boric acid esters [58].

2.4. Synthesis

Barriola and Valcarcel report the carbon dioxide laser induced synthesis of trialkylboranes [59]. Rees *et al.* described an *in situ* preparation of trimethylboron using trimethylaluminum [60]. Gurskii *et al.* synthesized 2,3-dimethylene-1,4-bis-(dipropylboryl)butane [61]. Treating thexene with butyllithium 50% yield of the targeted material. The reagent could be added to ketones which yielded diol products which were then subjected to Diels–Alder reactions.

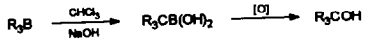


Flores-Parra *et al.* prepared a series of new quinic acid boron esters in aprotic media [62]. These boron heterocycles are useful intermediates, since they provide an alternative to dioxolane derivatives for functionalizing quinic acid.

3. Carbon–carbon bond formation

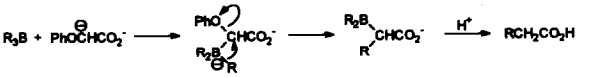
3.1. Homologation

Bai and Ding report the first phase-transfer catalyzed reaction of trialkylboranes with chloroform, which provides an economical and convenient method for the synthesis of trialkymethanols [63].

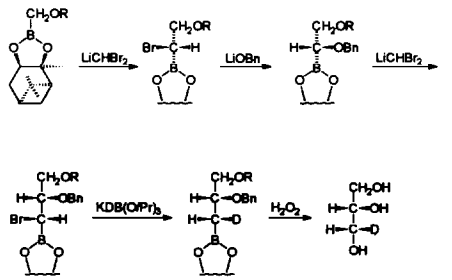


Brown *et al.* report the successful ring enlargement of boracyclanes *via* sequential one-carbon homologation [64]. The procedure represents the first synthesis of boracyclanes in the strained medium-ring range. The sequential one-carbon homologation of B-methoxyboracyclanes was achieved utilizing the successive reaction of B-methoxyboracyclanes with *in situ*-generated (chloromethyl)lithium. The yields achieved are in the range of 75%–85%.

Hara *et al.* developed a direct synthesis of carboxylic acids from organoboranes [65]. The synthesis involves a two-carbon atom homologation with the dianion of phenoxyacetic acid. Alkanoic, alkenoic, or alkynoic acids can be synthesized from the corresponding alkenes, dienes, or enynes, respectively, *via* hydroboration. The reaction is tolerant of various functional groups present in alkenes, thus giving corresponding carboxylic acids with chloro, sulfide, ether, acetal, and thioacetal functionalities in good yields.



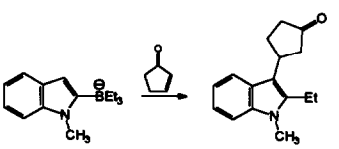
Matteson *et al.* developed a synthesis of asymmetrically deuterated glycerol and dibenzyl glyceraldehyde *via* boronic esters [66]. (*S*)-Pinanediol [(benzyloxy) methyl]boronate was converted, *via* an improved procedure, to (*S*)-pinanediol(1*R*)-[(1,2-bis(benzyloxy)ethyl]boronate in 96% diastereomeric excess (de), which with Br_2CHLi yielded (*S*)-pinanediol (1*S*,2*S*)-[2,3-bis (benzyloxy)-1-bromopropyl]boronate. This was then converted to the desired products.



Matteson and Beedle also prepared (1-methoxyvinyl)boronic and (1-chlorovinyl)boronic esters [67]. The methoxy derivative was synthesized from (1-methoxyvinyl)lithium and triisopropyl 1-methylpentyl)boronate. Reaction of the chloro derivative with (dichloromethyl)lithium yielded (*S*)-pinanediol (1*S*)-(1,2-dichloroallyl)boronate in 92% diastereomeric excess.

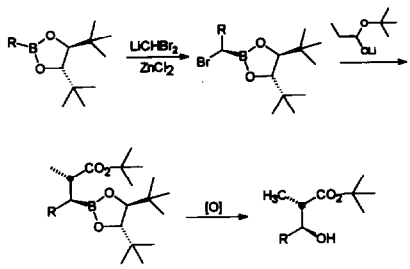
Gurskii *et al.* investigated the reactions of 1-boraadamantane with triethyl orthoformate at 20–70°C to give a borabicyclononane derivative. Bubnov *et al.* report an unusual reaction of triorganoboranes with ethyl orthoformate [68]. The reaction of R_3B with orthoformate at 135–140°C gave ethyl borinate and boronate esters in a ratio of approximately 1:1.

Ishikura and Terashima report the conjugate addition reaction of triethyl(1-methylindol-2-yl)borate, prepared from 1-methylindole by lithiation followed by reaction with triethylborane to 2-cycloalkenones [69].



Matteson and Michnick reported a stereoselective reaction of an enolate with chiral α-haloboronic acid esters [70]. Reaction of tert-butyl *trans*-lithiopropionate

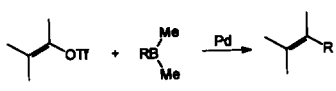
with (*S,S*)-diisopropylethanediol (DIPED) (1*R*)-(1-bromopentyl)boronate yielded semipurified tert-butyl (2*S*,3*S*)-3-hydroxy-2-methylheptanoate (*threo*) in a 60:1 ratio to the *erythro* diastereomer. These reactions are sluggish and α-bromoboronic esters generally give better yields than the corresponding chloro compounds. Less hindered ester enolates appear to undergo Claisen condensation under the reaction conditions, and only the tert-butyl ester proved useful. An efficient synthesis of (3*S*,4*S*)-2,5-dimethoxy-2,5-dimethyl-3,4-hexanediol and its use as an achiral director for chain extension of boronic esters are described.



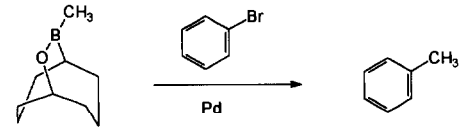
Tripathy and Matteson also reported the asymmetric synthesis of each of the four stereoisomers of 4-methyl-3-heptanol in very high purity [71]. Tayano *et al.* report the stereoselective synthesis of δ-iododienyl ketone ethylene acetals by the reaction of B-(2-iodo-1-alkenyl)-9-borabicyclo[3.3.1]nonanes with β-methoxy-α,β-unsaturated ketones [72].

3.2. Alkenylborate and arylborate

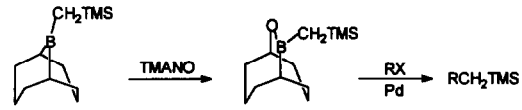
The chemistry of alkenyl and aryl boron derivatives is dominated by modifications and applications of the Suzuki coupling reaction. In a continuation of their development of this valuable reaction, Oh-e and Suzuki described the palladium-catalyzed coupling reactions of aryl or 1-alkynyl triflates with alkyl-, aryl-, and 1-alkenylboron compounds in the presence of potassium phosphate, which takes place in high yield under mild conditions [73]. The reaction provides a simple method for the preparation of alkenes, 1,3-alkadienes, arylalkenes, and biaryls and should make the Suzuki reaction even more useful in organic synthesis.



Soderquist and Santiago report a clean, efficient Pd-catalyzed cross-coupling of vinyl, alkynyl and aryl bromides with the air-stable organoborane, 10-methyl-9-oxa-10-borabicyclo[3.3.2]decane [74]. This report offers the possibility of carrying out Suzuki coupling reactions with alkyl groups in the absence of base.

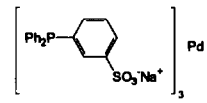


Soderquist *et al.* also describe an efficient Pd-catalyzed cross-coupling of viny, alkynyl and aryl bromides with the air-stable organoborane, [(trimethylsilyl) methyl]oxaborabicyclodecane [75]. The reaction produces excellent yields of the corresponding silylmethylated products, proceeding with complete retention of configuration.

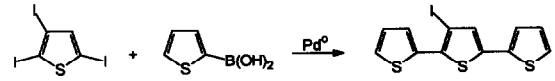


Roush *et al.* developed a stereoselective synthesis of (*Z,E*)-2-bromo-1,3-dienes *via* the palladium(0)-catalyzed cross-coupling reactions of 1,1-dibromoolefins and vinylboronic acids [76]. The syntheses are accomplished in the presence of $Pd(PPh_3)_4$ and TlOH. The reactions are most efficient when the dibromoalkene has an allylic alkoxy group.

Casalnuovo and Calabrese developed palladium-catalyzed alkylations in aqueous media using vinylboronic acids [77]. A water soluble palladium complex was isolated and characterized. Hydrophobic or hydrophilic aryl and heteroaromatic halides underwent coupling reactions with aryl or vinylboronic acids, alkynes, an alkene, and a dialkyl phosphite. Examples of the alkylation of biomolecules in aqueous media included the coupling of alkynes with unprotected iodonucleotides, iodonucleosides, and an iodoamino acid.



Siddiqui and Snieckus developed a concise syntheses of the Amaryllidaceae alkaloids ungerimine and hippadine *via* the Suzuki aryl–aryl cross-coupling reaction [78]. Gronowitz and Peters developed a convenient synthesis of various terheterocyclic compounds using palladium(0)-catalyzed coupling reactions with heterocyclic boronic acids [79].



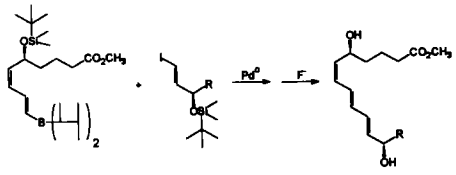
Cramer and Percec described a phase transfer palladium(0)-catalyzed polymerization involving cross-coupling of alkyl–boron compounds and aromatic halides

catalyzed by $PdCl_2$(dppf) and bases [80]. The polymerization sequence of 1,7-octadiene involved hydroboration with 9-borabicyclo[3.3.1]nonane followed by intermolecluar cross-coupling with 1,4-dibromo-benzene or 1,4-diiodobenzene in presence of palladium. Cramer and Percec also report phase transfer palladium(0)-catalyzed polymerization reactions consisting of hydroboration of a diolefin with 9-borabicyclo[3.3.1]nonane followed by the intermolecular cross-coupling of the resulting α,ω-bis(B-alkanediyl-9-borabicyclo[3.3.1] nonanes) with dihaloarenes [81].

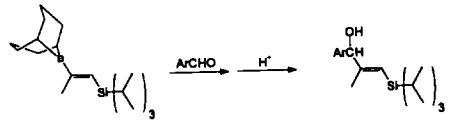
Fu and Snieckus describe a new and general Pd^0-catalyzed cross-coupling reaction of aryl boronic acids with aryl triflates to give biaryls [82].

Suri and Nair report the synthesis of 2-aryl-7-methoxytropones using a palladium(0)-catalyzed organoborane reaction [83]. Catellani *et al.* outlined a palladium-catalyzed carbon–carbon coupling reaction with tetra-arylborates [84]. Bumagin *et al.* describe the palladium-catalyzed cross-coupling of arylboric acids and sodium tetraphenylborate with aryl halides in aqueous solutions [85]. Crisp and Macolino used the palladium-catalyzed coupling of both 5-iodouridine and 5-iodo-2′-deoxyuridine derivatives with functionalized and non-functionalized arylboronic acids to produce moderate to good yields of the corresponding 5-aryluridines and 5-aryl-2′-deoxy-uridines [86].

Kobayashi *et al.* describe a highly stereocontrolled synthesis of leukotriene B4, 20-hydroxyleukotriene B4, leukotriene B3, and their analogues [87]. The sequence involves the Pd-catalyzed coupling reaction of a vinylborane, derived from the C(1)–C(9) fragment.



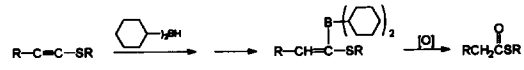
Soderquist and Vaquer used the Brown vinylation of aromatic aldehydes to provide a simple, efficient route to pure (*E*)-3-silylallyl alcohols [88]. Although the reaction is limited to aryl aldehydes, it provides a useful entry to stereodefined allylic alcohols containing the silyl functionality.



Vinyl and aryl borane reagents were also utilized in non-coupling reactions which have potential applications in a number of synthetic transformations. Larock and Stolz-Dunn report that organoboranes effect facile ring opening of vinylic oxetanes to give homoallylic alcohols [89]. In general, boron reagents react in a completely regioselective fashion, with preference for formation of the (*E*)-isomer.

Mikhail and Kaufmann describe the synthesis of optically active vinylboronates starting with (−)-2,3-pinanediol or (+)-diethyl tartrate and dichlorovinylborane, vinylboronic acid, and dibutylvinylboronate [90]. Singleton and Martinez described the synthesis and Diels–Alder reactions of 9-vinyl-9-borabicyclo[3.3.1] nonane (vinyl-9-BBN) [91]. The Diels–Alder reactions of vinyl-9-BBN with butadiene, isoprene, *trans*-piperylene, 1-vinylcyclohexene, and cyclopentadiene are reported. The endo-stereoselectivity generally rivals or exceeds that observed in the corresponding Lewis acid catalyzed Diels–Alder reactions on methyl acrylate. A steric effect in the reaction with *trans*-piperylene results in the regiospecific formation of the normally disfavored *meta* isomer.

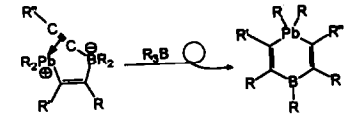
Hoshi *et al.* hydroborated 1-alkylthio-1-alkynes with dicyclohexylborane or bis(1,2-dimethylpropyl)borane [92]. The resulting alkenylboranes afforded either *S*-alkyl alkanethioates on controlled oxidation in the presence of *N,N,N,N′*-tetramethylethylenediamine or (*Z*)-1-alkylthio-1-alkenes on basic protonolysis, successive treatments with methyllithium, CuI and water in the presence of hexamethylphosphoric triamide.



3.3. Alkynylborate

Chen *et al.* describe the stereoselective allylation of lithium trialkylalkynylborates by allyl carbonate in the presence of $Pd(PPh_3)_4$ [93]. Interestingly, the (*E*)-isomer forms predominantly, in contrast to the results obtained in earlier studies utilizing allyl halides.

Wrackmeyer and Horchler report that the organoboration of bis(alkynyl)plumbanes leads to intermediates in which a triorganolead cation is stabilized by intramolecular side-on coordination to the carbon–carbon triple bond of an alkynylborate function [94]. These compounds decomposed rapidly at room temperature or rearrangement to give 1,4-plumbabora-2,5-cyclohexadienes.

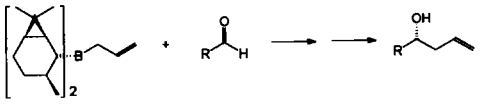


3.4. Propargyl(allyl)boranes

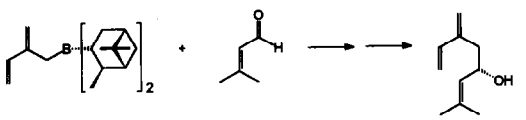
Allylborane reagents are beginning to play a key role in the syntheses of numerous ager with stereodefined centers. This year, the activity in this area of

organoborane chemistry was rather remarkable. The allylboron reagents include those based on organoboranes, which generally are chiral due to the incorporation of stereodefined alkyl groups, as well as a wide assortment of boronic acid derivatives. Brown and his co-workers have been most active in the organoborane arena. As an example, Brown *et al.* found that the hydroboration of (+)-2-carene, readily available *via* the base-induced isomerization of (+)-3-carene, provides bis(2-isocaranyl)borane, which can be readily transformed into B-allylbis(2-isocaranyl)borane [95]. This new reagent asymmetrically allylborates a variety of aldehydes and gives the respective homoallylic alcohols in 94%–99% ee. The enantioselectivities realized with this reagent are significantly higher than those realized with the previously explored reagents, *e.g.* B-allyldiisopinocampheylborane and B-allylbis(4-isocaranyl)borane. Interestingly, the new reagent affords products of opposite stereochemistry than those obtained using B-allylbis(4-isocaranyl)borane.

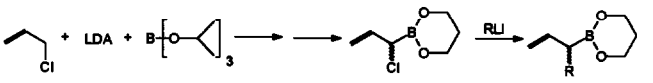
Brown and Randad also describe the synthesis and use of B-(*Z* and *E*)-crotylbis(2-isocaranyl)boranes as valuable reagents for the asymmetric crotylboration of aldehydes [96].



Brown *et al.* devised an efficient synthesis of isoprenyl derivatives of borane which are valuable reagents for the isoprenylboration of aldehydes [97]. Brown and Randad also prepared B-2′-isoprenyldiisopinocampheylborane by metalation of isoprene with potassium 2,2,5,5-tetramethylpiperidide followed by sequential treatment with B-methoxydiisopinocampheyl borane and boron trifluoride-etherate [98]. Condensation of this reagent with aldehydes provides isoprenylated chiral alcohols. This methodology is utilized for an efficient one-pot synthesis of both enantiomers of the pheromones of the bark beetle *Ips paraconfusus Lanier*, ipsenol and ipsdienol.

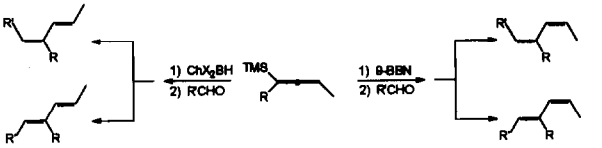


Brown and Rangaishenvi describe a successful application of α-haloallyllithium for a simple, convenient preparation of α-haloallylboronate ester [99]. They then utilized the reagent in a simple procedure for the synthesis of three-carbon homologated boronate esters and terminal alkenes *via* nucleophilic displacement [100]. The transfer reactions of α-haloallylborane esters with representative organolithium and Grignard reagents provide α-alkyl- or α-aryl-substituted allylboronate esters which are readily converted into C3-homologated boronate esters *via* a thermally induced boratropic rearrangement and terminal alkenes *via* protonolysis.



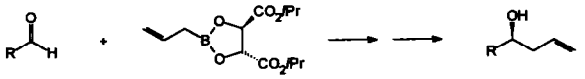
Prasad and Rich describe a general and stereoselective method to (produce) statine and ketomethylene and hydroxyethylene dipeptide isosteres [101]. The key reaction is the diastereoselective allylboron addition to α-amino aldehydes. Knoerzer *et al.* studied novel allylborane and allyldiborane derivatives [102].

Wang *et al.* developed a stereoselective synthesis of all four geometric isomers of internal 1,3-butadienes by the condensation reaction of aldehydes with δ-trimethylsilyl-substituted allylboranes [103]. Hydroboration of 2-(trimethylsilyl)-2,3-pentadiene or 4-(trimethylsilyl)-2,3-octadiene with 9-borabicyclo[3.3.1]nonane or dicyclohexylborane produced the corresponding δ-trimethylsilyl-substituted allylborane which condensed smoothly with aldehyde to afford, after elimination of hydroxytrimethylsilane by either basic or acidic workup, a variety of internal 1,3-butadienes. Apparently, high diastereoselectivity was obtained during the condensation step and therefore allowed an easy control of the geometry of one of the two resulting double bonds by simply employing either basic or acidic workup conditions to promote the Peterson olefination reaction. The geometry of the other double bond could also be controlled by selecting either 9-borabicyclo[3.3.1]nonane or dicyclohexylborane as the hydroborating agent. Consequently, all four geometric isomers of several representative internal 1,3-dienes were synthesized with high isomeric purity by utilizing different combinations of the hydroborating agents and the workup conditions. The authors carried out a detailed ^{1}H-NMR investigation of the allylborane intermediates and discovered unexpectedly facile [1,3]-sigmatropic rearrangements.



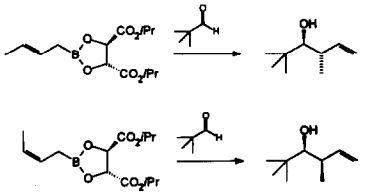
Roush *et al.* investigated the factors influencing stereoselectivity of the reactions of allyl boronates with chiral and achiral aldehydes [104]. The stereoselectivity of the reactions is sensitive to variables such as reaction temperature, solvent and moisture but not (on) the structure of the tartrate ester. Tartrate allylboronate has been found to be exceptionally reactive compared

to other, previously studied allylboronates, and even the reactions of very hindered substrates (*e.g.* pivaldehyde) are complete within several hours at −78°C.

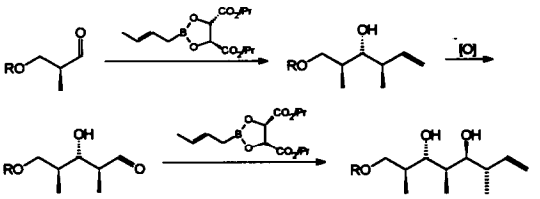


Roush *et al.* used the reactions of tartrate allylboronates with chiral and achiral alkoxy-substituted aldehydes for single and double asymmetric reactions with alkoxy-substituted aldehydes [105]. Conformationally unrestricted α- and β-alkoxyaldehyde substituents have a significant, negative impact on the stereoselectivity of the asymmetry allylborations. In contrast, chiral aldehydes containing alkoxy groups that are conformationally constrained by incorporation in rings, as in glyceraldehyde acetonide 4-deoxythreose ketal and α,β-epoxyaldehydes, are excellent allylboration substrates, with diastereoselection in certain cases being significantly greater than that obtained with simpler achiral substrates. A model that rationalizes this alkoxy effect is presented. A simple method for the analysis of the average diastereofacial selectivity of a chiral reagent in a pair of double asymmetry reactions is also presented. This analysis, which is independent of the intrinsic diastereofacial bias of the chiral aldehyde, enables one to make direct comparisons of the relative diastereoselectivities of a range of chiral substrates.

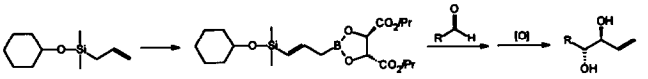
Roush *et al.* prepared chiral crotylboronates and reacted them with achiral aldehydes [106]. Diisopropyl tartrate modified (*E*)- and (*Z*)-crotylboronates are easily prepared with very high isomeric purity *via* the metalation of (*E*)- and (*Z*)-2-butene followed by treatment of the (*E*)- and (*Z*)-crotylpotassiums with triisopropylborate aqueous hydrolysis, and esterification with diisopropyl tartrate (DIPT). (*E*)-Crotylboronate has been prepared on 400 mmol scales with excellent results. A procedure for the preparation and standardization of solutions was also described. The reaction diastereoselectivity closely parallels the reagent isomeric purity especially for reactions performed at −78°C. The results in each case are consistent with the asymmetry crotylboration reaction proceeding preferentially through a transition state in which the R of RCHO has priority over the crotyl group that is transferred.



Roush *et al.* then studied double asymmetric reactions with tartrate ester-modified crotylboronates and carried out the synthesis of the C(19)–C(29) segment of *rifamycin S* [107]. An empirical model was presented which predicted the situations in which maximum effectiveness is achieved in complex synthetic problems, *e.g.* in the highly diastereoselective synthesis of the C(19)–C(29) segment of the ansa bridge of *rifamycin S*. This synthesis features four carbon–carbon bond forming reactions involving the chiral crotyl- and allylboronate technology.

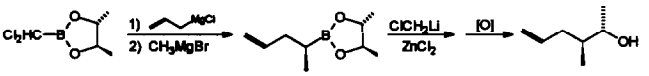


Roush and Park described an efficient kinetic resolution of racemic complexes and the highly enantiotopic group and face selective allylboration of a meso substrate [108]. Roush and Grover used diisopronyl tartrate (*E*)-δ-(dimethylphenylsilyl)allylboronate, a chiral allylic alcohol, β-carbanion equivalent for the enantioselective synthesis of 2-butene-1,4-diols from aldehydes [109]. Roush *et al.* developed an enantioselective synthesis of *anti*1,2-diols *via* the reactions of aldehydes and the tartrate ester modified δ-(alkoxysilyl)allylboronate [110].



Roush and Park discovered a significant improvement in the enantioselectivity of the asymmetry allylborations of certain unsaturated aldehydes by using metal carbonyl derivatives as substrates [111].

Matteson and Campbell utilized (*R*,*R*)-2,3-butanediol and (*S*)-pinanediol allylboronates in chiral synthesis of (2*S*,3*S*)-3-methyl-5-hexen-2-ol [112].

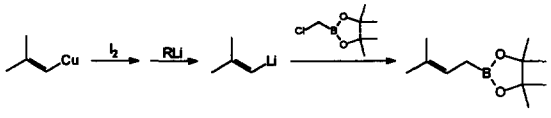


Hoffmann and Sander report that the reaction of isomers of (methylcrotyl)boronate with acetone gave mixtures. Unsymmetrical ketones yield mixtures of diasteriomers [113]. Bubnov *et al.* found that allylboration of aldehydes and ketones a well as mono- and diallyboration of glyoxal with allylic dimethoxyboranes can be achieved in water to give the corresponding homoallylic alcohols [114]. Zhou *et al.* synthesized 2-amino-1,2-oxaborolanes *via* reaction of allylox-

aborolane with various amines [115]. Brinkmann and Hoffmann examined the direction (Cram/anti-Cram) and the extent of asymmetric induction on addition of crotylboronates to chiral aldehydes [116]. A reversal in the sense of the asymmetric induction on changing from the (*Z*)- to the (*E*)-crotylboronate was found for aldehydes having polar α substituents and for some of the non-polar chiral aldehydes.

Hoffmann *et al.* found that the diastereoselectivity on addition of δ-substituted allylboronates to α-methylbutyraldehyde did not depend on the size of the substituent in the reagent but only on its location in the *Z* or *E* position [117]. This finding required a reinterpretation of the reasons for the attendant reversal in diastereoselectivity.

Hoffmann and Schlapbach investigated the stereoselective generation of homoallylic alcohols having quarternary stereogenic centers [118]. δ,δ-Disubstituted allylboronates (*E*- and *Z*-isomers) were generated by the carbocupration of alkynes and subsequent homologation. These allylboronates add to aldehydes to form homoallylic alcohols with 88%–99% simple diastereoselectivity. The highest diastereoselectivity was obtained with α-branched aldehydes.

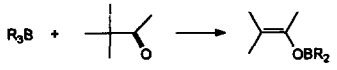


Stuermer and Hoffmann described an enantioselective allylboration of aldehydes with (4*R*,5*R*)-2-[(*S*)-1-chloro-2-propenyl]-4,5-dicyclohexyl-1,3,2-dioxaborolane [119].

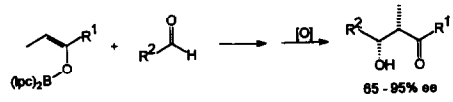
Guyot *et al.* report that pinacol-*E*-1-trimethylsilyl-1-propene-3-boronate regiospecifically reacts with aldimines and ketimines [120].

3.5. Enol borinates

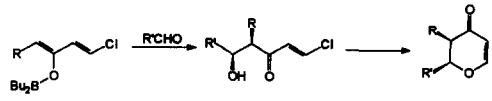
Maruoka *et al.* described a new preparative method for boron enolates [121]. The enolates were prepared from α-iodocarbonyl compounds under mild condition. The enolates thus obtained have been utilized for the stereoselective aldol reaction with aldehydes with the object of elucidating the influence of solvent effects on the *erythro/threo* selectivity.



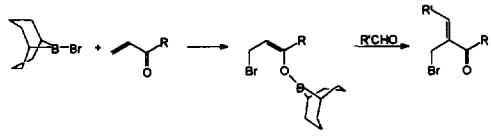
Paterson *et al.* studied the use of enol diisopinocampheylborinates in enantio- and diastereoselective aldol reactions of achiral ethyl and methyl ketones with aldehydes [122]. The reagents employed are easily prepared in enantiomerically pure form. The aldol reaction with ethyl ketones and aldehydes *via* the *Z*-enol gives product ketones in good enantiomeric excess (66%–90% ee) and with a diastereoselectivity approaching 95%. In contrast, the anti-selective aldol reaction of diethyl ketones *via* the *E*-enol proceeds with negligible enantioselectivity. Use of both the triflate and chloride reagents in the aldol reaction of methyl ketones with aldehydes gives β-hydroxy ketones in moderate enantiomeric excess (53%–78% ee) with a reversal in the enantioface selectivity of the aldehyde compared to the corresponding ethyl ketone syn aldol. This variable selectivity is interpreted as evidence for the participation of competing chair and boat transition states. Other chiral dialkylboron triflate reagents led to reduced enantioselectivities.



Paterson and Osborne described a synthesis of dihydropyrones involving the stereoselective aldol reactions of β-chlorovinyl ketones [123].



Shimizu *et al.* generated boron enolates *via* the 1,4-addition of B–Br-9-BBN to α,β-unsaturated ketones [124].



4. Carbon–heteroatom bonds

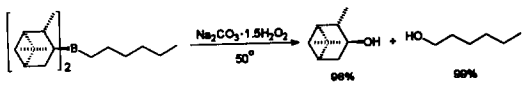
4.1. Group VII

The halogenation of organoborane derivatives has been rather well defined. There were few interesting reports related to this synthetic transformation. Pan *et al.* utilized the selective hydroboration–iodination of terminal alkenes containing functional groups to synthesize two insect sex pheromones [125].

Symes *et al.* synthesized (*E*)-17α-[^{131}I]iodovinyl estradiol using the vinylboron precursor and evaluated its use as radiotracer for estrogen receptor-positive breast tumors [126]. The material is metabolically stable and has been shown to accumulate in estrogen sensitive tissues of rodents. Clough *et al.* described a route to fluoroaromatics from boronic acids and cesium fluoroxysulfate [127].

4.2. Group VI

Kabalka *et al.* outlined a simple oxidation methodology suitable for the oxidation of organoboranes containing functional groups [128]. The method utilizes sodium percarbonate, a readily available, inexpensive, and easily handled reagent for efficiently oxidizing organoboranes. The product yields compare favorably with those obtained by use of the standard hydrogen peroxide methodology.



Bank and Longley describe an efficient and convenient method of preparing oxygen-17 enriched phenols using aryl boronic acids [129]. The boronic acids are oxidized with oxygen-17 enriched potassium hydroperoxide which is prepared from the autoxidation reaction of benzhydrol with oxygen-17 enriched oxygen gas in the presence of potassium tert-butoxide. ^{17}O-NMR spectra of the enriched phenols demonstrate the benefits of using enriched samples in reducing the total experiment time and greatly improving the signal-to-noise ratio.

4.3. Group V

Bubnov *et al.* report a new synthesis of 1-azaadamantane from 1-boraadamantane [130]. Reaction of a borabicyclononane, previously prepared from 1-boraadamantane, with lithium azide, followed by oxidation, gave azabicyclononane which, when treated with thionyl chloride, gave 1-azaadamantane.

Kabalka and Wang used the hydroboration/amination of *N*-trimethylsilyl protected olefin amines and diolefins to synthesize isomerically pure diamines [131]. Kabalka and Wang also prepared isomerically pure dialkylamines *via* the reaction of dimethylalkylboranes with chloroalkylamine [132]. Chlorination of a primary amine with hypochlorite followed by treatment with an alkyl dimethylborane gave dialkylamines.

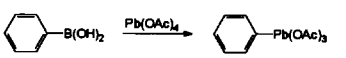
4.4. Metalation from B to M

Ramakrishnan and Chung carried out a NMR study of alkyl exchange reactions between boron and aluminum and evaluated the effect of such exchange reactions on the polymerizability of alkenyldialkylboranes by the Ziegler–Natta process. [133]. The reaction of a model borane, octyldimethylborane, with Et_3Al, Et_2AlCl and $EtAlCl_2$ was investigated. The transfer of the methyl group from boron to aluminum was monitored as a function of time. The rate of transfer was found to be rapid in the case of Et_3Al and decreased in the order: $Et_3Al > Et_2AlCl > EtAlCl_2$. The extent of this transfer at equilibrium, followed the same order and a maximum 92 mole% of the methyl group was transferred in the case of Et_3Al. Sterically hindered aluminum alkyls such as tri(isobutyl)aluminum were also found to undergo rapid exchange with octyldimethylborane. Sterically crowded boranes such as 1-hexenyl-9-BBN did not undergo an exchange reaction with Et_2AlCl.

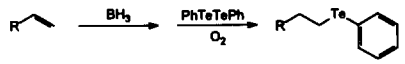
Snieckus reviewed three new methodologies based on the directed *ortho* metalation tactics; (i) silylated benzamides as dual *ortho*- and α-carbanion synthons for use in heteroannelation, lateral functionalization, alkaloid synthesis, and 1,3-dipolar cycloaddition; (ii) cross-coupling reactions of functionalized aryl boronic acids with aryl bromides leading to heteroaromomatics and alkaloids; and (iii) original 1,5-radical switch reactions providing new routes for heteroannulation and α'-amide functionalization [134].

Wrackmeyer and Horchler von Locquenghien studied the organoboration of monoalkynyllead compounds [135]. Alkynyllead compounds react with non-cyclic, monocyclic (B-t-hexylborolane), and bicyclic boranes (B-*R*-9-borabicylco[3.3.1]nonanes), to give organometallic-substituted alkenes. The reaction leads stereoselectively to the (*E*)-alkenes. If there is a second different organometallic group attached to the triple bond, the reaction with non-cyclic boranes affords a mixtures of (*E*/*Z*)-isomers. There are numerous examples in which the organoboration of the alkynyllead compounds readily gives the desired alkene derivative, whereas the corresponding alkynyltin compounds react very slowly or not at all. On the other hand, the alkenes bearing the boryl and the Me_3Pb group are thermally less stable than the corresponding tin compounds.

Huber and Pinhey prepared aryllead triacetates *via* boronic acid reactions with lead tetraacetate [136].



Nozaki *et al.* studied the triethylborane induced stereoselective radical addition of triphenylgermane to carbon–carbon multiple bonds [137]. Abe *et al.* report the oxygen-induced transmetalation of organoboranes with diphenyl ditelluride in the presence of oxygen to give alkyl phenyl tellurides in high yields [138]. The facile reaction proceeds *via* a free-radical mechanism induced by a stoichiometric amount of oxygen. A combination of this transmetalation with hydroboration provides an alternative method for hydrotelluration of olefins.



5. General synthetic methods

Chujo *et al.* reported the preparation of novel organoboron polymers by polyaddition between boron tribromide and a terminal diyne [139]. The polyaddition between 1,7-octadiyne and BBr_3 produced the corresponding poly(organoboron halide) as a brown solid soluble in common organic solvents such as chloroform and having a number-average molecular weight of 5200 and a weight-average molecular weight of 15,500 as determined by GPC. The structure of the polymer was supported by its ^{1}H-NMR, ^{11}B-NMR, IR, and UV spectra. The haloboration polymerization proceeded by *cis*addition of B–Br to the carbon–carbon triple bond.

Reddy and Periasamy reported a new, simple procedure for the generation and addition of hydrogen iodide to alkenes and alkynes using boron triiodide/*N,N*-diethylaniline complex and acetic acid [140]. HI, generated *in situ* from a BI_3-amine complex, readily adds to alkenes and alkynes in Markovnikov fashion to form alkyl and alkenyl iodides in high yield under mild conditions.

Dahlhoff *et al.* outlined the synthesis and stereoselective glycosylations of 3-O-acetyl-2,4-O-phenylboranediyl-β-D-ribopyranosyl bromide [141]. The reagent was prepared by an easy four-step synthesis from D-ribose, the first three steps of which are realized in one-pot. The material reacts stereoselectively with sodium methoxide and phenoxide to give, after deboration and deacetylation, the pure ribopyranosides.

Kaufmann and Boese developed a borate propeller compound as a chiral catalyst for an asymmetrically induced Diels–Alder reaction [142]. Acrolein underwent asymmetric Diels–Alder reaction with cyclopentadiene in presence of the hexanaphthohexaoxadiborabicycloeicosahexaene to give the (+)-*exo*-methylbicycloheptenecarboxaldehyde.

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