BORON I. CARBORANES AND HYDROBORATION
ANNUAL SURVEY COVERING THE YEAR 1977

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CONTENTS

Boron I. Carboranes and Hydroboration: Annual Survey Covering the Year 1976, see J. Organomet. Chem., 147 (1978) 17-62.

I. CARBORANES

A. Introduction

Metallacarborane chemistry has continued to provide the greatest number of new types of structures, with Grimes' research group now publishing the largest number of papers in this area. The total rate of research in this area has slowed considerably compared to a few years ago. Icosahedral carborane chemistry is still being pursued vigorously in the U.S.S.R., with Zakharkin's group continuing to provide a substantial number of papers.

As usual, the reviewer has included papers dealing with boron hydrides that are of possible interest to carborane chemists. Although patents as recorded in Chemical Abstracts have been included in previous Surveys, they have been omitted this year.

B. Metallacarboranes

Grimes and coworkers have reported the synthesis of a series of tetracarbon metallacarboranes derived from $(CH_3)_4C_4B_8H_8$ by way of the anion $(CH_3)_4C_4B_8H_8^{2-}$ and suitable transition metal compounds, including $FeCl_2$ + NaC_5H_5, the complex of $Ph_2PCH_2CH_2PPh_2$ with $NiCl_2$, $Mo(CO)_6$, and $W(CO)_6$ [1]. The iron compounds include two nido isomers of $(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ (Figure 1) as well as another nido compound resulting from loss of one boron atom from the cage and introduction of only one iron atom (Figure 2). The nido structures (I) and (II) were unexpected, since theory predicts that closo cages should be thermodynamica more stable for this composition.

Thermal isomerization of the nido isomers (I) and (II) does lead to the closo isomer (VII) and finally (VIII) [2]. The structures of (I), (II), intermediate (V), and (VIII) have been established by X-ray diffraction, and (VIII) has been assigned on the basis of NMR data (Figure 3).

Maxwell, Wong, and Grimes have reported reactions of the ferracarborane $[2,3-(CH_3)_2C_2B_4H_4]_2FeH_2$ [3]. With CO at 200°C, the major product is $Fe(CO)_3(CH_3)_2C_2B_7H_7$ (Figure 4). Treatment of $[2,3-(CH_3)_2C_2B_4H_4]_2FeH_2$ with NaH in THF results in removal of one proton from the iron, and the anion reacts with GeI_2 or $SnCl_2$ to form $GeFeC_4(CH_3)_4B_8H_8$ or $SnFeC_4(CH_3)_4B_8H_8$, which have structures different from the previously known Fe-Co series (Fig. 5). However, $PbBr_2$ yielded only $(CH_3)_4C_4B_8H_8$. Reaction of $[2,3-(CH_3)_2C_2B_4H_4]_2FeH_2$ with $CoCl_2$ cyclopentadiene, and KOH in ethanol yielded a mixture of products, including two new cobaltferracarboranes (Fig. 6) and a cobalt analogue of $(CH_3)_4C_4B_8H_8$ (Fig. 7)

The reaction of NaB_5H_8 with $CoCl_2$ and NaC_5H_5 in THF produces a mixture of cobaltaboranes, including $(C_5H_5)CoB_4H_8$, $1,2-(C_5H_5)_2Co_2B_4H_6$ and its 3- and 4-cyclopentenyl derivativies, $(C_5H_5)_3Co_3B_3H_5$, $(C_2H_5)_3Co_3B_4H_4$, $(C_5H_4)_4Co_4B_4H_4$, and a dicobaltacarborane having a cyclopentene ring fused onto the cage [4].

(Continued on p. 22)

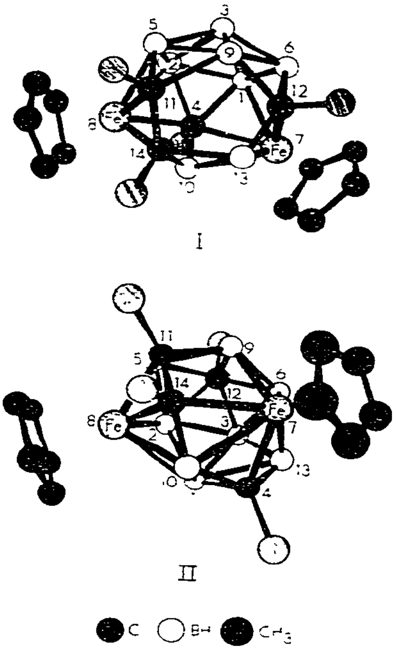


Figure 1. Structures of isomers (I) and (II) of $(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$. There is an open face on (I) defined by C11, B9, C12, B13, and C14, and an open face on (II) defined by C11, B9, Fe7, and C14. [Reprinted with permission from W. M. Maxwell, R. F. Bryan, and R. N. Grimes, J. Am. Chem. Soc., 99 (1977) 4008. Copyright by the American Chemical Society.]

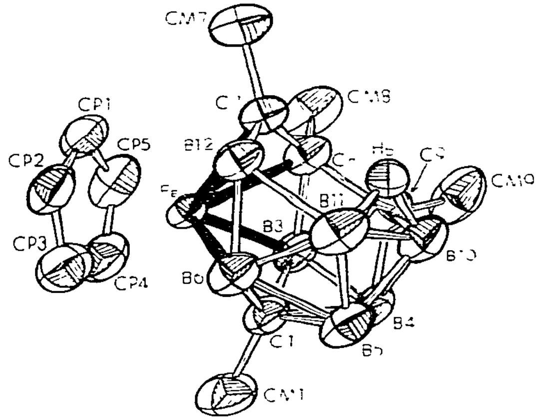


Figure 2. The structure of $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$. [Reprinted with permission from W. M. Maxwell, R. F. Bryan, and R. N. Grimes, J. Am. Chem. Soc., 99 (1977) 4008. Copyright by the American Chemical Society.]

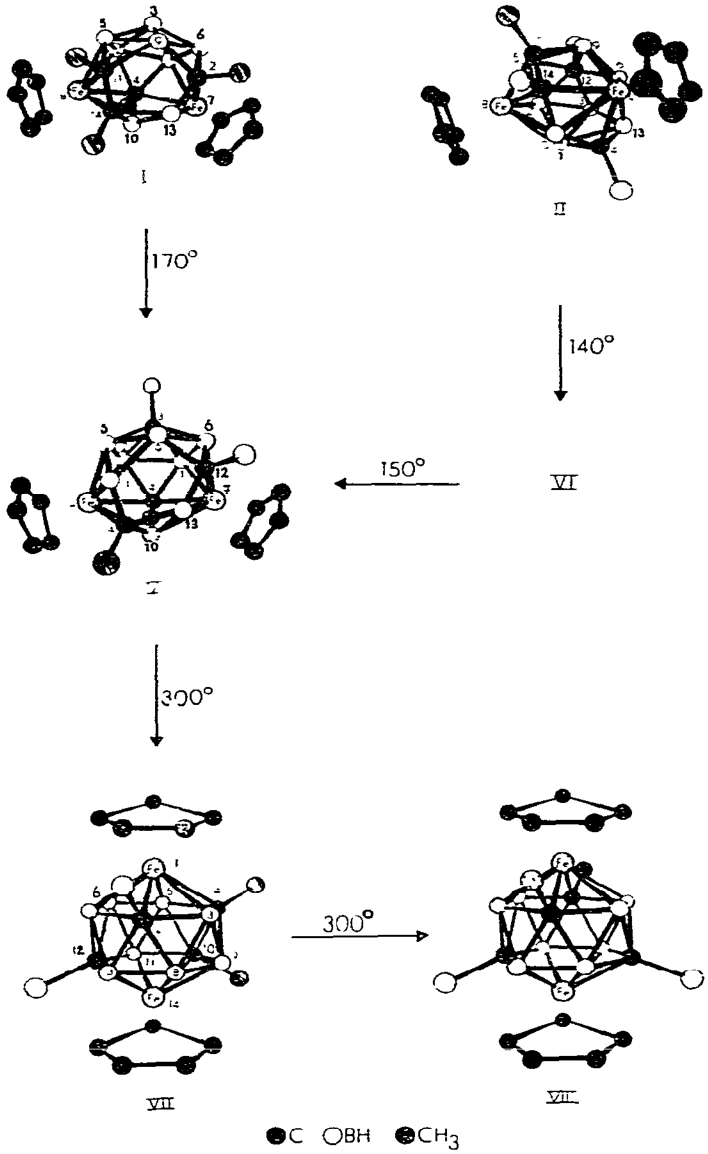


Figure 3. Thermal rearrangement of $(C_5H_5)_2Fe(CH_3)_4C_5B_8H_8$ isomers. [Reprinted with permission from W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, J. Am. Chem. Soc., 99 (1977) 4016. Copyright by the American Chemical Society.]

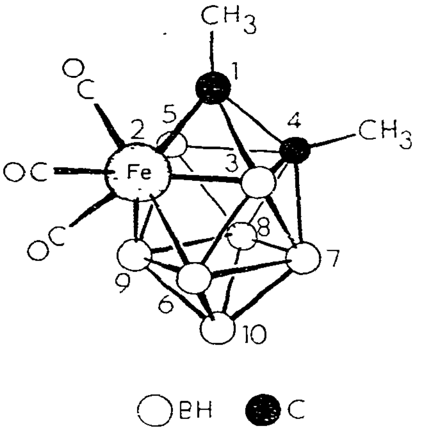


Figure 4. The proposed structure of 2,1,4-$Fe(CO)_3C_2(CH_3)_2B_7H_7$. [Reprinted with permission from W. M. Maxwell, K. S. Wong, and R. N. Grimes, Inorg. Chem., 16 (1977) 3094. Copyright by the American Chemical Society.]

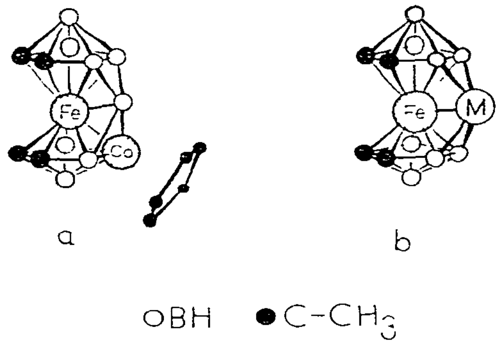
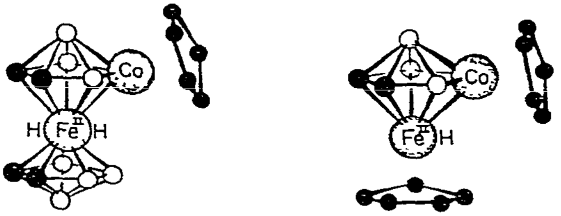


Figure 5. (a) Established structure of $(C_5H_5)CoFeC_4(CH_3)_4B_8H_8$ and (b) proposed structure of $MFeC_4(CH_3)_4B_8H_8$ where M = Sn or Ge. NMR spectra indicates fluxiona motion of the wedging metal atom in each case. [Reprinted with permission from W. M. Maxwell, K. S. Wong, and R. N. Grimes, Inorg. Chem., 16 (1977) 3094. Copyright by the American Chemical Society.]



IV

V

Figure 6. Proposed structures of $(C_5H_5)Co[(CH_3)_2C_2B_3H_3]FeH_2[(CH_3)_2C_2B_4H_4]$ (IV) and $(C_5H_5)_2CoFeH[(CH_3)_2C_2B_3H_3]$ (V). [Reprinted with permission from W. M. Maxwell, K. S. Wong, and R. N. Grimes, Inorg. Chem., 16 (1977) 3094. Copyright by the American Chemical Society.]

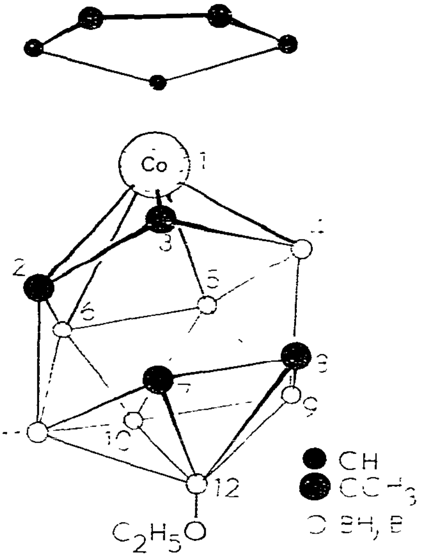
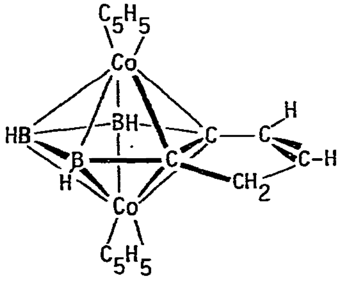


Figure 7. The structure of $(C_5H_5)Co[(CH_3)_4B_7H_6OC_2H_5]$. [Reprinted with permission from W. M. Maxwell, K. S. Wong, and R. N. Grimes, Inorg. Chem., 16 (1977) 3094. Copyright by the American Chemical Society.]



Reaction of $SnCl_2$ or $PbBr_2$ with $C_2B_4H_7^-$ or its C,C'-dimethyl homologue has yielded $SnC_2B_4H_6$, $PbC_2B_4H_6$ (Fig. 8), or their C,C'-dimethyl homologues [5]. The tin-cobalt carborane $(C_5H_5)CoSnC_2(CH_3)_2B_4H_4$ (Fig. 9) has been obtained as one of the products of the gas phase reaction of $SnC_2(CH_3)_2B_4H_4$ with $(C_5H_5)Co(CO)_2$.

The structure of $3,8\text{-}Me_2\text{-}2,2\text{-}(Et_3P)_2\text{-}2\text{-}Pt\text{-}3,8\text{-}C_2B_6H_6$ has been determined by X-ray crystallography [6]. The structure was illustrated in a previous Survey [JOM, 98 (1975) 319, Fig. 40]. Full details of the preparation and

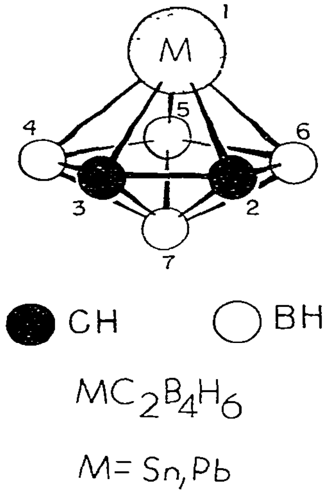


Figure 8. Proposed structures of $SnC_2B_4H_6$ and $PbC_2B_4H_6$. [Reprinted with permission from K. S. Wong and R. N. Grimes, Inorg. Chem., 16 (1977) 2053. Copyright by the American Chemical Society.]

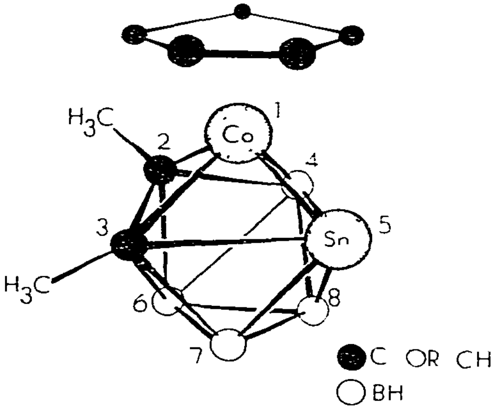


Figure 9. Proposed structure of $(C_5H_5)CoSnC_2(CH_3)_2B_4H_4$. [Reprinted with permission from K. S. Wong and R. N. Grimes, Inorg. Chem., 16 (1977) 2052. Copyright by the American Chemical Society.]

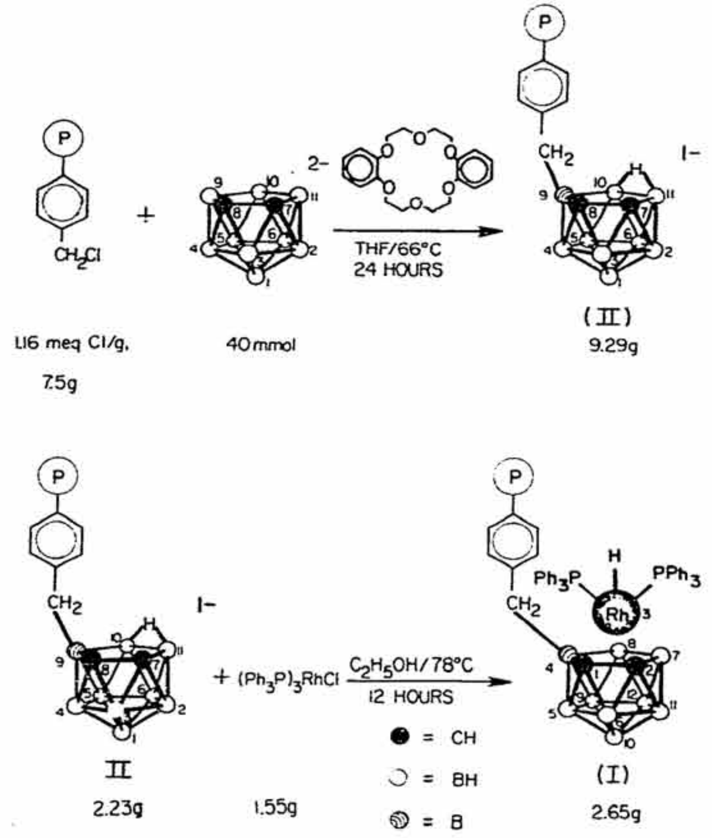


Figure 10. The synthesis of $[3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}4\text{-}(\text{polystyrylmethyl})\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$. (The circled "P" represents polystyrene resin.) [Reprinted with permission from B. A. Sosinksy, W. C. Kalb, R. A. Grey, V. A. Uski, and M. F. Hawthorne, J. Am. Chem. Soc., 99 (1977) 6768. Copyright by the American Chemical Society.]

characterization of a dicarbollyluranium(IV) complex, $(C_2B_9H_{11})_2UCl_2^{2-}$, have been reported [7]. The complex reacts with cyclooctatetraene to form uranocene, $(C_8H_8)_2U$. The structure of the complex was illustrated from the preliminary communication in last year's survey [JOM, 147 (1978) 30].

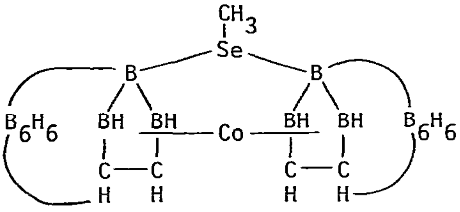
Hawthorne and coworkers have reported the synthesis of a rhodacarborane bound to a polystyrene resin (Fig. 10) [8]. The resin bound rhodacarborane shows activity as a hydrogenation catalyst, and shows promise of combining the advantages of uniform catalytic activity characteristic of homogeneous catalysts with the ease of separation from the product inherent in solid catalysts.

Hawthorne and coworkers have studied the exchange of deuterium (D_2 gas) with the hydrogen atoms of a series of carboranes and metallocarboranes catalyzed by a variety of transition metal complexes [9]. The general mechanism appears to involve oxidative addition of the B-H bond to the metal deuteride, followed by reversal. Effective catalysts included $(Ph_3P)_3RuHCl$, $(Ph_3P)_2(CO)IrCl$, $(Ph_3O)_2HRhC_2B_9H_{11}$, and related compounds.

Zakharkin and Grandberg have prepared optically active rhodacarboranes from optically active $1\text{-}Ph\text{-}C_2B_9H_{10}^-$ and $(Ph_3P)_3PhCl$ [10].

Pyrolysis of $Tl_2C_2B_9H_{11}$ or its mono- and di-C-methyl derivatives has yielded dimeric $(TlC_2B_9H_{12})_2$ or the corresponding C-methyl homologues [11]. The dimeric structure is believed to be linked through B-H-B bridges.

Treatment of bis(dicarbollyl)cobalt anion, $(C_2B_9H_{11})_2Co^-$, with H_2SeO_3 and acid followed by methylation with methyl sulfate introduces a CH_3Se bridging group between the 8 and 8' boron atoms [12]. Similar bridged species were obtained with oxygen, nitrogen, and tellurium bridging atoms.



B-Substituted dicarbolylcobalt cyclopentadienides have been prepared by base treatment of suitable substituted carboranes to remove a boron atom from the cage, followed by the usual treatment with $CoCl_2$, C_5H_5, and base [13]. The C-formyldicarbollycobalt $C_5H_5CoC_2B_9H_{10}CHO$ reacts with Grignard reagents RMgX to form alcohols $C_5H_5CoC_2B_9H_{10}CHOHR$ [14].

Heating $(1,2\text{-}C_2B_9H_{11})_2Ni$ under vacuum at 210°C results in cage isomerization and also in decomposition to $C_2B_7H_9$ and $C_2B_9H_{11}$ [15].

C. Four-Carbon Carboranes

The structure of the four-carbon carborane $(CH_3)_4C_4B_8H_8$ has been determined by X-ray diffraction [16] (Fig. 11).

Photolysis of $B_4H_8Fe(CO)_3$ in the presence of excess 2-butyne yields a four-carbon carborane, $(CH_3)_4C_4B_4H_4$, as well as a small amount of $(CH_3)_6C_6B_4H_4$ [17]. The four-carbon carborane is an air-stable liquid and shows a proton NMR spectrum consistent with a fluxional nido structure, which is expected on the basis of electron counting rules.

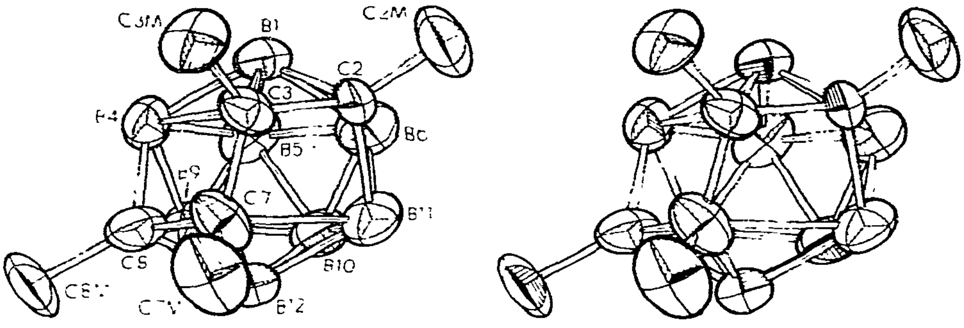
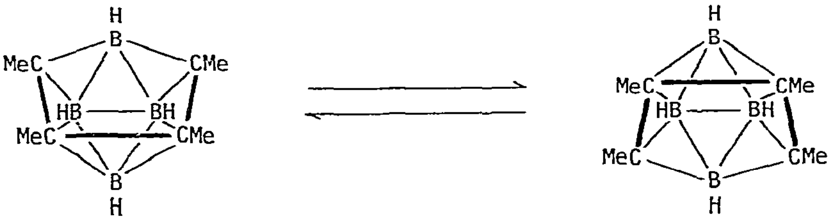
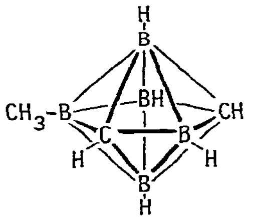


Figure 11. Stereodrawing of $(CH_3)_4C_4B_8H_8$, 50% probability ellipsoids, H atoms omitted. [Reprinted with permission from D. P. Freyberg, R. Weiss, E. Sinn, and R. N. Grimes, Inorg. Chem., 16 (1977) 1847. Copyright by the American Chemical Society.]

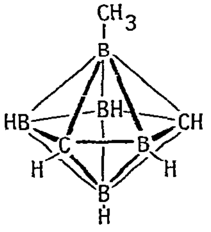


D. Small and Medium Carboranes and Metallaboranes

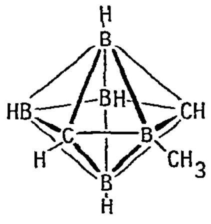
Fung and Onak have reported the isomerization of $5\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$ to an equilibrium mixture of 38% $1\text{-}CH_3\text{-}$, 34% $3\text{-}CH_3\text{-}$, and 28% $5\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$ at 300°C [18]. The mechanism is believed to involve boron migration in the cage not methyl migration from one boron to another.



$5\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$



$1\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$



$3\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$

The reaction of $2,3\text{-}C_2B_4H_7^-$ with $ClCH_2SiCl(CH_3)_2$ yields a μ-bridged sily derivative which can be rearranged to B-silyl and the B-silylmethyl derivativ which undergo further rearrangement at 690°C to form $(CH_3)_2SiClCH_2B_3C_2H_4$ and $(CH_3)_2SiClCH_2B_4C_2H_5$ [86] (Fig. 12).

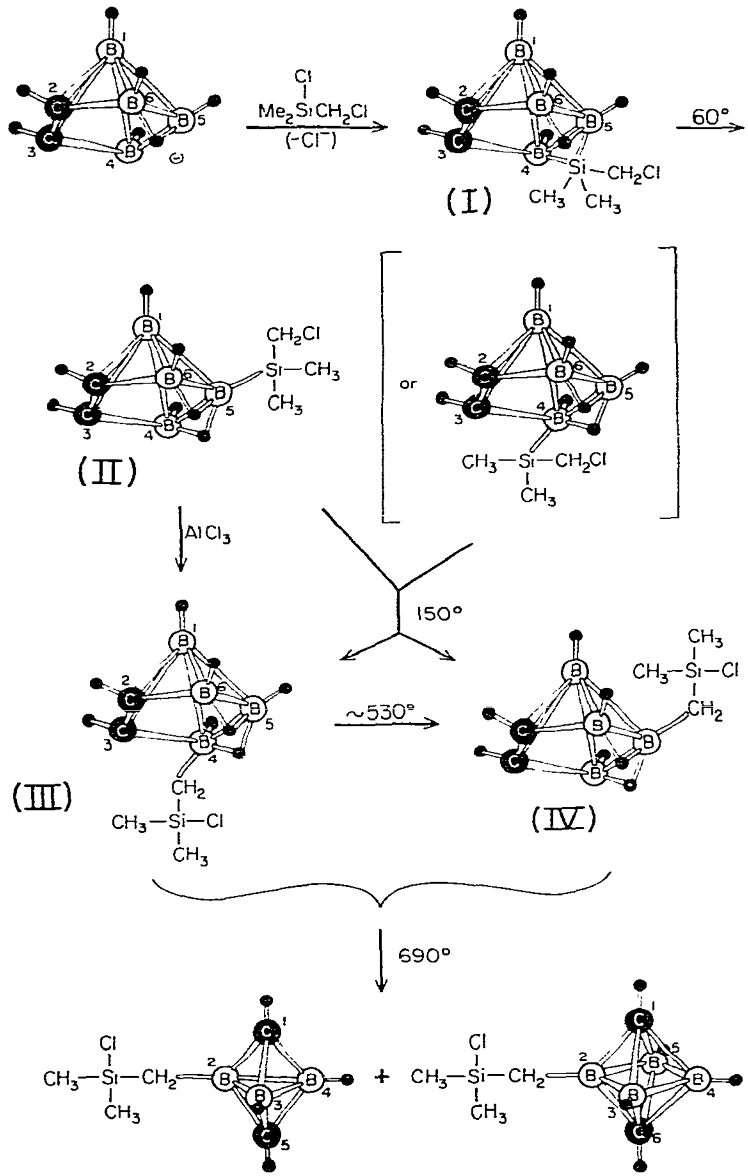
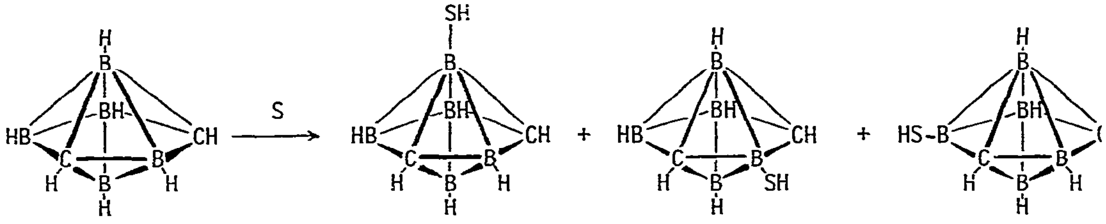


Figure 12. Reaction of 2,3-$C_2B_4H_7^-$ with $(CH_3)_2SiClCH_2Cl$ and subsequent rearrangements. [Reprinted with permission from C. B. Ungermann and T. Onak, Inorg. Chem., 16 (1977) 1428. Copyright by the American Chemical Society.]

The silylpentaborane μ-$ClCH_2Me_2Si$-B_5H_8 rearranges to 2- and then 1-substit silylpentaboranes, which in the presence of $AlCl_3$ rearrange to the C-bonded isomers, $Me_2SiClCH_2$-B_5H_8 [87]. Flash thermolysis of 2-($Me_2SiClCH_2$-)B_5H_8 yielded CB_5H_9 and CB_5H_7.

The small carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ have been found to react with atomic sulfur, which was generated by photolysis of COS, to form a series of B-mercaptocarboranes [19]. Photolysis of the three isomers of $C_2B_5H_6SH$ was found to yield the corresponding disulfides.



2,4-$C_2B_5H_7$ 1-SH-2,4-$C_2B_5H_6$ 3-SH-2,4-$C_2B_5H_6$ 5-SH-2,4-C_2H_5

The carborane derivative 2,4-$B_5H_5C_2[SiMe_2$-$C_5H_4Fe(CO)_2]_2$ has been synthesized as one of a series of complexes containing two transition metal atoms in close proximity [20].

The adamantane-like structure of $(HC)_4(BCH_3)_6$ has been determined by X-ray diffraction [21]. The cyclopentadienylboron compound $(Me_5C_5)BI^+$ BI_4^- is believed to have a carborane-like structure [22].

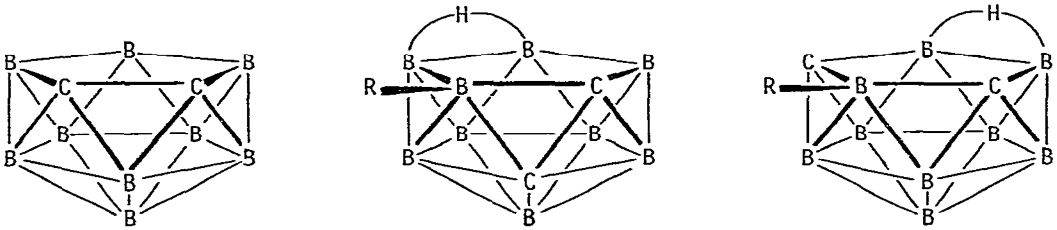
Reaction of cobalt atoms with B_5H_9 and cyclopentadiene in the gas phase has yielded several boron-cobalt cluster compounds, including $(C_5H_5)_3Co_3B_5H_5$ and cyclopentyl-$B_5H_4Co_3(C_5H_5)_3$ [88]. The structures of 5-$(C_5H_5)CoB_9H_{13}$ [89], $(C_5H_5)_3Co_3B_3H_5$, and $(C_5H_5)_3Co_3B_4H_4$ [90] have been determined by X-ray crystallogra

Two isomers of $(C_5H_5)FeB_5H_{10}$ have been prepared [91]. The more stable isomer has the iron atom midway between a B_5 ring and the C_5 ring. The structure of $Fe(CO)_4B_7H_{12}^-$ has been determined by X-ray [92].

The structure of 9,9-$(Ph_3P)_2$-6,9-$SPtB_8H_{10}$ has been determined [93].

E. Dicarbollide Ions

Treatment of 7,8-$C_2B_8H_{11}^{2-}$ with RX (R = Me, Et, Bu, allyl; X = halide) results in rearrangement of 11-R-2,7-$C_2B_9H_{11}^-$, which is stable below 0°C but at 25°C rearranges to 8-R-7,9-$C_2B_9H_{11}^-$ [23]. Protonation of the unstable



7,8-$C_2B_9H_{11}^{2-}$ 11-R-2,7-$C_2B_9H_{11}^-$ 8-R-7,9-$C_2B_9H_{11}^-$

(Terminal H's omitted, bridging H positions uncertain.)

methylated intermediate yields the nido carborane 11-CH_3-2,7-$C_2B_9H_{12}$ [24]. The structure has been determined by X-ray crystallography (Fig. 13). The reaction

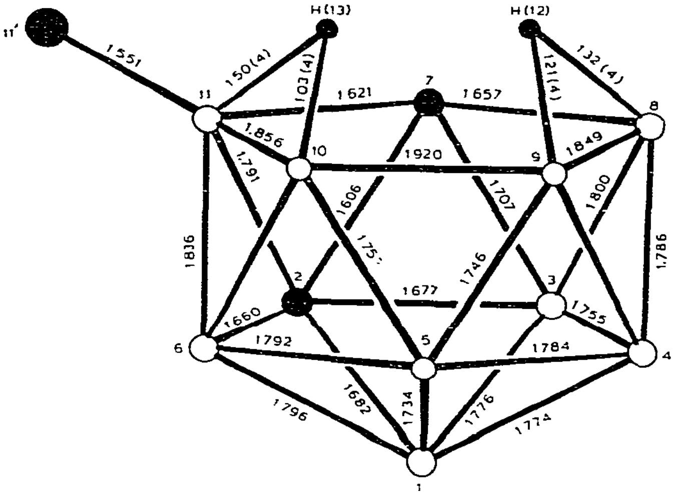


Figure 13. The structure of 11-CH_3-2,7-$C_2B_9H_{12}$. All hydrogens except those in the BHB bridges are omitted. [From Yu. T. Struchkov, M. Yu. Antipin, V. I. Stanko, V. A. Brattsev, N. I. Kirillova, and S. P. Knyazev, J. Organometal. Chem., 141 (1977) 133].

of methyl iodide with 7,8-$C_2B_9H_{11}^{2-}$ to form 11-CH_3-2,7-$C_2B_9H_{11}^-$ and the rearrangement of the latter to 8-CH_3-7,9-$C_2B_9H_{11}^-$ has been followed by ^{11}B NMR [25].

Treatment of 3-hydroxy-o-carborane or 2-hydroxy-m-carborane with base eliminates the hydroxylated boron atom in each case to form the dicarbollide anion [26]. The conversion of several C-substituted o-carboranes to dicarbollid derivatives by treatment with ammonia has been described [27].

F. Icosahedral Carboranes

1. *B-Substituted*. For numbering of the icosahedron, Fig. 14 may be consulted. o-Carborane is 1,2-$C_2B_{10}H_{12}$, m-carborane is the 1,7-isomer, and p-carborane is the 1,12-isomer.

Treatment of o-carborane with sulfur and aluminum chloride at 100-130°C has yielded 9-HS-o-carborane [28]. Similar treatment of m-carborane gave 9-HS-m-carborane, and from p-carborane the only possible B-substituted product because of symmetry, 2-HS-p-carborane, was obtained.

Zakharkin and coworkers have investigated the Friedel-Crafts alkylation of o- and m-carborane, o-arsacarborane, m-phosphacarborane, and $C_5H_5CoC_2B_9H_{11}$ with

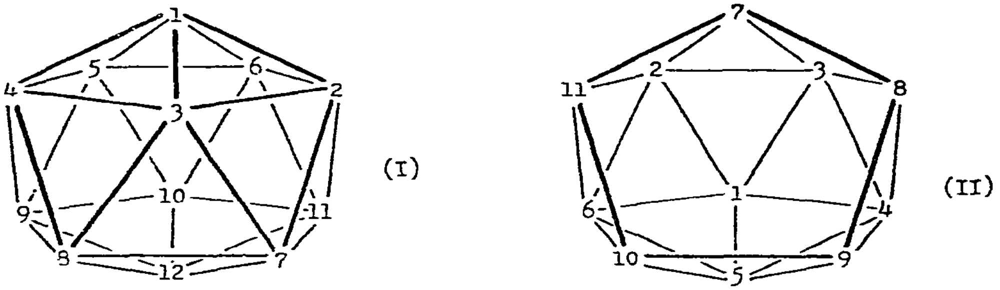


Figure 14. Numbering schemes for the icosahedron (I) and for the 11-atom icosahedral fragment (II) formed by removing atom number 3 from the icosahedron.

alkyl halides and aluminum chloride, which yields mixtures complex enough to keep several chemists employed for a while [29]. Treatment of $C_2B_{10}H_{12}^{2-}$ with RLi or RMgX followed by oxidation with $CuCl_2$ has given low yields of B-alkyl-o-carboranes [30].

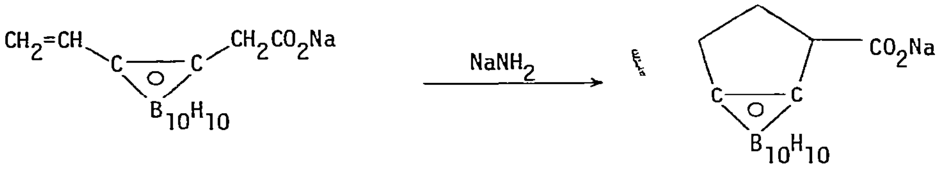
Carborane-B-carboxylic acids have been converted to -COCl, $-CO_2Me$, $-CH_2OH$, $-CH_2OAc$, and $-CO_2SiMe_3$ derivatives [31].

Zakharkin and Pisareva have reported that mercuration of o- and m-carboranes with mercury(II) trifluoroacetate attaches one or more mercury atoms to boron, with attack at the 9-position being fastest for both carboranes [32]. In a similar study, Bregadze and coworkers found 9-mercuration of o- and m-carborane and 2-mercuration of p-carborane (in which all B atoms are equivalent by symmetry) [33]. The boron-mercury bond is cleaved by bromine or by aqueous hydrochloric acid. Treatment of $H_2C_2B_{10}H_9HgO_2CCF_3$ with naphthalene anion-radical or with cadmium amalgam results in symmetrization to $H_2C_2B_{10}H_9$-Hg-$B_{10}H_9C_2H_2$. B-Mercurated o- and m-carboranes of the types $(C_2B_{10}H_{11})_2Hg$, $C_2B_{10}H_{11}HgEt$, and $C_2B_{10}H_{11}HgI$ have been prepared and found to have properties similar to aliphatic organomercury compounds [34].

The chlorination product of 9,10-dichloro-m-carborane was shown to be 4,9,10-trichloro-m-carborane by X-ray crystallography [35]. The structure of 1,7-$(Me_3Sn)_2$-10-$(Me_3SiCH_2CH_2)$-1,7-$C_2B_{10}H_9$ has been assigned by an X-ray determination [36]. Thermolysis of o-carborane under Ar is an ampoule at 600°C results in formation of a mixture of byproduct boron-linked bis(m- and p-carboranes) (9 to 15%) [37].

2. C-Substituted. Carboranylalanine has been prepared from N-phthaloyl-L-propargylglycine methyl ester and decaborane--acetonitrile [38]. N-(Alanyl-alanyl)-β-(1-o-carboranyl)alanine and N-acetyl-β-(1-o-carboranyl)alanine ethyl esters are good inhibitors of chymotrypsin, indicating that the carboranyl group interacts with the phenyl recognition site of the enzyme [39].

2-Vinyl-o-carboranyl-1-acetic acid cyclizes in the presence of sodamide [40]. Several naphtho[1,2]-o-carboranes have been prepared by cyclization of



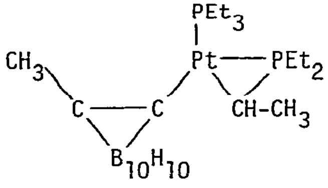
2-substituted 1-phenyl-*o*-carboranes using Friedel-Crafts type reactions [41]. Various vinylcarboranes have been hydrogenated by treatment with hydrogen, carbon monoxide, and cobalt or rhodium carbonyl [42]. Aldehydes were not obtained. Treatment of *C*-phenyl- and *C*-benzyl-*o*- and -*m*-carboranes with $Cr(CO)_6$ has given low yields of the tricarbonylchromium derivatives, where the chromium is π-complexed to the benzene ring [43].

C-Lithiocarborane has been oxidized by tri-*t*-butylphenoxy radical to form a reactive carboranyl radical, which abstracts hydrogen from the solvent [44]. *C*-Lithiation--carboxylation of 1,1'-bis(*o*- and *m*-carboranyl) and 1,2-bis(1-*o*-carboranyl)ethane has been reported, as well as treatment of the dilithio derivatives with formaldehyde [45].

Treatment of *o*- and *m*-$HCB_{10}H_{10}C\text{-}COCl$ with $HOO\text{-}CMe_3$ in pyridine yielded the peroxy esters $HCB_{10}H_{10}C\text{-}C(O)\text{-}O\text{-}O\text{-}CMe$ [46]. This success suggested the possibility of using $HOO\text{-}CMe_2Et$, and that worked, too. Meanwhile, another Russian group was making the *C*-phenyl analogues from $PhCB_{10}H_{10}C\text{-}COCl$ and $NaOO\text{-}CMe_3$, and went on to study kinetics of decomposition of carboranyl peroxyesters [47].

Phenathroline, bipyridyl, and other complexes of *o*- and *m*-$(HCB_{10}H_{10}C\text{-}CO_2\text{-})_2Hg$ have been prepared [48]. Choline esters of carboranecarboxylic acids have been reported [49].

1-Ph-2-Li-*o*-carborane reacts slowly with *cis*-$(Ph_2MeP)_2PtCl_2$ to form the 1-Ph-2-*o*-carboranylplatinum derivative in which one of the phosphorus-bound methyl groups has eliminated a hydrogen atom and formed a three-membered $Ph\text{-}CH_2\text{-}P$ ring [50]. The structure of a similar carboranylplatinum compound has been determined by X-ray crystallography [51].



The structure of 1,7-Ph_2-*m*-carborane has been determined by X-ray crystallography [52].

The carbon-metal bond of various $HCB_{10}H_{10}C\text{-}MMe_3$, where M = Ge, Si, or Sn, is cleaved by base, with relative rates in the *m*-carborane series Si > Sn > Ge [53]. Several carboranes bearing Me_2SiH- substituents on carbon have been chlorinated and found to react slowly because of the electron-withdrawing effect of the carborane group [54]. Halogenation of $HCB_{10}H_{10}C\text{-}CH_2\text{-}Fe(CO)_2C_5H_5$ has given $HCB_{10}H_{10}C\text{-}CH_2COFeX_2(CO)C_5H_5$ [55].

Addition of 2 electrons to 1,12-dimethyl-*p*-carborane followed by reoxidati yields the *m*- and *o*-isomers [56]. This type of rearrangement has been reported previously in earlier Surveys. Coupling of *m*-$HCB_{10}H_{10}C\text{-}CB_{10}H_{10}CLi$ with $CuCl_2$ has yielded the tetra-*m*-carboranyl, $H(CB_{10}H_{10}C)_4H$ [57]. Irradiation of *o*-carbo with gamma rays yields *m*-carborane and polymeric products [58].

Carborane derivatives show neurotropic activity [59]. The anion 7-Me-8-$(Et_2NCH_2CH_2)$-7,8-$C_2B_9H_{10}^-$ prolongs thiopental induced sleep in mice and shows an LD_{100} of 300 mg/kg, and related compounds show lesser activity or higher toxicity [60]. Carborane affects the orientation reaction of rats at an oral dosage of 45 mg/kg [61].

G. Theoretical Aspects

1. *Spectra and Physical Measurements*. Weiss and Grimes have studied the Fourier transform ^1H and ^{11}B NMR spectra of a series of carboranes and cobaltacarboranes containing three to six boron atoms [62]. ^{11}B relaxation times (T_1) were found to be a useful structural probe. Unexpectedly, decoupling of ^{11}B nuclei strongly affected the T_1 values of protons bound to cage carbon atoms.

Miller and Grimes have reported ^1H NMR spectra of a series of carboranes and metallocarboranes run under triple resonance conditions, in which decouplin of ^{11}B and selected ^1H nuclei was carried out while the ^1H spectrum was observe [63]. It was found that the broad lines often observed with boron-bound proton result from unresolved spin-spin splittings and not from ^{11}B quadrupolar relaxation, which is a significant factor only in the widths of the ^{11}B lines. Thus, with appropriate double decoupling, well resolved ^1H NMR spectra of carboranes can be observed and the coupling constants measured and identified, as illustrated in Fig. 15. Typical coupling constants found were 10-20 Hz for H-C-C-H, 1-10 Hz for H-C-B-H, and 0-4 Hz for H-B-B-H.

Onak and coworkers have reported that carbon-bound protons of carboranes show an upfield shift in the NMR spectrum on going from cyclohexane to benzene as solvent, and a downfield shift in perfluorobenzene [64]. Bridge hydrogens between boron atoms show similar shifts, and simple BH protons show generally smaller shifts which may be in either direction. The magnitude of the shifts correlate with hydrogen atom charges calculated by molecular orbital methods. Todd and coworkers have published an extensive study of carborane ^{13}C and ^{11}B NMR shielding values [65]. Stanko and coworkers have correlated the ^{11}B NMR chemical shifts of a series of substituted carboranes [66].

The structure of 1-Me_2NCS-*o*-$C_2B_{10}H_{11}$ as determined by X-ray crystallograph shows the C-C-C-S linkage to have a coplanar configuration, evidently as a result of π-bonding between the thiocarbonyl group and the cage [67].

Infrared spectra of a series of carboranes, including 1,5-$C_2B_3H_5$, 1,6-

$C_2B_4H_6$, 1,10-$C_2B_8H_{10}$, all isomers of $C_2B_{10}H_{12}$ and $H_2C_2B_{10}Cl_{10}$, have been correlated with physical properties [68]. The C-H stretching frequency decreases with increasing coordination of the boron (3165 cm^{-1} for $C_2B_3H_5$, 3060 cm^{-1} for p-carborane) and the intensity of the C-H absorption increases with increasing acidity of the proton, giving good linear correlations with pKa and

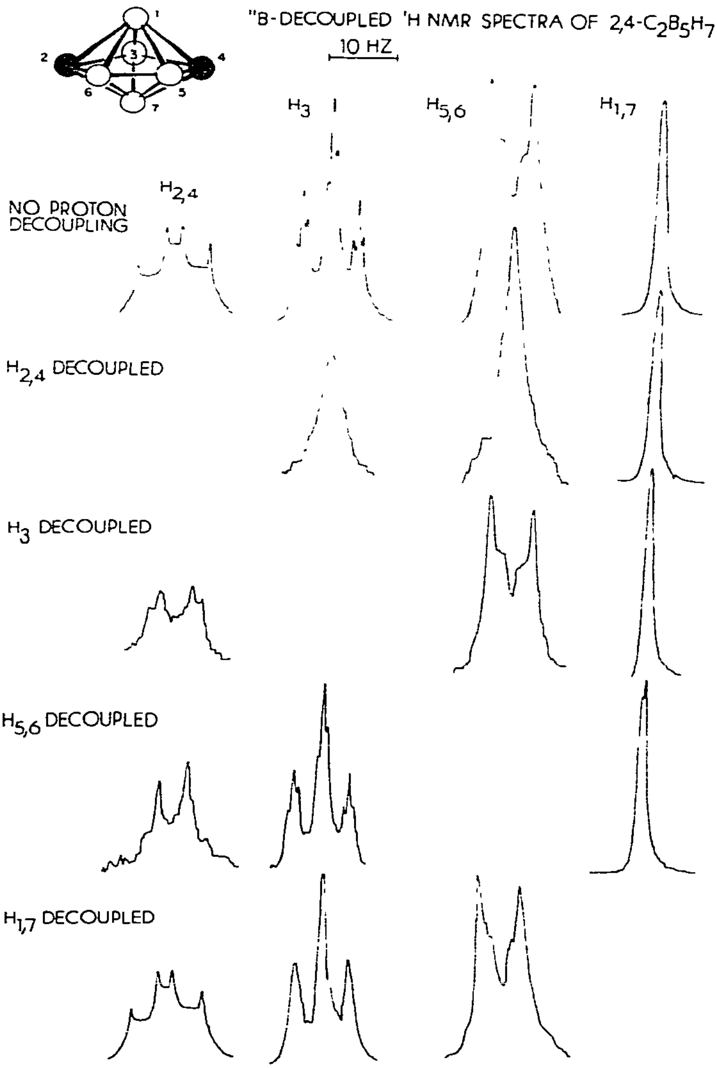


Figure 15. ^{11}B-Decoupled proton resonances of 2,4-$C_2B_5H_7$, with the decoupling frequency adjusted in each case to produce maximum resolution. In the top line, only boron is decoupled; in the remaining spectra, the boron nuclei and selected protons are decoupled simultaneously (triple resonance). [Reprinted with permission from V. R. Miller and R. N. Grimes, Inorg. Chem., 16 (1977) 15. Copyright by the American Chemical Society.]

enthalpy of hydrogen bond formation with DMSO. Infrared measurements have indicated that both the carboranyl CH and the cyclopentadienyl CH groups of $C_5H_5CoC_2B_9H_{11}$ and $C_5H_5FeC_2B_9H_{11}$ form weak hydrogen bonds (1.5 kcal/mol) with dimethyl sulfoxide [69]. Substituted o-carboranes show infrared evidence of CH hydrogen bonding to polar substituent groups or to solvent dimethyl sulfoxide [70].

The equilibrium CH acidities of a series of 3-substituted o-carboranes have been measured in 1,2-dimethoxyethane [71]. Effects of cation size in the series Li, K, and Cs on the acidity of carboranes toward triphenylmethide have been measured [72].

Dielectric constants of several o-carborane derivatives in the solid state have been measured at 80-300 K [73]. Polarographic potentials for reduction of bis(B-carboranyl)mercuries have been measured [74]. The kinetics of acylation of aniline by m-carboranecarbonyl chloride have been measured in 21 solvents [75].

2. Calculations. Lipscomb and coworkers have reported a series of calculations on all of the $B_nH_n^{2-}$ and $C_2B_{n-2}H_n$ polyhedra in the range n = 5 to 12, using the partial retention of diatomic differential overlap (PRDDO) approximation [76]. These are the most accurate wave functions to date for these molecules, and they correctly predict such trends as the increasing stability on rearranging o- to m- to p-$C_2B_{10}H_{12}$. The results are also interpreted in terms of localized molecular orbital structures, which correspond in principle to the familiar resonance structures used by organic chemists, except that three-center bonds have to be used in order to provide a rational basis for describing these polyhedral boranes.

Brown and Lipscomb have carried out self-consistent field calculations on a series of boron hydrides $B_{13}H_{13}^{2-}$ to $B_{24}H_{24}^{2-}$ and predicted the most stable of the possible geometries for each [77]. It was suggested that boranes and carboranes having these larger cage sizes can probably be synthesized.

Dewar and McKee have reported MNDO calculations on a long series of boron compounds, including polyhedral boranes and carboranes as well as trialkylboranes and other alkylboron compounds [78]. This method of calculation is much better than MINDO/3 for boron compounds and gives reasonably satisfactory heats of formation.

The distorted icosahedral metallocarboranes (t-BuNC)$_2$Pd(1-$Me_3NCB_{10}H_{10}$), ($PhMe_2P)_2$Pt(2,5-Me-2,5-$C_2B_9H_9$), and ($Et_3P)_2$Pt(3,4-$C_2B_9H_{11}$) have slipping and folding distortions where the metal atom is joined to the open face of the carboranyl group [79]. The magnitude and direction of the slip distortion as determined by X-ray crystallography depends on the substituents on the open face of the carboranyl group. Extended Hückel calculations correlate with the observed distortions in a satisfactory manner.

Geometry-optimized ab initio LCAO-MO-SCF calculations have been reported for 1,2- and 1,5-$C_2B_3H_5$ [80]. The electronic structure of $C_2B_3H_7Fe(CO)_3$ has been calculated by an ab initio method [81]. Calculations on unstable boron hydrides such as B_2H_4 and B_4H_{12} have been carried out, using PRDDO, STO-3G, and other methods [82]. Calculations on Lewis base adducts of B_3H_7, including B_3H_7CO, have been carried out using the PRDDO, STO-3G, and STO-4-31G methods [83]. A series of ab initio calculations on small molecules has included $CH_2(BH_2)_2$ and other boranes for comparison with carbonium ion structures [84].

A topological analysis of polyhedral boranes and carboranes correctly predicts stability for closed deltahedral systems having n vertices and 2n + 2 skeletal electrons [85].

H. Boron Cages Without Carbon

Several metallaboranes have been included in section D.

Friedel-Crafts alkylation of 1-SB_9H_9 yields mainly 6-alkylated product instead of the 10-alkyl product predicted by simple molecular orbital theory [94] Directive effects in the electrophilic halogenation of 1-SB_9H_9 and $SB_{11}H_{11}$ have been reported [95].

The reaction of decaborane with Na_2Se_4 yields $B_{10}H_{11}Se^-$, which can be protonated to $B_{10}H_{12}Se$ [96]. Metal complexes such as $Co(B_{10}H_{10}Se)_2^{2-}$ as well as the analogous tellurium series based on $B_{10}H_{13}Te$ were also prepared.

Oxidation of $B_{12}H_{11}SH^{2-}$ with iodosobenzoate yields $B_{12}H_{11}$-S-S-$B_{13}H_{11}^{4-}$, which yields a radical species on acidification [97].

The structure of $Me_2SB_{10}H_8$-$B_{10}H_8SMe_2$ has been determined by X-ray and shows three-center boron bridge bonds between the cages [98].

Reaction of Br_2 with $Me_2SnB_{10}H_{12}$ has yielded 5,10-$Br_2B_{19}H_{12}$ [99].

J. Reviews

Onak has reviewed carborane and metallocarborane chemistry [100]. Callahan and Hawthorne have reviewed metallocarboranes [101]. Rudolph has reviewed framework electron counting rules for polyhedral boranes and heteroboranes [102]. Burg has reviewed his own boron hydride chemistry [103].

The thermal neutron capture treatment of malignant melanomas using ^{10}B-dopa and $^{n}B_{12}$-chlorpromazine compounds has been reviewed [104].

Lipscomb's Nobel Lecture has appeared in German [105] and his work has been discussed in Danish [106].

II. HYDROBORATION

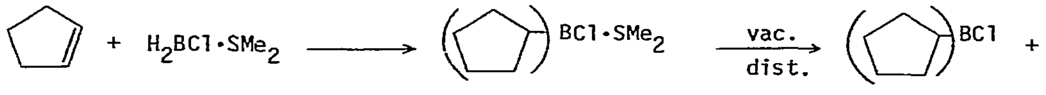
A. Hydroborating Agents

1. New Reagents. The major contributors to the hydroboration field continue to be H. C. Brown and his present and former students. Even though the field is becoming mature and the principles well understood, discoveries of new and useful reagents for hydroboration have been reported during 1977. Most of this work is a result of the commercial availability of borane--methyl sulfide, which

has an excellent combination of stability and reactivity properties.

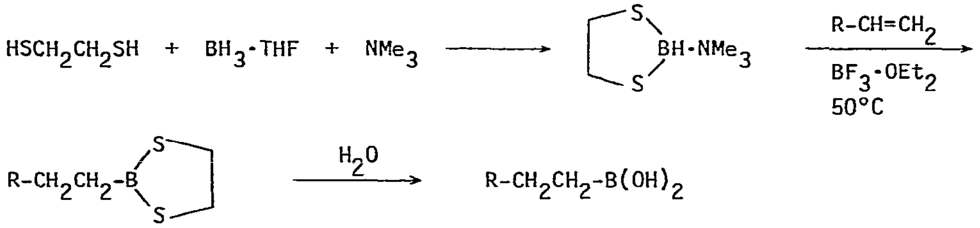
Brown and Ravindran have found that dibromoborane--dimethyl sulfide, $HBBr_2 \cdot S(CH_3)_2$, is a good hydroborating agent [107]. The resulting alkyldibromoboranes may serve as convenient precursors to boronic esters or acids. Similarly, $H_2BCl \cdot SMe_2$ and $HBCl_2 \cdot SMe_2$ are stable and highly useful hydroborating agents [108]. Their reactivity is similar to that of the corresponding etherates. The reagents $HBCl_2 \cdot SMe_2$, $HBBr_2 \cdot SMe_2$, and $H_2BBr \cdot SMe_2$ are easily made from $H_3B \cdot SMe_2$ and $Cl_3B \cdot SMe_2$ or BBr_3 + SMe_2 [109].

$$R\text{-}CH{=}CH_2 \;+\; HBBr_2 \cdot S(CH_3)_2 \longrightarrow RCH_2CH_2BBr_2 \cdot S(CH_3)_2$$



$$CH_3(CH_2)_5CH{=}CH_2 \;+\; HBCl_2 \cdot SMe_2 \xrightarrow{BCl_3} CH_3(CH_2)_7BCl_2$$

Thaisrivongs and Wuest have found that 1,3,2-dithiaborolane is an easily prepared and highly effective hydroborating agent for the preparation of boronic acids and their derivatives [110].

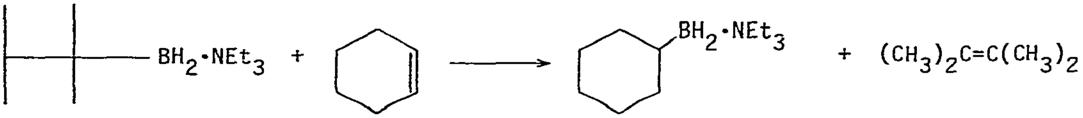


Deuterated diborane has been prepared using D_2O/DCl as the deuterium source, starting from trimethylamine-borane [111].

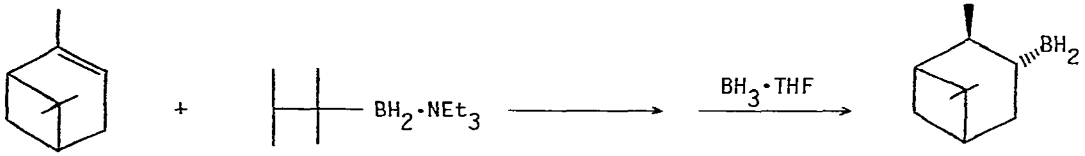
$$Me_3NBH_3 \xrightarrow{D_2O \;+\; DCl} Me_3NBD_3 \xrightarrow[CH_2Cl_2]{BF_3OEt_2} B_2D_6$$

Brown and coworkers have described in detail convenient preparations of the hydroborating agents thexylborane, disiamylborane, 9-BBN, catecholborane, diisopinocampheylborane, dicyclohexylborane, and 1,6-diboracyclodecane from borane--methyl sulfide [112].

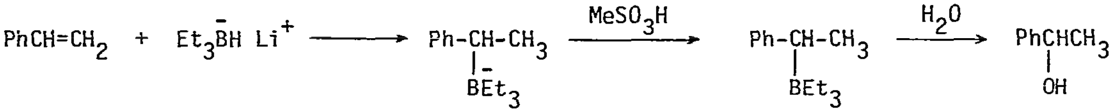
Tetramethylethylene is displaced from thexylborane--triethylamine by other moderately hindered olefins at 25°C, yielding monoalkylborane--triethylamine adducts [113]. Monoisopinocampheylborane has been prepared from



thexylborane-triethylamine and α-pinene, and has been found to be a useful chiral hydroborating agent for trisubstituted olefins [114].

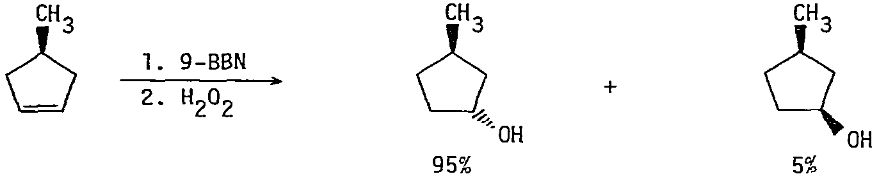


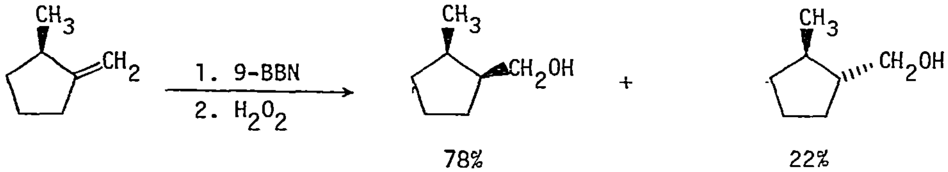
Lithium triethylborohydride adds to styrenes to place the boron on the carbon next to the ring [115]. The borate can be converted to the borane by treatment with methanesulfonic acid.



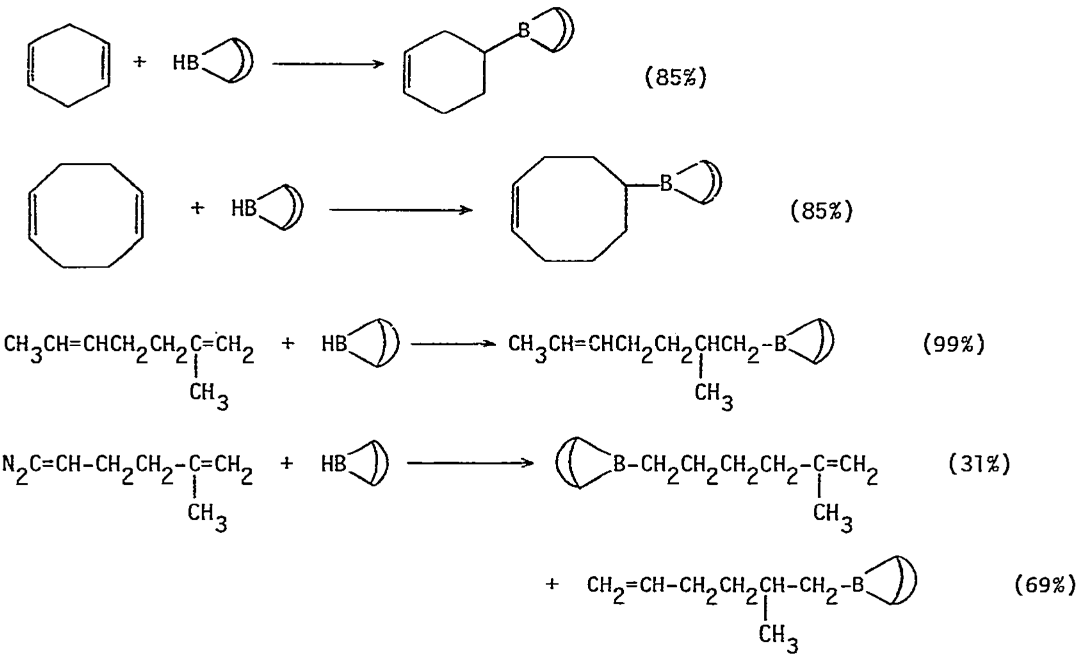
$$\mathrm{PhCH{=}CH_2} + \mathrm{Et_3\overset{-}{B}H\ Li^+} \longrightarrow \mathrm{Ph\text{-}\underset{\overset{|\,-}{BEt_3}}{CH}\text{-}CH_3} \xrightarrow{\mathrm{MeSO_3H}} \mathrm{Ph\text{-}\underset{\overset{|}{BEt_3}}{CH}\text{-}CH_3} \xrightarrow{\mathrm{H_2O}} \mathrm{Ph\underset{\overset{|}{OH}}{C}HCH_3}$$

2. Specificity. Several studies of the regio- and stereoselectivity of known hydroborating agents have appeared. The hydroboration of cyclic olefins with 9-borabicyclo[3.3.1]nonane (9-BBN) is exceptionally regioselective and stereoselective [116]. Brown and coworkers have reported in detail the isomer ratios obtained with a series of cycloalkenes and 9-borabicyclononane (9-BBN) and have compared these results with those obtained with other hydroborating agents. The 9-BBN hydorboration products are also unusually resistant to isomerization under the conditions of hydroboration. Two of the many examples which may have synthetic utility are illustrated below.

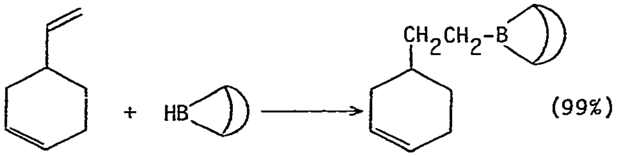




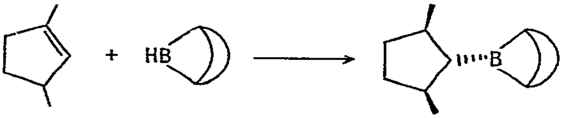
Liotta and Brown have studied the selectivity of the monohydroboration of a series of nonconjugated dienes by 9-borabicyclo[3.3.1]nonane (9-BBN) [117]. Where both double bonds are identical and well separated, as in $H_2C{=}CH{-}(CH_2)_2CH{=}CH_2$, the ratio of mono- and dihydroboration products is essentially statistical, but high selectivity was found whenever the two olefinic groups were in close proximity or differed in their degree of substitution.



(opposite preference of disiamylborane)



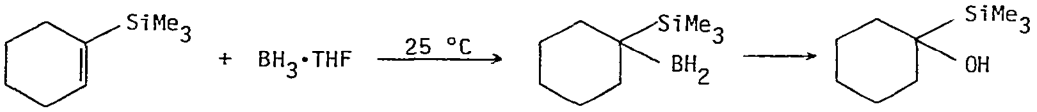
Hydroboration of 1,3-dimethylcycloalkenes with 9-BBN proceeds stereospecifically to form the borane with both methyl groups trans to boron [118].



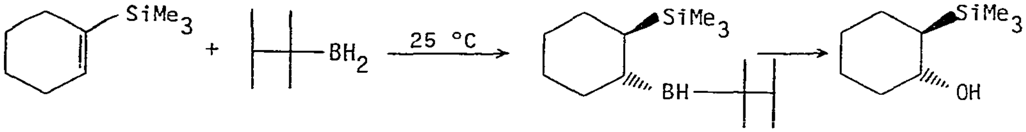
(similar results with 4- and 6-membered rings)

Hydroboration of $Cl_3SiCH=CH_2$, $MeCl_2SiCH=CH_2$, $Me_2ClSiCH=CH_2$, and $Me_3SiCH=CH_2$ has been studied [119]. With excess $BH_3{\cdot}THF$ and $Cl_3SiCH=CH_2$, the major hydroboration product is the 1,1-isomer (88% purity). With dicyclohexylborane and $Me_3SiCH=CH_2$, the product is 88%, 1,2-isomer. Other combinations give intermediate distributions of products

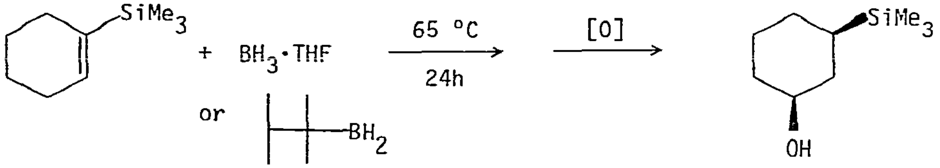
Hydroboration--oxidation of trimethylsilylcyclohexenes and cyclopentenes has been studied by Larson and coworkers [120]. Diborane and 1-trimethylsilylcycloalkenes under conditions of kinetic control yield mainly the 1-boryl-1-trimethylsilylcycloalkane.



Thexylborane yields β-boryl product.



At higher temperatures, the usual borane rearrangements occur and the thermodynamically controlled 1,3-borylsilyl product results.



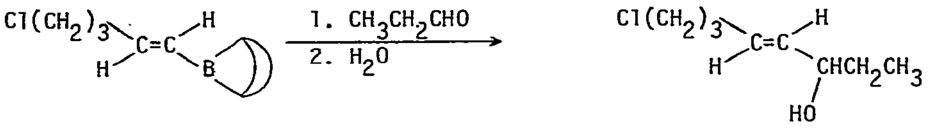
Hydroboration of 3- and 4-trimethylsilylcyclohexene under kinetically controlled conditions yielded mixtures containing mostly cis and trans 1,3-product, and the 4-isomer gave in addition some trans 1,4-product. Trimethylsilylcyclopentenes gave similar results, except that the thermodynamically controlled 1,3-product is trans.

B. Replacement of Boron

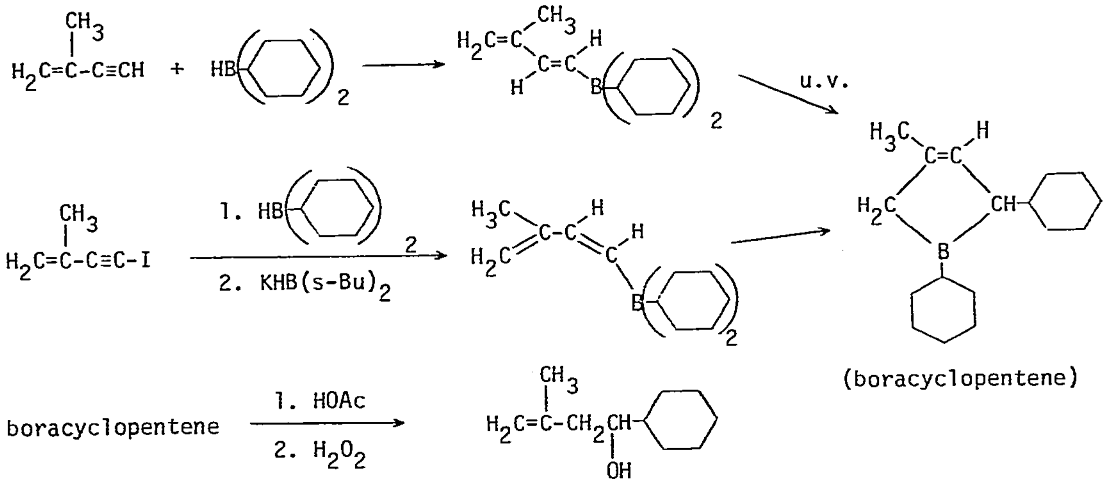
1. Alkenylboranes and Alkynylboranes. Boron is replaced from alkenylboranes relatively easily, and many such processes lead to useful carbon-carbon bond formation. As a result, there has been growing interest in the preparation and utilization of alkenylboranes. Most alkenylboranes are made either by hydroboration of acetylenes or by rearrangement of trialkylborane--acetylide ate

complexes, and the alkynylboranes are therefore treated in this same section as well. An alternative and not yet fully explored route to alkenylboranes is the reaction of boron-substituted carbanions, $R\text{-}C(BO_2C_3H_6)_2$ [121], with aldehydes, R'CHO, to form $R'CH{=}C(R)BO_2C_3H_6$.

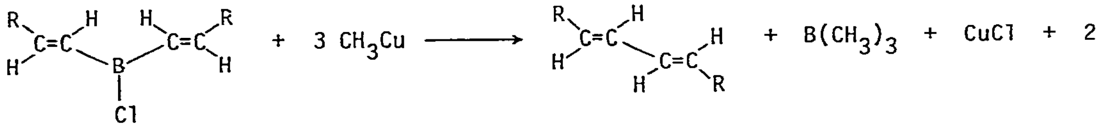
B-Alkenyl-9-BBN derivatives add to the carbonyl group of aldehydes to yield allyl alcohols with retention of the geometry of the alkenyl group [122].



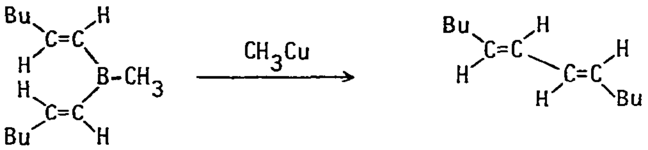
Zweifel and coworkers have studied the photocyclization of trans-1,3-dienylboranes, and have also discovered that cis-1,3-dienylboranes cyclize spontaneously [123]. Migration of an alkyl group from boron to carbon occurs during the cyclization. The boracyclopentenes are readily converted to homoallylic alcohols



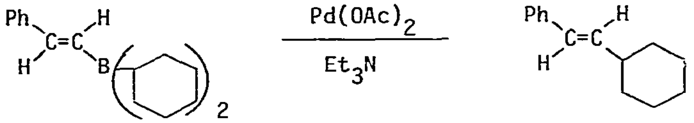
Methylcopper has been found to cause efficient coupling of the alkenyl groups of dialkenylchloroboranes [124].



Dialkenylmethylboranes couple in a similar manner [125].

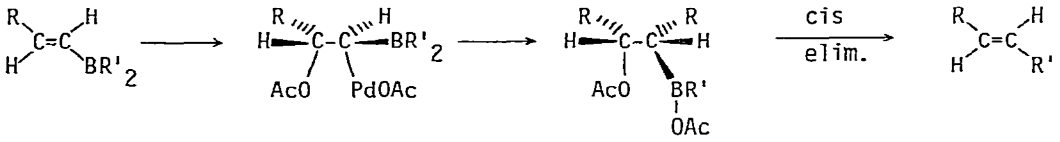


Treatment of trans-alkenylboranes with $Pd(OAc)_2$ and Et_3N in THF yields trans-alkenes [126].

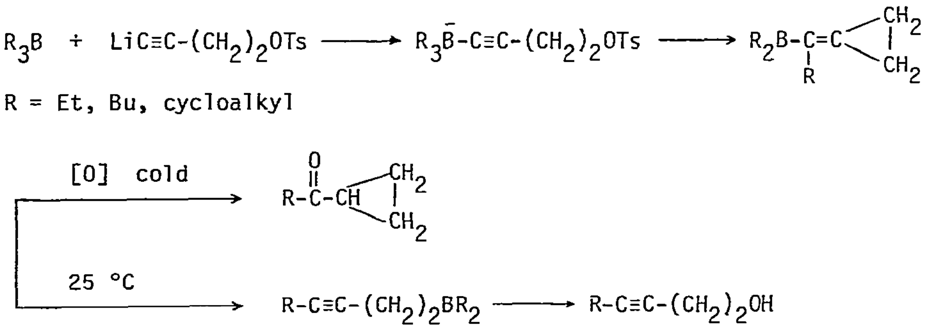


(The reaction illustrated fails with BrCN.)

The mechanism is postulated to involve oxypalladation, migration, and eliminati

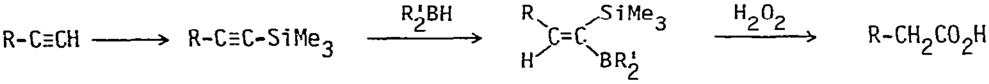


Trialkylboranes react with $LiC{\equiv}C(CH_2)_2OTs$ at -78°C to form alkenylborane intermediates that can be oxidized to cyclopropyl alkyl ketones or rearranged to acetylenic compounds by warming [127].

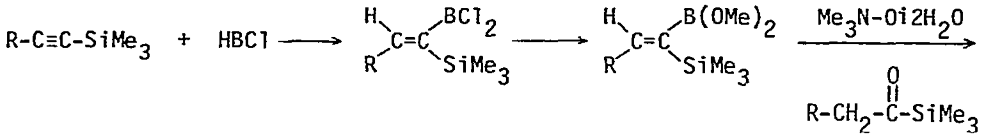


R = Et, Bu, cycloalkyl

Hydroboration of alkynylsilanes followed by oxidation yields carboxylic acids, thus accomplishing the synthetic conversion $R\text{-}C{\equiv}CH \longrightarrow RCH_2CO_2H$ [128].

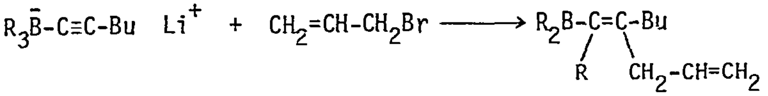


Hydroboration of trimethylsilylacetylenes with $HBCl_2$ yields 1-dichloroboryl-1-trimethylsilylalkenes, which can be oxidized to acylsilanes [129].



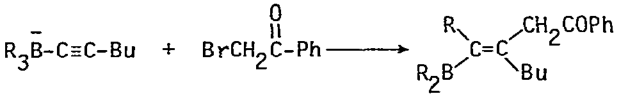
Reaction of $R_3\bar{B}\text{-C≡C-SiMe}_3$ with a series of electrophilic halides has yielded $R_2B\text{-CR=CR'SiMe}_3$, where R' is Et, $MeOCH_2$, Me_2NCH_2, Me_3Si, CH_3CO, or Ph_2P [130]

Pelter and coworkers have reported that alkylation of alkynyltrialkylbor with reactive alkylating agents such as methyl sulfate, allyl bromide, or ben bromide results in efficient rearrangement of vinylboranes [131].



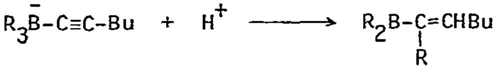
(E,Z-mixture)

Electrophiles such as α-bromoketones, ethyl bromoacetate, iodoacetonitrile, a propargyl bromide lead to stereospecific rearrangment [132].

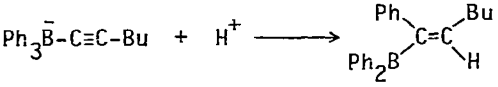


R = n-hexyl, cyclopentyl, etc.

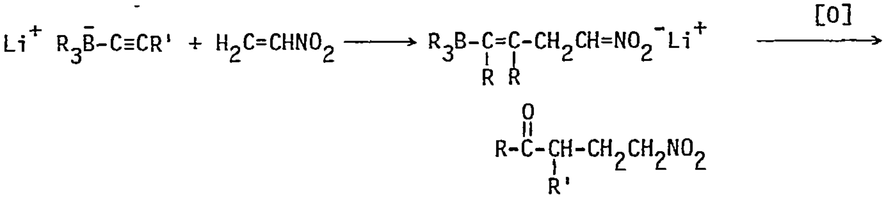
Since the R_2B group is cleaved stereospecifically by carboxylic acids, this provides a useful trisubstituted olefin synthesis. Protonation of alkynyltrialkylborates results in rearrangement to Z,E mixtures of alkenylboranes, excep when the migrating group is phenyl, which leads to Z-isomer exclusively [133].



$$R_3\bar{B}\text{-C≡C-Bu} + H^+ \longrightarrow R_2B\text{-}\underset{R}{\underset{|}{C}}\text{=CHBu}$$

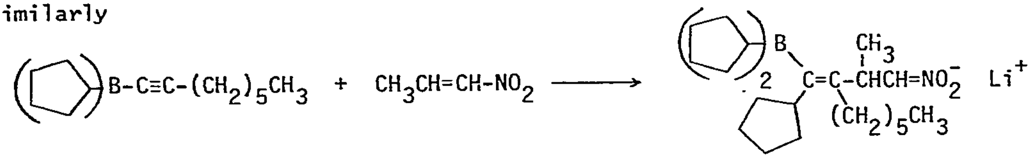


Lithium trialkylalkynylborates add to Michael acceptors with alkyl migration from boron to carbon [134].

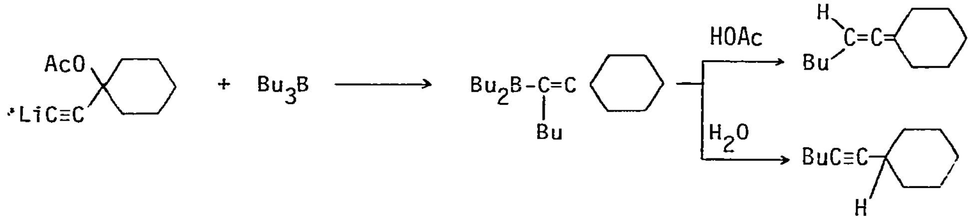


$$Li^+\ R_3\bar{B}\text{-C≡CR'} + H_2C\text{=CHNO}_2 \longrightarrow R_3B\text{-}\underset{R}{C}\text{=}\underset{R}{C}\text{-CH}_2\text{CH=NO}_2{}^-Li^+ \xrightarrow{[O]} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R'}{CH}\text{-CH}_2\text{CH}_2\text{NO}_2$$

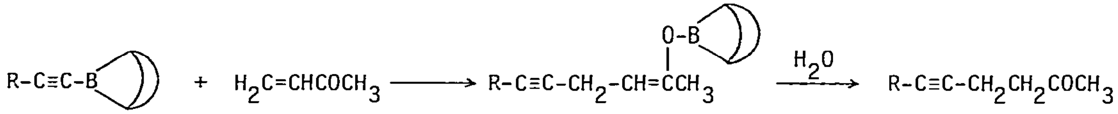
similarly



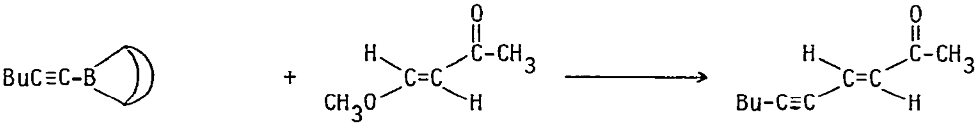
Treatment of propargyl acetates with butyllithium followed by a trialkylborane yields allenic boranes, which can be protonated with acetic acid to form allenes or with water to form acetylenes [135].



Alkynyldialkylboranes, R_2B-C≡C-R', have been prepared from R_2BOMe and LiC≡C-R'[136]. Alkynyl 9-BBN derivatives readily undergo conjugate addition to methyl vinyl ketone and other α,β-unsaturated ketones capable of adopting a cisoid conformation [137]. Cyclohexenone and cyclopentenone fail to react.

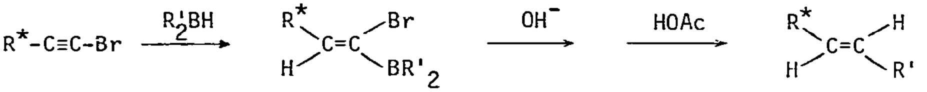


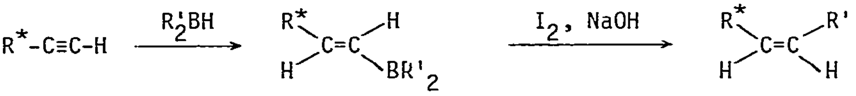
B-Alkynyl-9-BBN's react with 4-methoxy-3-buten-2-one to form enynones [138].



Reaction of LiC≡C-OEt with R_3B followed by cleavage with iodine gives mediocre yields of R-C≡C-OEt [139]. Using allyl iodide in place of iodine yielded some CH_2=$CHCH_2C$≡C-OEt.

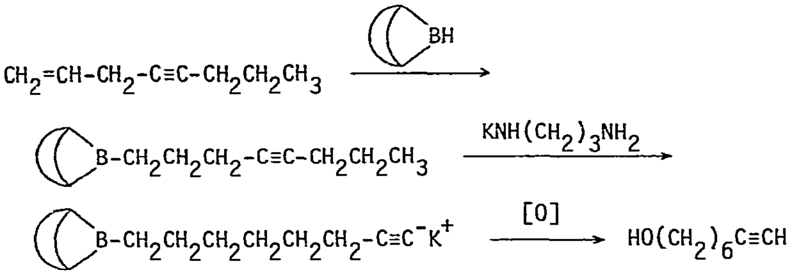
Olefins having optically active substituents have been prepared from acetylenes by known sequences of hydroboration and rearrangement [140].



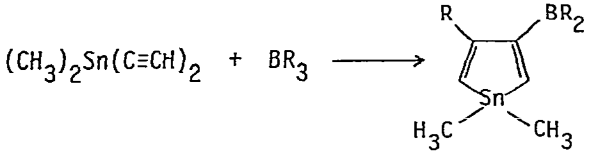


Deprotonation of $R_3\bar{B}C{\equiv}CH$ with butyllithium followed by alkylation with butyl bromide yields $R_3\bar{B}C{\equiv}C\text{-}Bu$ [141].

Hydroboration of the readily available 1-octene-4-yne with 9-BBN yields a borane which undergoes rearrangement to the terminal acetylenic borane, 7-octyn-1-yl-9-BBN, on treatment with potassium 3-aminopropylamide [142]. The acetylenic group does not move adjacent to the C-B bond, since $R\text{-}C{\equiv}C\text{-}BR'_2$ cleaves under the reaction conditions.



Reaction of diethynyldimethylstannane with trialkylboranes yields stannoles [143].

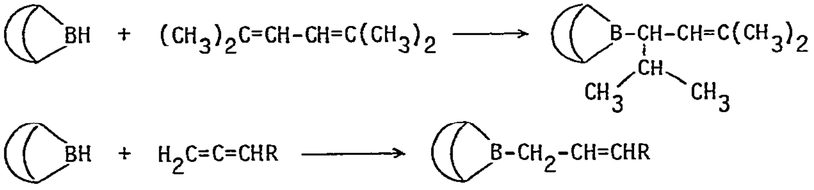


Hydroboration of alkynes $R\text{-}C{\equiv}C\text{-}R$ followed by treatment with alkaline silver(I) yields predominantly trans alkenes RCH=CHR [144].

Bromoboration of $HC{\equiv}C\text{-}C_4H_9$ yields thermodynamically controlled *E,Z*-isomer mixtures unless low temperatures (-80°C) are used, where *cis* addition (*Z*-product) is favored (98%) [145].

2. *Rearrangement of Boranes*. Included in this section are various rearrangements which lead to carbon-carbon bond formation, including reactions of allylboranes. Rearrangements of alkenylboranes and alkynylboranes have been covered in the preceding section.

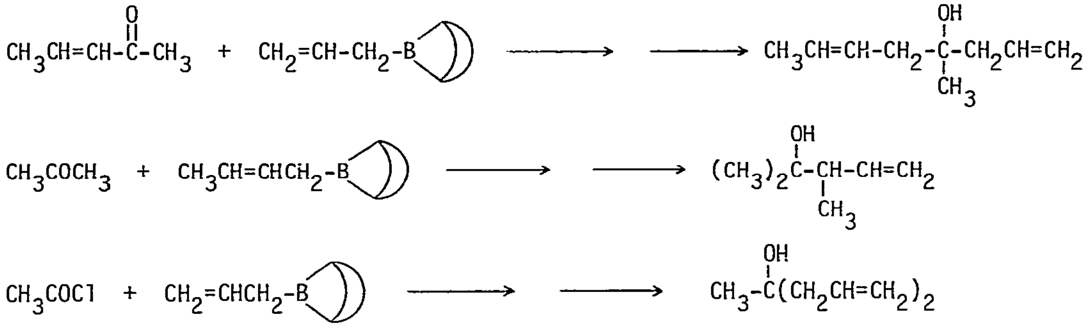
Hydroboration of allenes and certain 1,4-dienes with 9-BBN yields B-allylic 9-BBN derivatives [146].



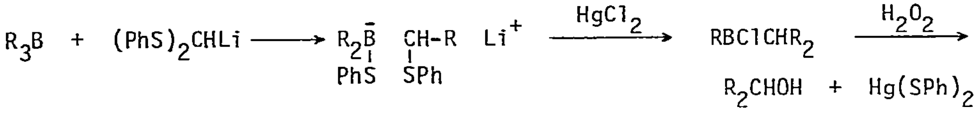
Allylic rearrangements occur readily, and both ends of the allyl group of

$CH_2=CH-CH_2$-9-BBN become equivalent on the NMR time scale at about 10°C. Electrophilic cleavages of the allylic groups from boron occur readily.

B-Allyl-9-BBN allylates aldehydes and ketones, yielding boronic esters which hydrolyze to homoallylic alcohols [147]. From experiments with B-crotyl-9-BBN, complete allylic rearrangement occurs during the reaction. α,β-Unsaturated carbonyl compounds react exclusively in a 1,2-manner. Acid chlorides undergo diallylation.

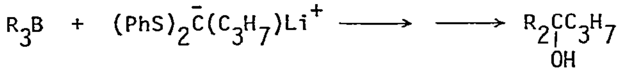


Secondary and tertiary alcohols are readily obtained by treatment of trialkylboranes with bis(phenylthio)methyllithium of 1,1-bis(phenylthio)-alkyllithium followed by rearrangement with mercuric chloride and oxidation [148].



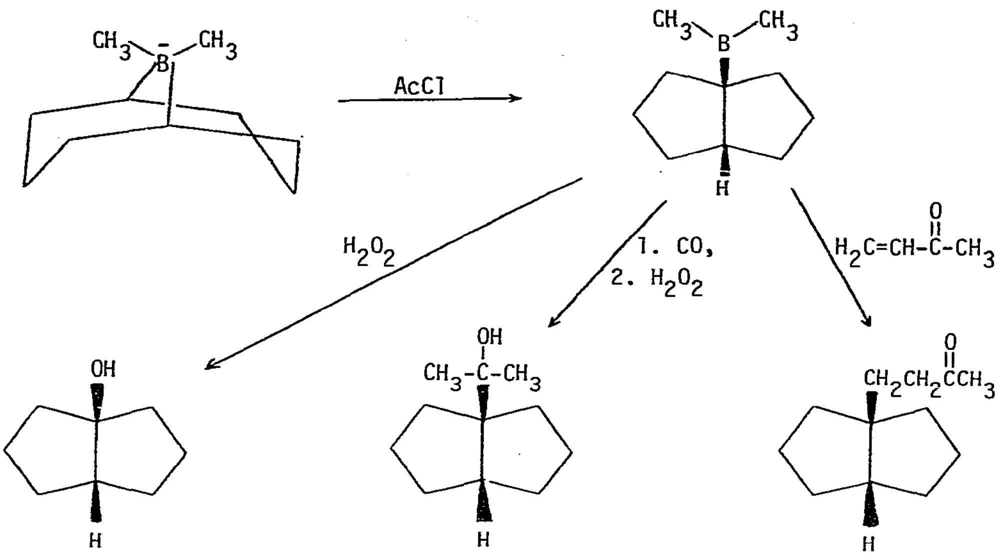
$$R_3B + (PhS)_2CHLi \longrightarrow \underset{PhS}{R_2\bar{B}}-\underset{SPh}{CH}-R\ Li^+ \xrightarrow{HgCl_2} RBClCHR_2 \xrightarrow{H_2O_2} R_2CHOH + Hg(SPh)_2$$

R = n-hexyl, cyclopentyl, etc.

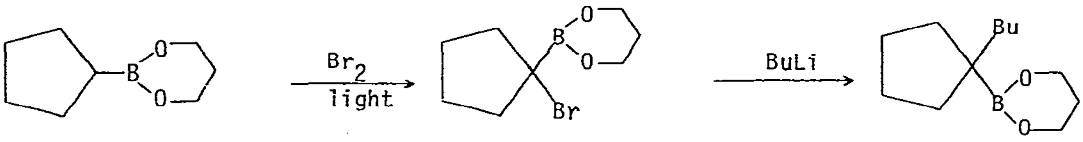


$$R_3B + (PhS)_2\bar{C}(C_3H_7)Li^+ \longrightarrow \longrightarrow R_2\underset{OH}{C}C_3H_7$$

Lithium B,B-dialkyl-9-BBN ate complexes undergo hydride transfer from and rearrangement of the 9-BBN group on reaction with acetyl chloride. This rearrangement has been used to synthesize the intermediate 1-dimethylboryl-bicyclo[3.3.0]octane, from which a series of 1-substituted bicyclo[3.3.0]-octanes have been prepared by known organoborane reactions [149].

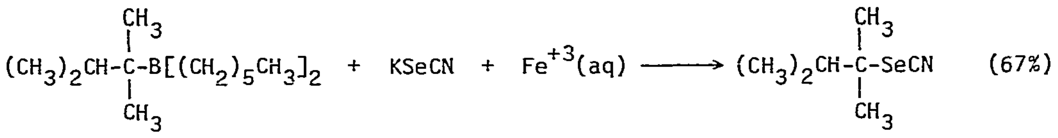


Reaction of secondary alkaneboronic or cycloalkaneboronic propanediol esters with bromine is initiated by light and provides an efficient synthesis of α-bromo boronic esters [150], which react with lithium reagents or even with hindered Grignard reagents to form carbon-carbon bonds [151].



3. Oxidative Replacements. Kabalka and Slayden have reported that the commercially available trimethylamine oxide dihydrate is an effective reagent for oxidizing trialkylboranes to the corresponding alcohols [152]. The reaction is slow and can be controlled to oxidize 1, 2, or all 3 alkyl groups. The order of rates of oxidation is tertiary > secondary > primary.

Reaction of mixed trialkylboranes with ferric thiocyanate or selenocyanate preferentially cleaves the more highly substituted alkyl group to form the alkyl thiocyanate or selenocyanate [153]. Treatment of R_3B with iron(III) azide



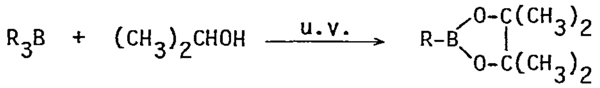
$$(CH_3)_2CH-\underset{CH_3}{\overset{CH_3}{C}}-B[(CH_2)_5CH_3]_2 + KSeCN + Fe^{+3}(aq) \longrightarrow (CH_3)_2CH-\underset{CH_3}{\overset{CH_3}{C}}-SeCN \quad (67\%)$$

and hydrogen peroxide gives good yields of alkyl azides, RN_3, where R is n-alkyl, cyclopentyl, or 2-butyl [154].

Nitrogen trichloride readily cleaves R_3B stepwise to RCl and, apparently, $B(NCl_2)_3$ [155]. The reaction is believed to be a free radical process, as shown by the fact that tris-exo-5-norbornylborane gives a 77/23 ratio of exo- and endo-5-chloronorbornane.

Hydroboration--mercuration of allene has been used to make $ClHgCH_2CH_2CH_2HgCl$, a useful precursor to the Grignard reagent $BrMg(CH_2)_3MgBr$ [156].

Irradiation of trialkylboranes in isopropyl alcohol with a high-pressure mercury vapor lamp yields pinacol boronic esters [157]. The yield is improved by passing oxygen (air) through the reaction mixture, and the results indicate a radical mechanism.



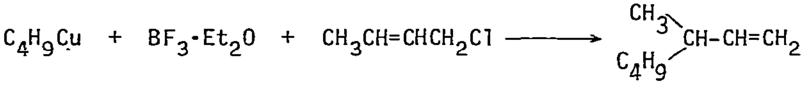
$$R_3B + (CH_3)_2CHOH \xrightarrow{u.v.} R\text{-}B\begin{matrix} O\text{-}C(CH_3)_2 \\ | \\ O\text{-}C(CH_3)_2 \end{matrix}$$

Reactions of copper(I) methyltrialkylborates with allylic or propargylic halides yield alkylation products [158].

$$[CH_3(CH_2)_5]_3\bar{B}CH_3Li^+ + CuBr + CH_2{=}CH\text{-}CH_2Cl \longrightarrow CH_3(CH_2)_5CH_2\text{-}CH{=}CH_2 \quad (87\%)$$

$$[CH_3(CH_2)_4]\ \bar{B}CH_3Li^+ + CuBr + HC{\equiv}CCH_2Br \longrightarrow CH_3(CH_2)_4CH{=}C{=}CH_2 \quad (54\%)$$

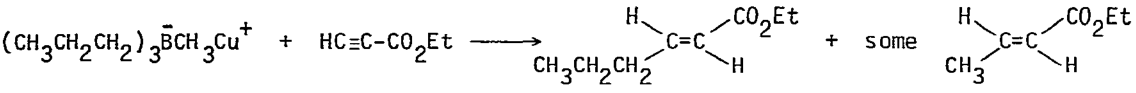
The reaction of $RCu{\cdot}BF_3$ with allylic halides is believed to proceed by way of an alkylboron ate complex, $R\text{-}BF_3^-Cu^+$ [159].



$$C_4H_9Cu + BF_3{\cdot}Et_2O + CH_3CH{=}CHCH_2Cl \longrightarrow \begin{matrix} CH_3 \\ C_4H_9 \end{matrix}\!\!>CH\text{-}CH{=}CH_2$$

98% this isomer, 80% isolated

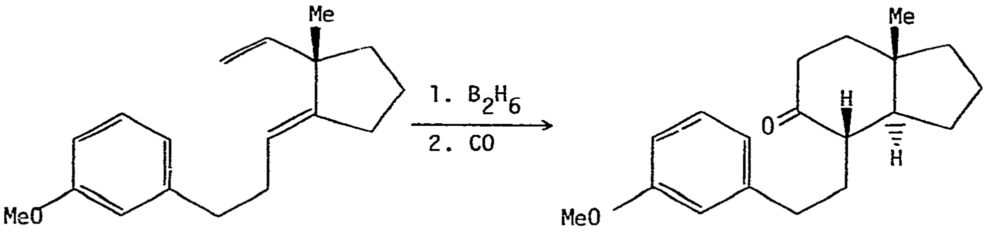
The reaction of ethyl propiolate with copper(I) methyltrialkylboranes yields, after hydrolytic workup, α,β-unsaturated acids which are 94-100% E isomer [160].



$$(CH_3CH_2CH_2)_3\bar{B}CH_3Cu^+ + HC{\equiv}C\text{-}CO_2Et \longrightarrow \begin{matrix} H \\ CH_3CH_2CH_2 \end{matrix}\!\!>C{=}C<\!\!\begin{matrix} CO_2Et \\ H \end{matrix} + \text{some} \begin{matrix} H \\ CH_3 \end{matrix}\!\!>C{=}C<\!\!\begin{matrix} CO_2Et \\ H \end{matrix}$$

C. Hydroboration of Natural Products and Miscellaneous

Hydroboration--carbonylation has been used as a key step in the synthesis of a steriod, 3-methoxyestra-1,3,5(10)-triene [161].

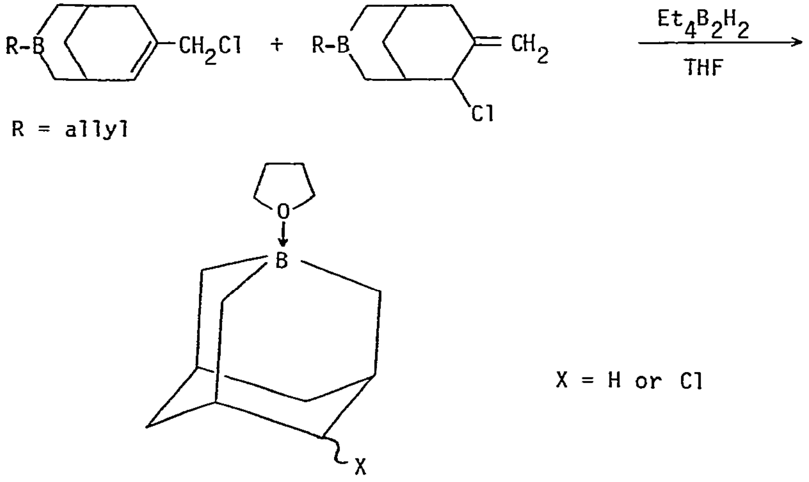


Hydroboration--oxidation has been used in the conversion of a $C{=}CH_2$ side chain of a steroid to a $CH{-}CH_2OH$ group [162]. Thermal isomerization of boranes derived from steroids has been reported [163, 164].

Hydroboration-oxidation has been used to convert $CH_2{=}CH{-}(CH_2)_2CH{=}CH(CH_2)_2{-}CO_2Et$ to $HO(CH_2)_4CH{=}CH(CH_2)_2CO_2Et$ in a synthesis of bee royal jelly acid [165].

Hydroboration--oxidation of monoterpenes, myrtenic acid [166] and 2-caren-4-ol [167], have been reported. Hydroboration of pinenes and related terpenes with monochloroborane has been reported [168]. The use of hydroboration--oxidation in the synthesis of a terpenoid, trihydroxylupane, has been reported [169].

Hydroboration of the propargyl chloride--trialkylborane adduct mixture with $Et_4B_2H_2$ in THF has given boraadamantane--THF complexes [170].

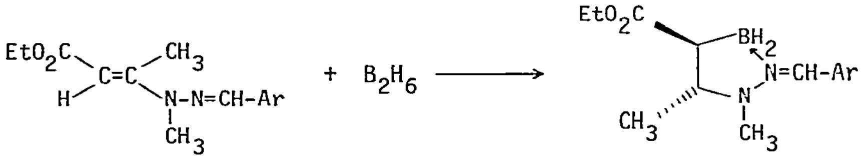


R = allyl

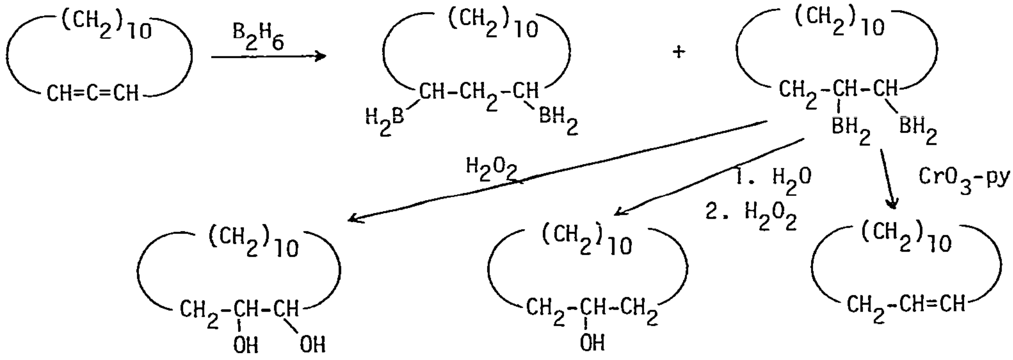
X = H or Cl

This work has been extended to related compounds, and the boraadamantanes have been treated with carbon monoxide and oxidized to yield hydroxyadamantanes [171] Hydroboration of bicyclo[3.3.1]nona-2,6-diene with B_2H_6 and $Et_4B_2H_2$ followed by heating with trimethyl borate has yielded a 2-boraadamantane [172].

Hydroboration of a series of enehydrazones has yielded stable heterocyclic chelates [173].



The dihydroboration--oxidation of a cyclic allene, 1,2-cyclotridecadiene, has been studied in considerable detail [174]. Substantial amounts of 1,2-diboryl product are formed, which leads to 1,2-cyclotridecanediol (both stereoisomers) on oxidation with hydrogen peroxide, or to Z- and E-cyclotridecene on oxidation with CrO_3. Hydrolysis before oxidation removes one of the boryl groups and leads to cyclotridecanol as the major product.



Hydroboration-oxidation of 1,1-diphenyl-2-vinylcyclopropane gives the expected product, 1,1-diphenyl-2-(2-hydroxyethyl)cyclopropane [175]. Hydroboration of tricyclo[5.3.1.$0^{3,8}$]undec-2-ene is not highly regioselective [176]. Hydroboration--oxidation of 9-phenylsulfonyl-9-azabicyclo[3.3.1]nona-2,6-diene has yielded a mixture of exo 2,6- and 2.7-diols [177]. Hydroboration and oxidatio of 1,1'-dicyclohexenyl gives a diastereomeric mixture of the two possible trans-1,1'-dicyclohexyl-2,2'-diols [178]. Reaction of $MeOCH_2CH=CHCH_2OMe$ with $Bu_4B_2H_2$ yields Bu_2BOMe, $MeOCH_2CH_2CH=CH_2$, and $MeOCH_2CH_2CH_2CH_2BBu_2$ [179]. The mechanism of hydroboration of ethylene and propylene on alumina involves dissociative adsorption of the diborane [180]. The progress of air oxidation of trialkylboranes has been followed by NMR [181].

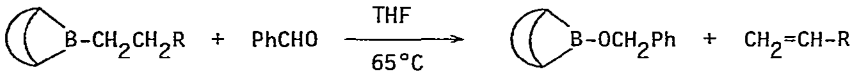
Hydroboration of ethylene with $[(CH_3)_2BH]_2$ yields $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$, which are easily isolated and disproportionate only slowly (several days at room temperature) [182].

D. Alkylboranes as Reducing Agents

9-Borabicyclononane (9-BBN) formes complexes with tertiary amines such as trimethylamine, pyridine, and γ-picoline, but fails to form stable adducts with more highly hindered amines such as triethylamine or tetramethylethylenediamine or the weaker base dimethyl sulfide [183]. The 9-BBN pyridine complex is a highly selective, mild reducing agent, useful for reducing aldehyde groups in the presence of ketones [184]. It is a very slow hydroborating agent.

9-BBN reduces α,β-unsaturated aldehydes and ketones cleanly to allylic alcohols without attacking the carbon-carbon double bond [185].

B-Allyl-9-BBN derivatives reduce benzaldehyde readily, liberating a mol of alkene in the process [186].



$(R = C_6H_{13})$

Rearrangement of the 9-BBN unit is not involved in this process, and the rate of reaction is strongly dependent on the nature of the B-alkyl group. A cyclic mechanism is postulated. Midland and coworkers have used the hydroboration product from α-pinene and 9-BBN to reduce benzaldehyde, which with appropriate deuterium labeling yields the enantiomers of α-deutero benzyl alcohol in high optical purity [187]. The reduction regenerates α-pinene.

Hydroboration of α-pinene with 9-BBN followed by treatment of the borane with t-butyllithium yields the asymmetric trialkylborohydride, lithium B-isopinocampheyl-9-borabicyclo[3.3.1]nonyl hydride, which is useful for asymmetric reduction of ketones [188]. Diisopinocampheylborane of high optical purity has been prepared, with care taken to insure absence of chemical contaminants such as sodium borohydride, and has been found to give consistent and reproducible results in the asymmetric reduction of ketones [189].

Catecholborane hydroborates alkynes rapidly at room temperature, but reacts very slowly with 1-alkenes and is a useful selective reducing agent [190]. Catecholborane reducts ketones preferentially in the presence of reactive groups such as alkyl halides, acid chlorides, nitriles, and alkenes, reduces aldehydes in preference to ketones, and reduces tosylhydrazones to $-CH_2-$ under mild conditions. Reduction of tosylhydrazones with catecholborane introduces the second hydrogen as a proton, and the reaction may be used to introduce a deuteriu label [191].

Triethylborane and trimethylborane react with LiH in ether to form $R_3BH^-Li^+$ [192]. The reaction of LiH with BR_3 to form $LiHBR_3$ and LiR_3BHBR_3 in various ethereal solvents has been studied in detail [193].

E. Reviews

Brown has reviewed the use of organoborane in synthesis [194]. Negishi has reviewed organoboron compounds as nucleophiles in organic synthesis [195]. Organoborane heterocycles from hydroboration of dienes have been reviewed [196]. Cragg has reviewed hydroboration--oxidation [197]. Gupta has reviewed organoboron chemistry [198]. Aliphatic boron compounds have been reviewed [199]. Yamamoto has reviewed organoborane chemistry in Japanese [200, 201].

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