BORON

ANNUAL SURVEY COVERING THE YEAR 1972

PART II*

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CONTENTS

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*Part I follows in a later volume

1. REVIEWS AND SUMMARIES

"Boranes in Organic Chemistry" is the title of a new book by H. C. Brown (72) which is a "must" on the shelves of the organoboron chemist. A well illustrated review (56) describes hydroboration as a synthetic tool in organic chemistry; a review of syntheses via organoboranes is available in the Japanese language (78). Organic syntheses via free-radical displacement reactions of organoboranes have been summarized elsewhere (221). The organometallic aspects of the chemistry of diborane(4) derivatives (129), reductions of functional groupgs with sulfurated borohydrides (241), and a listing of organic boron compounds, their syntheses and reactions (59) have also been compiled.

In a recent book (64) about 300 pages are devoted to a review of syntheses, reactions, and properties of boron hydrides and volume 7 of "Preparative Inorganic Reactions" contains a section on polyhedral and heteroatom boranes (94). An excellent article discussing pharmaceutical aspects of boron chemistry lists 294 references, summarizes recent trends of research, and depicts future possibilities (87). The chemistry of iminoboranes containing the skeletal unit C=N-B has been reviewed by Meller (18) and the main lectures of an international meeting on boron compounds held in Prague in 1971 and covering various aspects of boron chmeistry have been published (149,235).

During the last decade, allylboron chemistry has developed as a new area of organoboron chemistry, which has now been reviewed by Mikhailov (209); also, a summary on light-sensitive tetraarylborates has been published (219). Other articles treat the use of organoboranes as alkylating and arylating agents (211), boron-nitrogen betaines (210), and the chemistry of trialkyloxonium tetrafluoroborates (188).

Finally, the reader's attention is called to an article on the nomenclature of inorganic boron compounds (192) and another on bonding in boron hydrides (193).

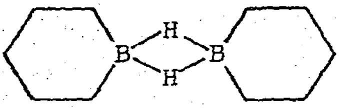
2. ORGANOBORON HYDRIDES

The role of hydroboration in organic chemistry is discussed in detail in Part I of this review. Hence, references to organohydridoboranes are limited herein to some basic studies.

In a recent note (196) the synthesis of tetraalkylammonium tetrahydridoborate has been described; this may be of interest for the synthetic chemist since this salt can be utilized for preparing solutions of diborane(6) in such non ethereal solvents as dichloromethane. In this context it should be noted that some recent studies on the hydrolysis of the tetrahydridoborate ion suggest the formation of an intermediate BH_5 species (215). Another novel hydroboration agent is the salt lithium tri-sec.-butylhydridoborate which can be obtained in quantitative yield from the interaction of tri-sec.-butylborane with lithium trimethoxyaluminohydride (232). The new reducing agent exhibits high stereoselectivity in the reduction of cyclic and bicyclic ketones.

New syntheses of organohydridoboranes include a novel preparatio of monoalkylboranes as triethylamine adducts, $(C_2H_5)_3N\cdot BH_2R$, via thexylborane (i.e., 2,3-dimethyl-2-butylborane) (184). It may be noted that thexylborane is readily available from the hydroboration of 2,3-dimethyl-2-butene with borane in a 1:1 molar ratio, which proceeds cleanly to the monoalkylborane stage (25).

Monomeric dialkylboranes are exceedingly rare; however, they are readily identified by a characteristic band near 2470 cm^{-1} in their infrared spectra and the lack of a typical B-H-B bridge absorption in the 1600-1500 cm^{-1} region (169). Dialkylboranes can be obtained by the reaction of thexylborane with an internal olefin (22). Also, it has been reported (240) that hydroboration of 1,4-pentadiene in a 3:2 molar ratio leads to a mixture of compounds. After thermal treatment of this product at 170° and subsequent reaction with an equimolar quantity of borane, bisborinane, 1, is obtained in 80% yield.



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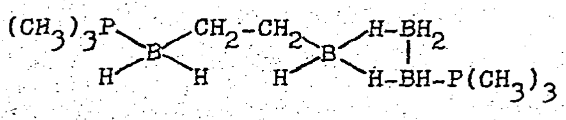
Tetraborane(10), B_4H_{10}, reacts with ethylene to yield 2,4-dimethylene-tetraborane (83). The base cleavage of the molecule proceeds in 2:1 molar ratio to yield a symmetrical product, 2.



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3. TRIORGANOBORANES

3.1 Syntheses

As noted above, the hydroboration of 2,3-dimethyl-2-butene proceeds cleanly to the monoalkylborane stage (25) and subsequent reaction with an internal olefin proceeds rapidly to the dialkylborane (22). Further treatment of the dialkylborane with a terminal olefin provides for unsymmetrical trialkylboranes. However, it should be noted that displacement reactions may occur in this last step, depending on the nature of the utilized terminal olefin. Apparently, steric requirements can force a reaction as depicted in the following equation:

$$\underline{c}\text{-}C_5H_9BRH \;+\; 2\; CH_2{=}CCH_3\text{-}CH_2\text{-}CH(CH_3)_2 \xrightarrow[\text{THF}]{3\ \text{hrs},\ 25^{\circ}}$$

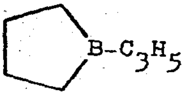
$$\underline{c}\text{-}C_5H_9B\left[CH_2\text{-}CHCH_3\text{-}CH_2\text{-}CH(CH_3)_2\right]_2 \;+\; (CH_3)_2C{=}C(CH_3)_2$$

$$R = C(CH_3)_2\text{-}CH(CH_3)_2$$

In principle, this development affords a highly convenient route to certain mixed trialkylboranes. Also, the experimental observations imply that displacement reactions may be quite common with increasing steric crowding of an organoborane.

A brief communication (60) reports the formation of organoboranes from Grignard reagents by reaction with borane in tetrahydrofuran. By this method several alkyl halides were converted to organoboranes which, without isolation, were oxidized to yield the corresponding alcohols.

The hydroboration of olefins with bisborinane, 1, provides a convenient synthesis of B-alkylborinanes (240). 1-Allylborolane, 3, is readily obtained by the reaction of 1-alkoxyborolanes with allyl



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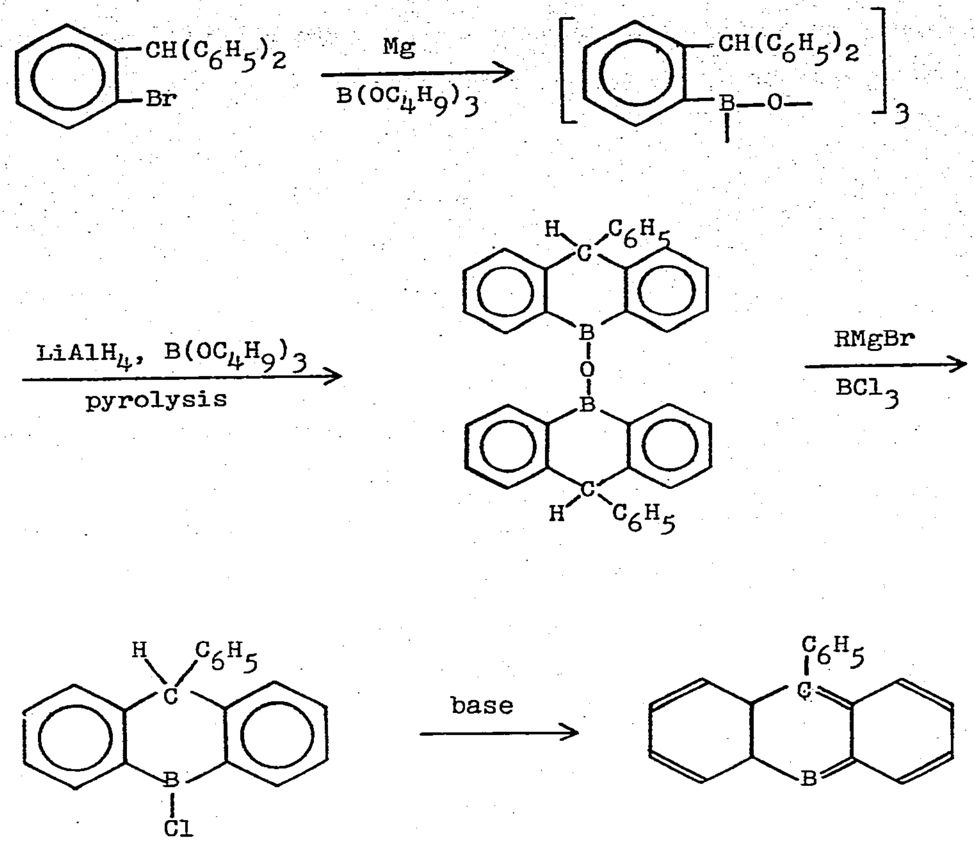
Grignard or with diallylaluminum bromide (139). Other specific reactions include the formation of ethyl(3-methyl-2-butenyl)boranes, $[(CH_3)_2C{=}CH{-}CH_2]_nB(C_2H_5)_{3-n}$, from tetraethyldiborane and 3-methyl-1,2-butadiene (234).

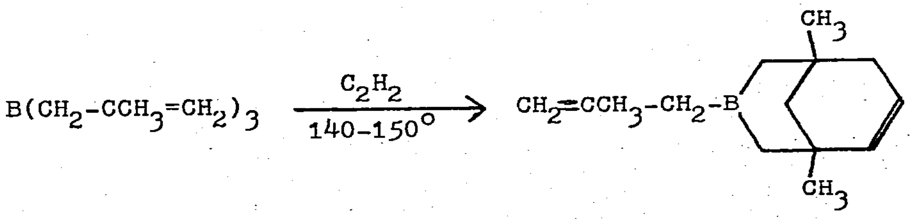
The mechanism of the transalkylation (elimination-addition) of triorganoboranes, first reported by Köster (30), has been studied by reacting tri-n-butylborane and tri-i-butylborane respectively with styrene and p-chlorostyrene (28). Also, the hydroboration of these latter olefins with tetra-n-butyldiborane(6) and tetra-i-butyldiborane(6) was investigated in that same work. The rate of transalkylation of tri-i-butylborane was found to be higher than that of tri-n-butylborane and theorientation in transalkylation reactions was found to be different from that observed in hydroboration reactions. These data were interpreted to support a mechanism for the transalkylation at boron of trialkylboranes proceeding through a six-center transition state with synchronous bond cleavage and formation of new ones. In this connection it is of interest to note that optically active trialkylaluminums have been prepared by alkyl exchange reactions between triethylaluminum and trialkylboranes (154). The data indicate that in this case alkyl exchange occurs stereospecifically and they also support a four-center transition state for the process.

Several p-substituted phenyldimesitylboranes have been synthesized by the reaction of dimesitylfluoroborane with substituted phenyllithiums (137). Derivatives of 10-phenyl-9,10-dihydro-9-boraanthracenes have been synthesized by pyrolysis of tris(2-benzhydryl)boroxin with lithium aluminum hydride and tris(butoxy)borane (227). Details are illustrated in the following reaction scheme.



3.2 Reactions of Triorganoboranes

The reaction of tris(2-methylallyl)borane with acetylene and derivatives thereof gives bicyclic derivatives as shown in the following equation (99):



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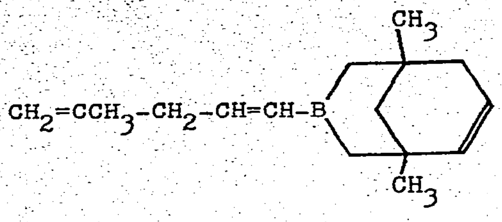
Additional action of acetylene on 4 produces 5, which reacts with methyl alcohol to yield the alkoxide 6.



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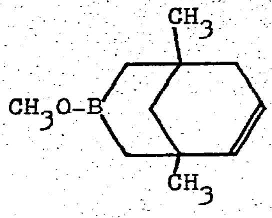

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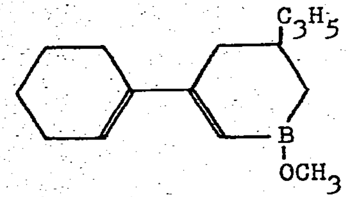
It should be noted that on the basis of infrared and proton magnetic resonance spectroscopic studies (144) tris(2-methylallyl)borane undergoes a permanent allylic rearrangement at temperatures above -40°. Presumably this rearrangement proceeds through a cyclic transition state and exchange is slow at room temperature. However, at 150° the exchange rate was found to exceed 10^3 sec^{-1} and the activation energy was calculated to be about 9.8 kcal/mole.

The reaction of triallylborane with 1-ethynylcyclohexene and subsequent methanolysis yields 5-allyl-3-(1-cyclohexen-1-yl)-1-methoxyboracyclohex-2-ene, 7 (158). This latter compound undergoes a diene condensation with maleic anhydride.



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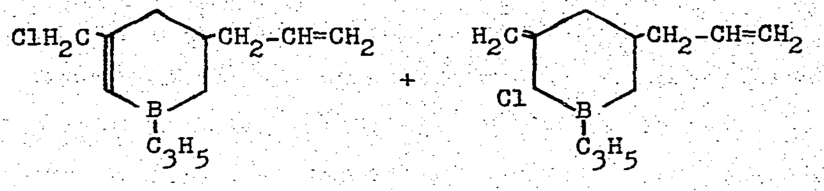
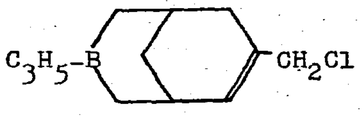
Triallylborane reacts very slowly with propargyl chloride at room temperature according to the following procedure:

$$HC\equiv C{-}CH_2Cl \quad + \quad B(C_3H_5)_3 \quad \xrightarrow[\text{20-25 days}]{}$$



If, however, the reaction is effected at 130° by adding the chloride to the hot borane over a period of 2-3 hours, a mixture of 8 and 9 is obtained (237).



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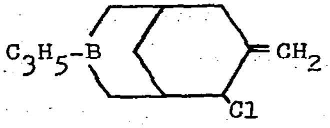

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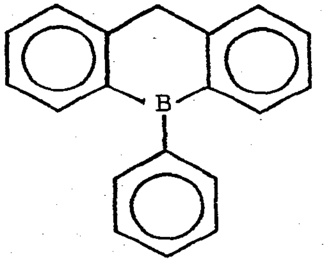
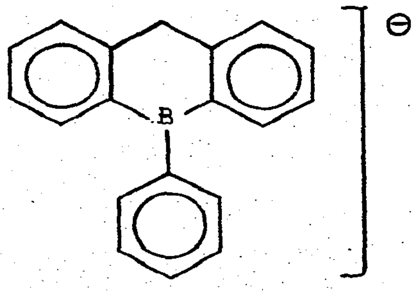
The reaction of 9-phenyl-9,10-dihydro-9-boraanthracene with t-butyllithium can yield, depending on the reaction conditions, either the acid-base type adduct 10 or the ion pair 11 (172).



· $LiC(CH_3)_3$

10



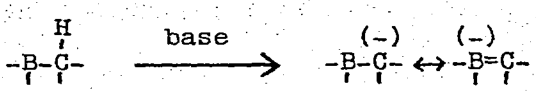
$Li^{\oplus}$ · 3.5 THF · C_4H_{10}

11

The thermal decomposition of tri-i-butylborane in the gas phase has been studied in the presence of excess of ethylene and over the temperature range of 407-469°K (43). Elimination of 2-methylpropene and rapid addition of ethylene to the resulting hydridoborane leads to the formation of ethyl-di-i-butylborane, diethyl-isobutylborane, and triethylborane by a consecutive mechanism. The results are consistent with a polar four-center transition state. Pyrolysis of trialkylboranes was also studied in the presence of polar compounds such as dimethyl sulfoxide, dimethyl formamide, acetophenone, benzaldehyde or furfural (84). Substantial elimination of an alkyl group as olefin was observed at temperatures higher than 120°. In dimethyl sulfoxide, dimethyl formamide or acetophenone only one of the three alkyl groups is eliminated while in benzaldehyde or furfural two of the alkyl groups of the trialkylborane are split off. Secondary alkyl groups are preferentially eliminated from mixed trialkylboranes and internal olefins are formed.

On gamma irradiation of trimethylborane or its adduct with ammonia (135), the formation of the free radicals $H_2\dot{C}\text{-}B(CH_3)_2$ and $H_2\dot{C}\text{-}B(CH_3)_2\cdot NH_3$ respectively has been observed by esr spectroscopy. Also, the esr spectrum of the trimesitylboran anion radical has been recorded (247).

Evidence has been presented for the formation of boron-stabilized carbanions by the interaction of selected trialkylboranes with bases of large steric requirements (217). For example, B-methyl-9-borabicyclononane was reacted with N-lithio 2,2,6,6-tetramethylpiperidine and the product was subsequently treated with deuterium oxide to give the monodeuterated (at the methyl group) borane. This observation was interpreted by a base-promoted removal of an alpha proton from an organoborane to give a boron-stabilized carbanion according to the following

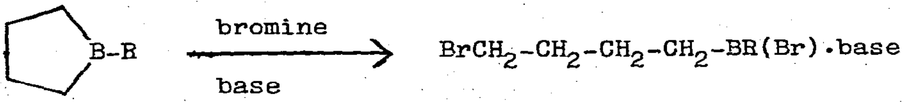


$$-\underset{|}{B}-\underset{|}{\overset{H}{C}}- \xrightarrow{\text{base}} -\underset{|}{B}-\underset{|}{\overset{(-)}{C}}- \leftrightarrow -\underset{|}{\overset{(-)}{B}}=\underset{|}{C}-$$

Dimethylchloromethylborane, $(CH_3)_2BCH_2Cl$, interacts with nucleophiles to yield boron-substituted methylethylboranes by alkyl rearrangement or alpha-substituted methylboranes without rearrangement (128). For example, reaction of $(CH_3)_2BCH_2Cl$ with dimethylamine provides for (dimethylamino)ethylmethylborane, $(CH_3)_2N-B(CH_3)(C_2H_5)$, in 89% yield whereas the same borane interacts with potassium iodide to yield dimethyliodomethylborane, $(CH_3)_2BCH_2I$. Alpha-bromoethyldiethylborane rearranges at 25° under the influence of aluminum tribromide and related electrophilic catalysts, in an almost instanteneous reaction, to yield s-butylethylbromoborane as shown in the following scheme (2):

$$CH_3-CHBr-B(C_2H_5)_2 \xrightarrow{AlBr_3} CH_3-CH(C_2H_5)-B(Br)(C_2H_5)$$

Bromination of 1-alkylborolanes in the absence of organic bases is not very selective (230). Cleavage of the endocyclic boron-carbon bond may occur as well as bromination of the borolane ring with evolution of hydrogen bromide. The latter may interact with the borolane or the 2-bromoborolane. In the presence of base, however, base adducts of alkylbromo(4-bromobutyl)boranes are obtained in high yield:



The light-induced bromination of thexyldialkylboranes has also been studied (239) and the photochemical iodination of triethylborane in cyclohexane was found to follow a simple free-radical mechanism in the temperature range of 50-90° (205). At lower temperatures and high iodine concentrations a more complex mechanism seems to prevail.

Monomeric formaldehyde at 0° reacts with tri-n-butylborane to produce 1-butene and di-n-butyl(methoxy)borane (216). However, in the presence of air, the one-carbon homologated ester is produced as is shown in the following equations. The homologation seems to occ via a free-radical chain mechanism and the two reactions appear to be common to other trialkylboranes.

$$BR_3 + CH_2O \longrightarrow R_2BOCH_3 + CH_3CH_2CH{=}CH_2$$

$$BR_3 + CH_2O \xrightarrow{O_2} R_2B{-}O{-}CH_2R$$

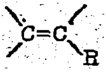
$$R = \underline{n}{-}C_4H_9$$

Trialkylboranes react with pivalamide under formation of (acylamino)dialkylboranes, $R_2B{-}NH{-}CO{-}C(CH_3)_3$, and generation of alkane (138). Trialkylboranes such as tri-n-propylborane, tri-n-butylborane or tribenzylborane were found to react with 1,4-naphthochinone by addition of the borane at only one of the two carbonyl groups (29).

Allylboranes react readily with vinyl ethers (31). This reaction provides for a simple method for the synthesis of 1,4-dienes and is illustrated by the following equation:

$$R'CH{=}CH{-}CH_2{-}BR_2 + CH_2{=}CHOR'' \xrightarrow{110-140^\circ} R''O{-}BR_2 + CH_2CH{-}CHR'{-}CH{=}CH_2$$

Tris(2-butenyl)borane reacts with vinyl ethers with allyl rearrangement Also, diene syntheses via vinylboranes of type 12 have been studied



$R = BCl_2,\ B(O{-}CH_2)_2,\ B(NCH_3{-}CH_2)_2$

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with special attention being devoted to configurational aspects of the resultant products (114). Vinylboranes derived from terminal and internal acetylenes <u>via</u> hydroboration with dicyclohexylborane undergo an instanteneous reaction with mercury(II) acetate at 0° to give the corresponding vinylmercury(II) acetates (82).

In this context it is of interest to note a detailed study on the mercury-deboronation of trialkylboranes delineating the wide scope of this procedure (155). The reaction can be described by the following basic equations:

$$BR_3 + 3\ Hg(OAc)_2 \xrightarrow{THF} B(OAc)_3 + 3\ RHgOAc$$

$$BR_3 + 3\ RHgOAc \longrightarrow B(CAc)_3 + 3\ HgR_2$$

However, $RB(OAc)_2$ appears as a side product. In principle, the first two of the boron-bonded alkyl groups react rapidly at room temperature while the third one is more sluggish. It is noteworthyy that organoboranes derived from internal olefins <u>via</u> hydroboration are unreactive towards various mercury(II) salts under these same conditions.

Some new studies on the hydroboration-carbonylation reaction include a general multi carbon homologation of olefins (162); also, it was found that a tertiary alkyl group can be transferred from boron to carbon without isomerization (163) to provide a ready synthesis of highly branched alcohols. Finally, it was found that the hydroboration of methylchlorosilylalkenes with diborane(6) gives adducts <u>via</u> attack of the olefinic double bond and the Si-Cl bond is kept intact (119). The cocondensation of difluorosilane with diborane(6) yields some new polyfluoropoylsilanes (196).

3.3 Physicochemical Studies

Last year (270) an indirect measurement of ^{11}B-H coupling constants in organoboron compounds was proposed; some experimental data on various vinylboron derivatives utilizing this approach have now been presented (242). Detailed proton magnetic resonance studies on diborane(6) and methylated and chlorinated derivatives thereof have been reported (69). The bridge hydrogen chemical shift moves -0.40 ppm per methyl group and -1.1 ppm with a chlorine substituent.

Chemical shifts in boron 1-s electron bonding energies for gaseous boron trifluoride, boron trichloride, tris(methoxy)borane, diborane(6), trimethylborane, borane-carbonyl and trimethylamine-borane were shown to be linearly related to boron atom charges as estimated by Pauling, CNDO and extended Hückel methods (110). However, there is no apparent correlation between the 1-s binding energy chemical shifts and the boron-11 nuclear magnetic resonance shifts. It is of interest to note that molecular orbital calculations on trimethylborane indicate virtually complete sigma character for the boron-carbon bonds (226).

Ultraviolet spectra of tribenzylboranes p-substituted at the benzene ring have been studied (165) and experimental data were correlated with semiempirical molecular orbital calculations.

The quantum yields of fluorescence of several p-substituted phenyldimesitylboranes (in cyclohexane) vary with the nature of the p-substituent in the order

$$Br \approx Cl < CN < CH_3 \approx H < N(CH_3)_2 < N(C_6H_5)_2$$

and were found to be sensitive to solvent polarity (137).

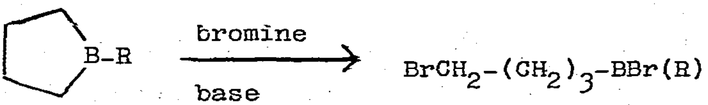
Tris(o-alkoxyphenyl)boranes form 2:1 complexes with diamines such as ethylenediamine, m-phenylenediamine, or toluene-2,4-diamine

(197). Only in the case of 1,6-hexanediamine, when it was reacted with tris(o-ethoxyphenyl)borane, was a 1:1 adduct obtained, apparently due to the low solubility of the material in ether. As a rule, the complexes of aliphatic diamines appear to be chemically more stable.

A computer method has been described which automatically and exactly determines the elemental composition of borane ions and the ions of borane derivatives from their polyisotopic mass spectra (175).

4. ORGANOHALOBORANES

A general synthesis for alkyldichloroboranes has been developed: It was noted that trialkylboranes derived from terminal, cyclic or bicyclic olefins via hydroboration in presence of a slight excess of borane, react with boron trichloride at 110° to give alkyldichloroboranes in excellent yield (225). s-Butylethylbromoborane, (s-C_4H_9)BBr(C_2H_5), has been obtained in an almost instantaneous rearrangement from bromoethyldiethylborane under the influence of aluminum tribromide at 25° (2), and propinyldifluoroborane, $CH_3C{\equiv}C\text{-}BF_2$, was prepared by reacting a gaseous mixture containing BF_2Cl with solid dipropinylmercury (17). In the presence of bases such as pyridine, 1-alkylborolanes can be brominated with the elemental halogen to give high yields of diorganobromoboranes (230) as shown in the following equation:



The organohaloboranes are obtained as base adducts.

Detailed procedures have been described for the preparation of dichlorophenylborane and chlorodiphenylborane from boron trichloride and tetraphenyl tin (200). Also, it was found that in the absence of solvents, p-substituted tetraaryl tins react with boron trichloride in a manner that all four tin-bonded aryl groups are effectively utilized as depicted in the following equation (272):

$$R_4Sn + 4\ BCl_3 \longrightarrow 4\ RBCl_2 + SnCl_4$$

Fluorophenylboranes, $(C_6H_5)_{3-n}BF_n$ (n = 1, 2) have been obtained by halogen metathesis from the corresponding chloro- and bromophenylboranes with titanium tetrafluoride (15).

It may also be noted that silicon tetrafluoride interacts with elemental silicon or silicon carbide at 1200-1850° to form gaseous species, which, on condensation with boron trifluoride at -196° yield (trifluorosilyl)difluoroborane, F_3Si-BF_2 (101).

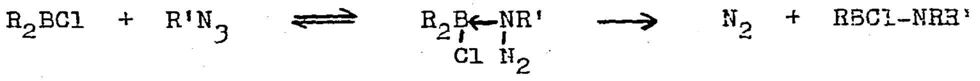
Tetrachlorodiborane(4), B_2Cl_4, which has been prepared on a 10 g scale by reaction of copper vapor with boron trichloride (133), was found to react with cyclopropanes to give ring cleavage addition compounds (24). Infrared and nuclear magnetic resonance data indicate the formation of structures with dichloroboryl groups in the 1,3-position of the resultant hydrocarbon chain. Some orbital overlap considerations have been described (95) in order to explain the unusual reactivity of trigonal diboron species as exemplified in the following equation:

$$Cl_2B-BCl_2 + H_2C=CH_2 \longrightarrow Cl_2B-CH_2-CH_2-BCl_2$$

The concept of having two formally empty p-orbitals participating in reactions which occur via pi-complex mechanisms was stressed. Tetrachlorodiborane(4) reacts with trifluoroethylene to give dichloro-2,2-difluorovinylborane and both isomers of dichloro-2-chloro-2-fluorovinylborane (206). Action of antimony(III) fluoride on these compounds results in displacement of chlorine by fluorine and a facile halogen exchange with B_2Cl_4 was observed for several fluoroolefins.

The vibrational spectrum of tetrabromodiborane(4) has been studied (246) and the infrared spectra of phenylhaloboranes have been recorded in the 4,000-250 cm^{-1} frequency range (15). Assignments for the fundamental vibrations were suggested and characteristic frequency trends were discussed. On that basis it was concluded thatthe inner vibrations of boron-bonded phenyl groups are not significantly influenced by the boron-bonded halogen; boron-halogen frequency shifts were related to mass and electronegativity differences. Also, the infrared spectrum of propinyldifluoroborane was recorded and an assignment of the fundamental modes of vibration was suggested (17).

Di-*n*-butylchloroborane reacts with sodium/potassium alloy to give an alkali metal species of di-*n*-butylboron of yet unknown structure (26). When the latter is treated with alkyl iodides in ether at room temperature, very little alkylation occurs at the boron atom (23). Organic azides react readily with dialkylchloroboranes (120). The reaction proceeds *via* a reversible coordination of the azide with the borane followed by an alkyl group transfer from boron to nitrogen:



$$R_2BCl + R'N_3 \rightleftharpoons R_2\underset{\displaystyle Cl}{\overset{}{B}}\leftarrow\underset{\displaystyle N_2}{N}R' \longrightarrow N_2 + RBCl\text{-}NRR'$$

Dialkylchloroboranes react with ethyl diazoacetate at low temperatures; protonolysis of the product yields the corresponding ethyl alkylacetate (170).

A series of adducts of alkylfluoroboranes with trialkylphosphines have been prepared (54) and nuclear magnetic resonance data on the compounds were evaluated in terms of the donor strength of phosphorus to boron. The stability of the complexes decreases in the order

$$R_3P{\cdot}BF_3 > R_3P{\cdot}RBF_2 > R_3P{\cdot}R_2BF > R_3P{\cdot}BR_3.$$

It is of interest to note that xenon was found to react with dioxygenyl tetrafluoroborate under liberation of oxygen and fluorine and formation of $FXe-BF_2$, containing a covalent xenon-boron bond (171 Finally, it should be mentioned that the crystal structure of dichloroazidoborane, Cl_2BN_3, has been elucidated by X-ray techniques (189) and that the role of boron tribromide and boron triiodide as reagents for the synthesis of anhydrous metal halides by a halogen exchange reaction has been evaluated (42).

A kinetic study of the halogen exchange between alkyl halides and boron trihalides (251) provided evidence for the formation of adducts between the two cited species.

5. ORGANOBORON-CHALCOGEN DERIVATIVES

5.1 Organoboron-Oxygen Compounds

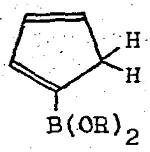
Monomeric fomaldehyde at 0^{o} reacts with tri-n-butylborane to produce 1-butene and di-n-butyl(methoxy)borane (216). However, in the presence of air, the one-carbon homologated ester is produced.

$$BR_3 + CH_2O \longrightarrow R_2BOCH_3 + C_4H_8$$

$$BR_3 + CH_2O \xrightarrow{O_2} R_2B-O-CH_2-R$$

The homologation seems to occur via a free-radical chain mechanism and the two cited reactions appear to be common to other trialkylboranes.

Reaction of cyclopentadienylmagnesium bromide with chloro(dimethoxy)borane, $ClB(OCH_3)_2$, in ether at -5^{o} yields cyclopentadienyldimethoxyborane (145). On the basis of infrared and proton magnetic resonance date, a mixture of the two isomers 13 and 14 is obtained



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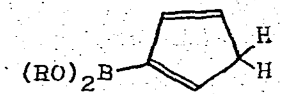
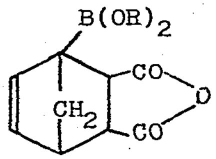


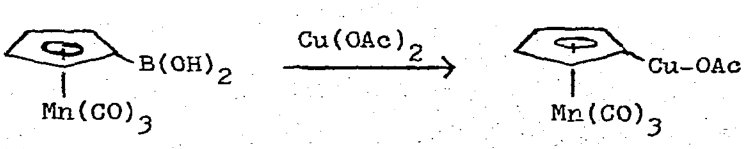
14

in a 10:1 molar ratio. The ester mixture readily enters into a Diels-Alder reaction as a diene but only 15 was obtained and identified from the reaction with maleic anhydride. Other esters of cyclopentadienylborane are accessible by the same basic preparative procedure



15

In this context it seems of interest to note that (cyclopentadienylmanganesetricarbonyl)dihydroxyborane, 16, reacts with copper(II) acetate by displacement of the dihydroxyborane group from the ring (146). On the other hand, 1-(1'-bromoferrocenyl)boric acid reacts with copper tetraphenylborate in acetone to yield phenylferrocene as the major product (156).



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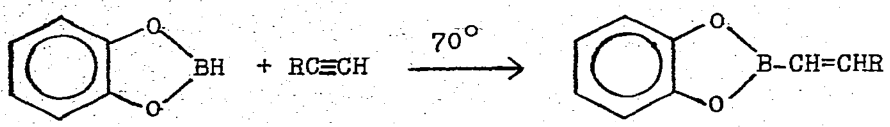
Catecholborane, 17, has been evaluated as a new and general reagent for the monohydroboration of alkynes (166). This novel reagent provides a particularly easy route to alkeneboronic esters according to the following equation:



17 18

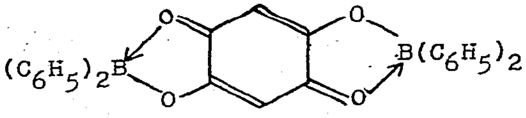
$$\xrightarrow{ROH} (RO)_2B\text{-}CH{=}CHR$$

It should be noted that the intermediate 18 reacts with mercury(II) acetate to provide a convenient and stereospecific procedure for the synthesis of alkenylmercury(II) salts (167).

$$\underline{18} \xrightarrow{Hg(OAc)_2} RHC{=}CH\text{-}HgOAc$$

A series of sterically hindered diaryl-n-butoxyboranes, $RR'BOC_4H_9$, has been synthesized by the reaction of di-n-butoxyarylboranes with aryllithium reagents (34). Steric shielding of the boron renders these compounds hydrolytically stable and interttowards many chemical reactions such as transesterification or oxidation. Proton magnetic resonance data on these compounds indicate (35) a barrier of internal rotation about the $B\text{-}C_{aryl}$ bond in the order of 11.5 to 12.5 kcal/mole which is due primarily to steric hindrance; no significant effect of $B\text{-}C_{aryl}$ pi-bonding can be deduced from the spectral data.

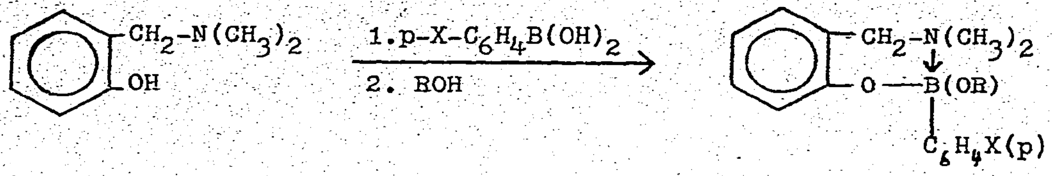
Bis(dibenzylboryl) oxide, $[(C_6H_5CH_2)_2B]_2O$, reacts with 1,4-naphthochinone and with p-chinone with formation of 2-benzyl-1,4-naphthalenediol and 2-benzylhydrochinone respectively (29). Polarographic reduction of the diphenylboryl ester of 2,5-dihydroxy-p-benzochinone, 19, yields a B-O-C heterocyclic radical as evidenced by esr data (147). In the anodic oxidation of trihexylmethoxyborates in the presence of butadiene both species seem to be simultaneously oxidized and the resulting radicals interact to form a variety of boron-free products (173).



19

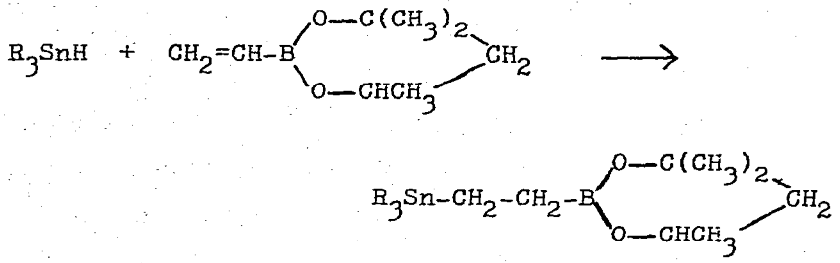
On the basis of infrared and boron-11 magnetic resonance data on (acyloxy)dialkylboranes, $R_2B{-}O{-}CC{-}R'$, these compounds are present in nonpolar solvents as monomeric and dimeric species (140). The dimers are formed by coordination between boron and the oxygen of a carbonyl group. In contrast, oxybis [(acyloxy)alkylboranes], $O(BR{-}O{-}CO{-}R')_2$, exist in solution only as monomers since intramolecular coordination occurs to give an unstrained six-membered ring system. This is particularly evident by the great lowering of the carbonyl stretching frequency.

The reaction of o-dimethylaminomethylphenols with p-substituted dihydroxyphenylborane in acetone yields intermediates which form the corresponding phenol esters, 20, upon treatment with alcohol (107). These esters are very stable towards hydrolysis; this observation can be accounted for by the tetrahedral environment about the boron atom.



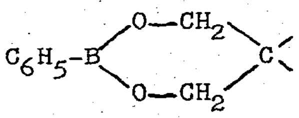
20

Hydrostannation of 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane with triorganotin hydrides (R_3SnH, R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5) provides derivatives with the organotin species at the beta-carbon atom of the vinyl group (212). A free-radical mechanism was advanced for this process described in the following equation:



Polymers containing a system of conjugated bonds have been prepared by polymerization of $HC{\equiv}C\text{-}B(OC_4H_9)_2$ (106). The presence of the electron-accepting boron in the polymer structure was found to affect only the resistivity value without changing the general temperature dependence of the electroconductivity of the material. Also, it might be mentioned here that the light-induced bromination of dialkylborinic acids (dialkylhydroxyboranes) provides a simple procedure for the synthesis of highly-substituted tertiary alcohols (238).

Proton and boron-11 nuclear magnetic resonance studies (180) on 2-phenyl-1,3,2-dioxaboracycloalkanes of type 21 suggest the existence of rapidly inverting chair-type conformation for the six-membered ring system. The mass spectra of various similar heterocycles, 22, have been examined in detail (134). The formation



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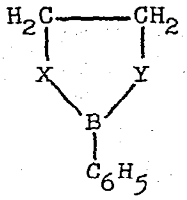


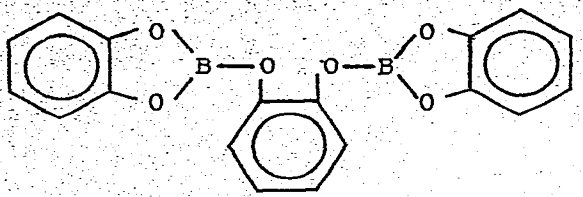
22

X = O, S
Y = O, S

hydrocarbon ions from these heterocycles by electron impact-induced rearrangement was discussed in terms of the relative bond energies between the various annular atoms. The mass spectra of some corticosteroid boronates have also been studied (49). The compounds were found to undergo characteristic fragmentation which is hardly influenced by the boron substituent.Other mass spectroscopic studies report on the fragmentation of dihydroxyphenylborane and B-triphenylboroxin, $(-BC_6H_5-O-)_3$ (256).

Several t-butoxyboranes have been prepared by displacement of amino groups from aminoboranes with t-butoxy groups (203).In other studies on tris-oxyborane systems it was found that boron tribromide reacts with phenoxyalkanes, C_6H_5OR, to yield phenoxyboranes and alkyl bromide (182); the reaction was interpreted by a bimolecular mechanism.

Catechol reacts with boron sulfide to give 2,2'-o-phenylenedioxybis(1,3,2-benzodioxaborole),23 (199). On the other hand, boron sulfide does not interact with the carboxylic group of salicylic acid and only tris(o-carboxylphenoxy)borane, 24, is obtained.



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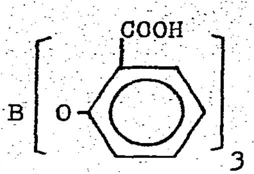


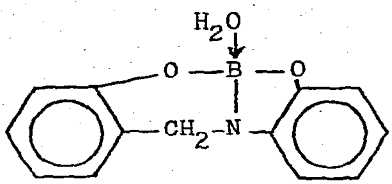
24

Though phthalic acid is being dehydrated by the action of boron sulfide, succinic acid and maleic acid were found to be completely inert towards this same reagent.

Boron-11 and proton magnetic resonance spectra of mixtures of tris(methoxy)borane and tris(dimethylamino)borane were utilized to study some ligand exchange reactions. The exchange equilibrium was found to be virtually random and all possible species $B(OCH_3)_{3-n}[N(CH_3)_2]_n$ were identified in the mixture (250). The dipole moments of the boron-oxygen bond in tris(alkoxy)boranes have been studied (195) and it has been reported that tris(methoxy)borane can be hydrolized in organic solvents and in the presence of cesium-t-butylate to yield various polyborates (81).

Last year the crystal structure of triethanolamine borate, $B(OCH_2CH_2)_3N$, was studied by X-ray diffraction techniques (160). A more accurate study has now shown that the B-N bond distance of the cited compound, which has a threefold symmetry along the intermolecular boron-nitrogen coordinate bond, has a length of 1.677 ± 0.006 Å (153). Vibrational and magnetic resonance studies on triethanolamine borate and its 1:1 adduct with antimony(V) chloride have confirmed a pyramidal structure for the O_3BN grouping of the molecule (152).

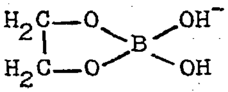
Schiff bases containing o- or o'- hydroxy groups can be reduced to benzaniline derivatives with sodium tetrahydridoborate (115). However, in the case of o,o'-dihydroxy Schiff bases boron chelates such as 25 were isolated after acidification of the reaction mixture. Sublimation of the product in vacuum readily



25

yields the dehydrated material. On the other hand, if steric factors prevent the formation of the borane derivative, the normal reduction path will be followed.

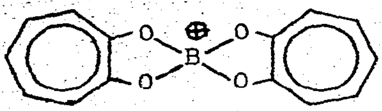
The electrophoretic mobilities of various polyols such as aldoses, ketoses, glycosides, etc. in diphenylborate at pH 10 closely parallel those obtained in borate (273). Raman spectra of aqueous solutions containing $B(OH)_4^-$ and various polyols have also been studied (61). The experimental data were interpreted by assuming chelate formation, e.g., 26, and observation of a



26

boron-oxygen stretching frequency near 760 cm^{-1} seems to be a reliable diagnostic means to establish a five-membered ring size, whereas this same vibration is observed near 720 cm^{-1} in six-membered chelates.

An X-ray crystal structure study of bistropolonatoboron(III) bromide hydrate, $[(C_7H_5O_2)_2B]^+Br\cdot H_2O$, has shown (96) that the two tropolonato rings are planar and the individual bond distances can best be explained by a delocalized structure, 27.



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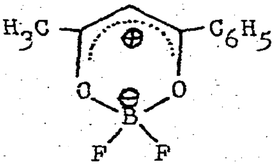
The crystal structure of benzoylacetonatoboron difluoride has also been studied by X-ray spectroscopy (245). Individual bond lengths were found to be B-F = 1.37 Å and B-O = 1.49 Å and the boron of the compound, 28, has an approximately tetrahedral environment.

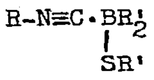


28

Several quinazirin borates have been prepared (191) and the synthesis and some properties of borodicitric acid have been described (51). Also, boric esters of substituted pyrans (52) and zinc and cadmium boropentaerythritols have been reported (53). Transesterification of monosaccharides can be accomplished with a large excess of tris(alkoxy)boranes but is accompanied by homogenization of the reaction mixture (100). Finally, new methods for the preparation of borosiloxanes (263) and particular of some of high boron contents (264) have been reported.

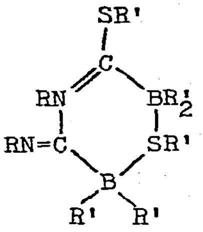
5.2 Sulfur and Selenium Derivatives

A new synthesis of organoboron sulfolenes has been reported (269) and some reactions of isonitriles with thioboranes have been studied (159). Interaction of isonitriles with diethyl(phenylthio)borane or diethyl(ethylthio)borane yields 1:1 adducts, 29, which can dimerize under the formation of species such as 30. These adducts can undergo 1.3-cycloaddition of an additional thioborane to yield heterocycles of type 31, which thermally isomerize to 32.



$R{-}N{\equiv}C{\cdot}\underset{SR'}{BR'_2}$

29



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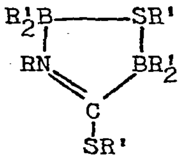

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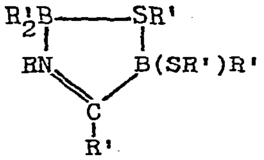

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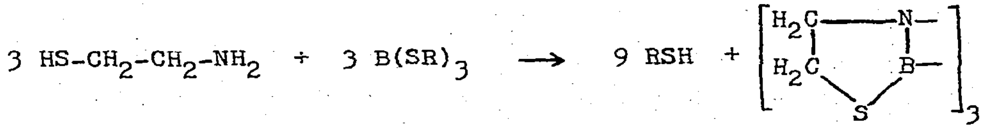
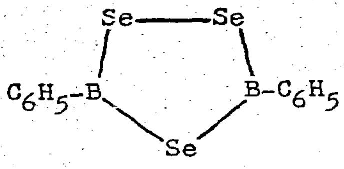
Tris(alkylthio)boranes react with hydroxy- or mercapto-amines under formation of borazines (40) as depicted in the following equation:



Proton magnetic resonance studies of the pyridine and gamma-picoline complexes of tris(methylthio)borane and tris(ethylthio)-

borane provide strong evidence that the pi-bonding in the boron-sulfu bond is much weaker than that in the boron-oxygen bond (259).

Arylselenodihaloboranes, ArSe-BX_2, are thermally unstable (105). For example, phenylselenodiiodoborane decomposes quantitatively to yield phenyldiiodoborane, elemental iodine and the five-membered heterocycle 33. On the other hand, phenylselenodichloroborane rearranges on thermal treatment to yield boron trichloride and tris(phenylseleno)borane, $B(SeC_6H_5)_3$. Methylselenoboranes such as $CH_3Se\text{-}BI_2$ or $CH_3Se\text{-}BI\text{-}CH_3$ are readily obtained by redox reactions of iodoboranes with dimethyldiselenane (104). The two cited compounds form stable trimers, whereas bis(dimethylseleno)iodoborane and species such as $(CH_3Se)_nBR_{3-n}$ ($R = CH_3$, C_6H_5) as well as the (methylseleno)phenyliodoborane, $CH_3Se\text{-}BI\text{-}C_6H_5$, are monomeric.



33

6. BORON-NITROGEN CHEMISTRY

6.1 Aminoboranes

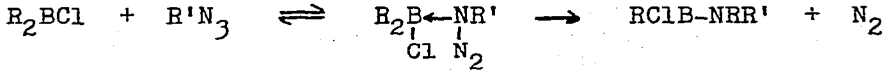
Trimeric methylaminoborane, $(CH_3HN\text{-}BH_2)_3$, hydroborates 1-hexene in the presence of pyridine to yield the (methylamino)-hexylborane trimer (98). On rapid heating of the latter compound to temperatures above 200° dehydrogenation occurs yielding B-tri-hexyl-N-trimethylborazine. However, if the aminoborane trimer is kept at lower temperatures (120-180°) for prolonged periods of time, (methylamino)dihexylborane appears as major reaction product.

Hexafluoroisopropylidenimine, $(CF_3)_2CNH$, reacts with phenylhaloboranes in a 1:1 molar ratio to yield (perhaloalkylamino)boranes (181):

$$C_6H_5BX_2 + (CF_3)_2CNH \longrightarrow (CF_3)_2CX\text{-}NH\text{-}BX\text{-}C_6H_5$$

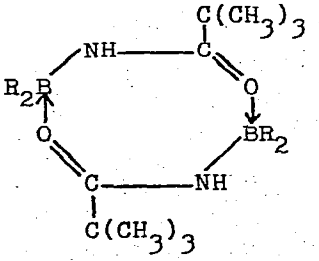
N-Alkylated hexafluoroisopropylidenimines, $(CF_3)_2CNR$, were found to react with boron trihalides, BX_3, either according to this same scheme or with formation of 1:1 adducts, $(CF_3)_2CNR \cdot BX_3$. In the case of $R = C_2H_5$ and $X = Br$, both of the cited reactions occur simultaneously.

Organic azides react readily with dialkylchloroboranes (120). The initial adduct formation is reversible; alkyl group transfer from boron to nitrogen with simultaneous elimination of nitrogen yields (amino)chloroboranes as depicted in the following equation:



$$R_2BCl + R'N_3 \rightleftharpoons R_2\underset{Cl}{B} \leftarrow \underset{N_2}{N}R' \longrightarrow RClB\text{-}NRR' + N_2$$

(Acylamino)dialkylboranes have been obtained by the reaction of trialkylboranes with pivalamide (138) to yield $R_2B\text{-}NH\text{-}CO\text{-}C(CH_3)_3$ under elimination of alkane. The structure of the acylamindoboranes was confirmed by their infrared spectra; the compounds tend to dimerize with the formation of a coordinated cyclic species, 34.



34

(Dialkylamino)haloboranes react with lithium phosphines, arsines or stibines under elimination of lithium halide and formation of a bond between boron and the Group V element (151). Compounds such as $[(CH_3)_2N]_2B\text{-}P(CH_3)_2$ and $[(CH_3)_2N]_2B\text{-}As(C_2H_5)_2$ have been obtained by this procedure and boron-11 chemical shift data on the materials were reported.

The reaction of boron trichloride with methylamine can be directed to yield either tris(methylamino)borane, $B(NHCH_3)_3$, or B-tris(methylamino)-N-trimethylborazine, $(\text{-}BNHCH_3\text{-}NCH_3\text{-})_3$, as major product (4). The vibrational spectrum of tris(methylamino)-borane and of its N-deuterated derivative were recorded and an assignment of the fundamentals has been suggested. The valence force constant k_{BN} of the molecule was calculated to be 4.51 mdyn/Å.

Tris(dimethylamino)borane reacts with carbonyl sulfide by 1,2-addition of the borane to the carbonyl group (20).

$$B[N(CH_3)_2]_3 \;+\; 2\ OCS \;\longrightarrow\; (CH_3)_2N\text{-}B\ O\text{-}CS[N(CH_3)_2]_2$$

In contrast, the same borane interacts with phosgene or thiophosgene under formation of bis(dimethylamino)chloroborane and substituted carbamides. Bis(dimethylamino)chloroborane reacts with carbonyl sulfide according to the following equation:

$$ClB[N(CH_3)_2]_2 \;+\; OCS \;\longrightarrow\; (CH_3)_2N\text{-}BCl\text{-}O\text{-}CS\text{-}N(CH_3)_2$$

Tris(2,2-dimethylhydrazino)borane, $B[NH\text{-}N(CH_3)_2]_3$, does not react with either CS_2 or OCS (20). However, reaction of the cited hydrazinoborane with three equivalents of carbon dioxide leads to a carbamoyloxyborane according to:

$$B[NH\text{-}N(CH_3)_2]_3 \;+\; 3\ CO_2 \;\longrightarrow\; B[O\text{-}CO\text{-}NH\text{-}N(CH_3)_2]_3$$

It may also be noted that aminoboranes have been utilized to prepare sulfenamides from sulfenic esters:(224):

$$B(NR_2)_3 + 3\ C_6H_5SOCH_3 \longrightarrow B(OCH_3)_3 + 3\ C_6H_5SNR_2$$

Boron trifluoride reacts with hexamethyldisilazane below 0° to yield the adduct $(R_3Si)_2NH{\cdot}BF_3$ (97). Above 0°, elimination of R_3SiF occurs and $R_3SiNH_2{\cdot}BF_3$, B-trifluoroborazine and N-trimethylsilylated derivatives of the latter are formed. If the two cited BF_3 adducts are reacted with ethyldiisopropylamine-trifluoroborane, $(R_3Si)_2N\text{-}BF_2$ and $(\text{-}BF\text{-}NSiR_3\text{-})_3$ ($R = CH_3$) respectively are obtained in good yield. Bis(trimethylsilyl)amino-difluoroborane is a quite versatile reagent since both the B–N and the B–F bonds can be reactive. For example, at 150° dialkyl(trimethylsilyl)amines will cleave a boron-fluorine bond as is depicted in the following equation:

$$(R_3Si)_2N\text{-}BF_2 + R_3SiNR'_2 \longrightarrow R_3SiF + (R_3Si)_2N\text{-}BF\text{-}NR'_2$$

Bis(trimethylsilyl)alkylamines react in analogous fashion; however, silylamines containing a proton bonded to the nitrogen preferentially undergo a transamination reaction:

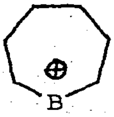
$$(R_3Si)_2N\text{-}BF_2 + HNR(SiR_3) \longrightarrow (R_3Si)_2NH + R_3SiRN\text{-}BF_2$$

Silylamines of the type R_3SiNHR react with boron trifluoride at 0° to yield unstable adducts which readily decompose with the elimination of R_3SiF. The resultant aminoboranes, $RHN\text{-}BF_2$, are also unstable und undergo cyclization to give B-trifluoroborazines and adducts of primary amines with boron trifluoride (118). However, in the presence of HF acceptors, dehydrofluorination can also be accomplished leading to compounds such as $R_3SiRN\text{-}BF_2$. Thermal decomposition of the latter yields B-trifluoroborazines, $(\text{-}BF\text{-}NR\text{-})_3$, in virtually quantitative yield.

Excess diborane reacts with heptasulfur imide, S_7NH, under formation of $S_7N\text{-}BH_2$ (179). The latter compound is stabilized as ether adduct or as a 1:1 adduct with tetrahydrofuran or pyridine.

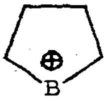
Studies on the nitrogen-14 chemical shift of a large number of simple aminoboranes have been reported (220) and were discussed in terms of neighboring group anisotropy effects and the order of the boron-nitrogen bond in the compounds. Apparently, increasing B-N bond strength results in a decrease in the shielding of the nitrogen-14 nucleus. Molecular properties such as bond energies, overlap population and group charges appear to permit ready distinction of a covalent boron-nitrogen bond in aminoboranes <u>vs.</u> a coordinate bond as exemplified in the amine-borane system (55).

The formation of the tropylium ion from organoboranes by electron impact has aroused quite some interest (276). Acyclic and cyclic derivatives of organoboranes containing at least one boron-nitrogen sigma bond were now found to give peaks in their mass spectra (71) which can be assigned to the boratropylium, <u>35</u>, and boracyclopentadienyl ; <u>36</u>, ions.



<u>35</u>

(m/q 89)



<u>36</u>

(m/q 63)

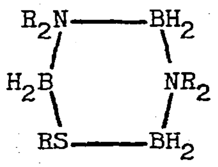
Boron trichloride or dichlorophenylborane react with SPF_2NH_2 or $P_3N_3F_5NH_2$ under elimination of hydrogen chloride and formation of the aminoboranes $B[NH\text{-}P(S)F_2]_3$, $C_6H_5B[NH\text{-}P(S)F_2]_2$ and $B[NH\text{-}P(N\text{-}PF_2)_2N]_3$ respectively. All three compounds are solid at room temperature and are extremely sensitive to moisture (150).

Both sodium heptahydridoborate, NaB_2H_7, and alkali metal trialkyltetrahydridoborates, $MB_2R_3H_4$, can be utilized for the hydroboration of anils with resultant formation of substituted trisaminoboranes (27). This observation illustrates the structural similarities of the two cited types of hydridoborates; furthermore, the reaction provides fairly ready access to substituted derivatives of tris(benzylphenylamino)borane.

Hexafluoroisopropylideniminolithium, $(CF_3)_2C{=}N{-}Li$, was found to react with boron trichloride to yield $B[N{=}C(CF_3)_2]_3$ (3). Surprisingly, the CF_3 groups of the latter compound are magnetically nonequivalent at 30° though at -30° a single sharp fluorine-19 resonance line is observed. Several new ketiminoboranes of the type $R_2C{=}N{-}BX_2$ (R = $\underline{t}$-C_4H_9; X = Cl, C_6H_5, $\underline{n}$-C_4H_9) have been prepared (132). The compounds are monomeric in benzene solution in agreement with the observation of a boron-11 nuclear magnetic resonance line at -32 ppm (relative to BF_3-etherate). The C=N(-B) group frequency of the various compounds was observed in the 1812-1839 cm^{-1} range. The linear configuration of the C-N-B grouping is indicated by observation of only one proton magnetic resonance line for the $\underline{t}$-butyl protons.

6.2 Coordinate Heterocycles

The interesting cotrimer 37 is readily obtained by the interaction of dimethylaminodiborane(6) with CH_3SH and dimethylamine or



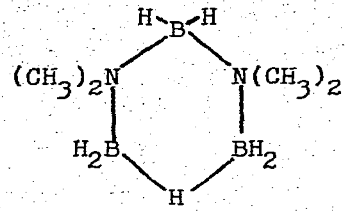
R = CH_3

37

by reaction of dimethylaminodiborane(6) with tris(methylthio)-

borane and (dimethylamino)borane (204); the compound is chemically quite inert.

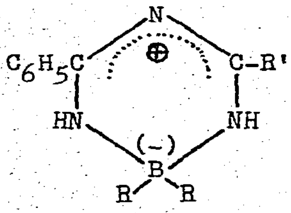
Tris(dimethylamino)alane reacts with diborane(6) to yield the aminolysis products $[(CH_3)_2NBH_2]_2$ and $(CH_3)_2NB_2H_5$ amongst other products (168). Most interesting appears to be a higher aggregated species for which, on the basis of boron-11 nuclear magnetic resonance data, the hydrogen-bridged structure 38 was proposed.



38

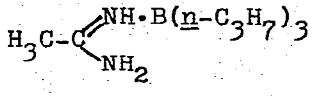
On heating of a mixture of benzamidine, benzonitrile and a trialkylborane, good yields of dialkylborylimidoylamidinates, 39, have been obtained (65). These compounds are stable in air and are not hydrolized by boiling water or by base. The synthetic reaction can be illustrated by the following equation:

$$BR_3 + C_6H_5C(NH)NH_2 + R'CN \xrightarrow[100\text{-}120^{\circ}]{-RH}$$



39

For analogous reactions involving low boiling nitriles, the trialkylborane can conveniently be replaced by (alkylthio)dialkylboranes, R"SBR$_2$. Though aliphatic amidines are fairly unstable, it was possible to obtain the complex of acetamidine with tri-n-propylborane, 40. The latter was reacted with acetonitrile to give 41.



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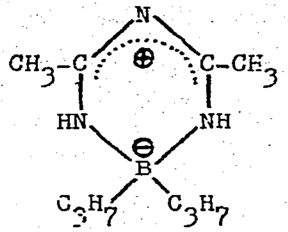

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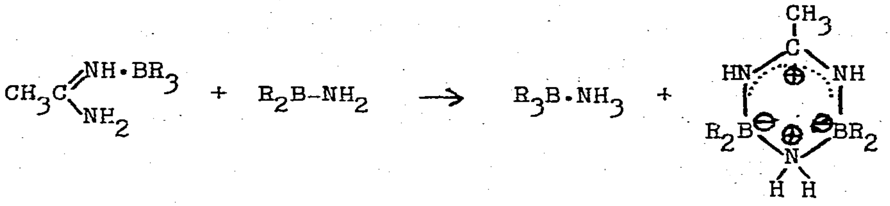
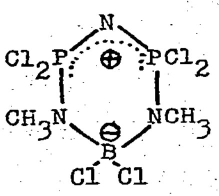
On treatment of the acetamidine complex of tri-n-propylborane with amino-di-n-propylborane reaction occurs according to the following scheme (141):



The cyclic species 42 can be reacted with antimony(III) fluoride or arsenic(III) fluoride to provide for complete replacement of chlorine by fluorine (265). Nuclear magnetic resonance data establish that the compound must be considered as an inner salt containing four-coordinate boron.



42

6.3 Borazine Chemistry

A mechanism for the formation of borazine, $(-BH-NH-)_3$, by the interaction of diborane(6) with ammonia has been suggested (4). Several reaction steps involving covalent and ionic species were formulated and some experimental data seem to support the postulated mechanism. Also, the effect of ortho-substitution at the aromatic ring on the formation of N-triarylborazines has been studied (131). In the reaction of substituted arylamines with triethylamine-borane or boron trichloride, the presence of two substituents in the ortho-position prevents the formation of the corresponding borazine. Rather, bisaminoboranes, $XB(NHR)_2$, and aminodichloroboranes as well as linear triazaboranes, RHN-BX-NR-BX-NHR, are formed. A possible reaction path to yield borazines via similar intermediates was formulated.

New preparative studies describe the synthesis of B-tris(methylamino)-N-trimethylborazine, $(-BNHCH_3-NCH_3-)_3$, by direct interaction of boron trichloride with methylamine (4) and B-cyclopentadienyl as well as B-methylcyclopentadienyl derivatives of N-trimethylborazine were readily obtained from the interaction of the corresponding B-trichloroborazine with potassium cyclopentadienide (127). Analogous reactions of B-trichloroborazine apparently lead to polymeric materials. Several B-chlorinated N-monomethylborazines have been prepared by the reaction of N-monomethylborazine with mercury(II) chloride (45). Subsequent aminolysis of the boron-halogen bonds gives access to such compound as $B_3H_2N(CH_3)_2N_3H_2CH_3$ and isomeric species could be isolated. Details on the preparation of such unsymmetrically substituted borazines have been desribed elsewhere (164) and all possible B-phenyl, -methyl and -chloro substituted derivatives of N-trimethylborazine have been prepared by the reaction of B-trichloro-N-trimethylborazine with Grignard reagents (142). Correlation techniques were used to establish characteristic frequency trends for the fundamental vibrations of the boron and nitrogen substituents. Detailed procedures have been described for the preparation of B-trichloroborazine and B-trichloro-N-trimethylborazine (201) and the formation of borazines by reaction of tris(alkylthio)boranes with hydroxy- or mercapto-amines (40) has already been noted in the above section on boron-sulfur compounds.

Hydrolysis of 25 borazines has been studied under homogeneous conditions in 90% THF / 10% H_2O (257). A marked steric effect of o-substitution in the phenyl groups of N-arylborazines was observed which tended to enhance the hydrolytic stability of the compounds.

Photolysis of borazine produces hydrogen, borazanaphthalene, diborazinyl and a non-volatile polymer (109). The experimental results were interpreted by assuming the intermediate formation of a borazyne species, $B_3N_3H_4$. The quantum yields for B-monoaminoborazine and hydrogen in the photochemical reaction of borazine with ammonia were found to increase with increasing ammonia to borazine ratio, reaching limiting values at approximately an equimolar mixture (258). The reacting intermediate appears to be a vibrationally excited borazine molecule. Similar experiments with mixtures of borazine with methyl bromide lead to the formation of monobromoborazine.

Chemical ionization studies of several other reaction mixtures containing borazine have been studied (5). Two classes of reactions were investigated:

a. Reactions of a proton donor with borazines through the sequence

$$CH_5^+ + R \longrightarrow RH^+ + CH_4$$

$$RH^+ + B \longrightarrow BH^+ + R$$

B = borazine
R = proton acceptor

b. Reactions of protonated borazine with a proton acceptor through the sequence

$$CH_5^+ + B \longrightarrow BH^+ + CH_4$$

$$BH^+ + R \longrightarrow RH^+ + B$$

The resultant data indicate that the proton affinity of borazine is greater than that of phosphine, cyclopropane, allene or 2-butyne but is less than the proton affinity of ammonia. Thus, borazine can be considered as a relatively strong base and it should be possible to stabilize the cation $(B_3N_3H_7)^+$ under appropriate reaction conditions.

The photoelectron and gas phase far UV spectra of several borazines, $(-BX-NY-)_3$ with X = H, F, Cl, CH_3 and Y = H, CH_3, have been recorded and some molecular orbital calculations were presented (248). On the basis of nuclear magnetic resonance studies on borazine, nitrogen and boron spin-lattice relaxation data were obtained (261); the following quadrupole coupling constants were reported: boron-10, 7.6 ± 2.9 MHz; boron-11, 3.6 ± 1.3 MHz, nitrogen-14, 1.4 ± 0.5 MHz. The proton magnetic resonance spectra of borazine and boron-10 enriched borazine have been studied at various temperatures in the -40 to $+59^\circ$ range (91). The observed line width data were interpreted by a combination of quadrupole relaxation effects resulting from the high-spin nuclei present and from long-range spin coupling. The aromatic character of some substituted borazines was evaluated by studying nuclear magnetic resonance solvent effects caused by anisotropy (249). Also, an interpretation and some calculations of the vibrational spectra of N-trimethylborazines have been presented (255).

Experimental details on the previous (271) structural study of tricarbonylhexaethylborazine-chromium have now become available

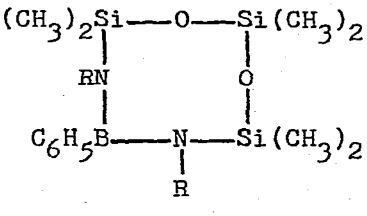
(268) and the crystal structure of hexachloroborazine has been studied (207) by X-ray diffraction. The molecular symmetry is C_3 and the following bond length data were obtained:

B-N, 1.398, 1.451 Å; B-Cl, 1.724 Å; N-Cl, 1.749 Å.

The exocyclic bonds are not exactly parallel to the ring plane and the puckered configuration of the chlorine atoms might well be due to steric factors.

In the present context it may also be noted that the ground-state electronic and geometric structure of the yet unknown iminoborane, HN=BH, has been investigated by ab initio SCF-LCAO molecular orbital calculations (1). The molecule is predicted to be linear with a B-N distance of 1.23 Å and with a dipole moment of 0.86 D. Analysis of the calculated wave functions indicates that the B-N bond of the iminoborane is indeed isoelectronic with the carbon-carbon bond of acetylene and is best represented as a truly triple bond.

Two new compounds have been synthesized which may be considered as heteroborazines (190). It was found that dichlorophenylborane reacts with the N-lithio silicon derivatives $(CH_3)_2Si[O-Si(CH_3)_2-NRLi]_2$ and $O[Si(CH_3)_2-NRLi]_2$ under formation of 43 and 44 respectively, containing boron, nitrogen, silicon and oxygen as annular atoms.



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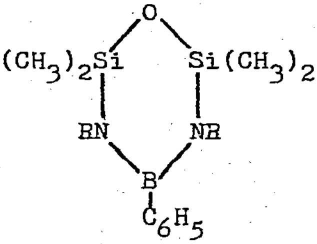
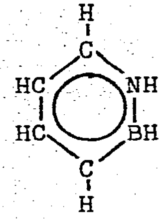


44

6.4 Boron-Nitrogen-Carbon Heterocycles

In an attempt to synthesize 2,1-borazarobenzene, 45, various reactions of buten-(3)-ylamine and its N-methyl derivative with various boranes have been studied (202). The cited amine interacts with diborane(6) under formation of tris(tetramethylene)borazine, 46, and polymeric materials. Replacing diborane(6) with the less reactive trimethylamine-borane gave similar results and utilization of monochloroborane yielded an ionic species, $[(CH_2=CH-CH_2-CH_2-NH_2)_2BH_2]Cl$. Buten-(3)-ylamine reacts with boron trichloride under formation of a borazine, $(-BCl-NC_4H_7-)_3$, and interaction with organohaloboranes was found to provide for acyclic aminoboranes such as $C_4H_7NH-BClC_6H_5$ as well as borazine derivatives. In high dilution trimethylamine-borane was found to react with N-methyl-buten-(3)-ylamine to give N-methyl-tetrahydro-2,1-borazarobenzene, 47, as well as an unidentified dimeric material. Compound 47 can in hydroboration reactions and several B-alkyl derivatives of 47 were prepared by this route.



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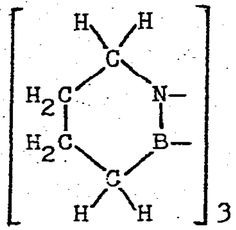

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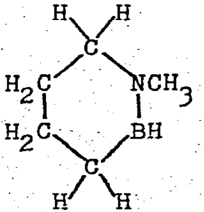
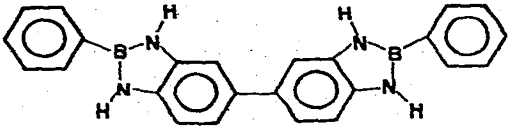


47

Polycyclic organoboron-nitrogen systems have been obtained by the interaction of aromatic diamines and tetraamines with bis(dimethylamino)phenylborane (223). Reaction occurs quite readily even if one of the reacting species (primarily or completely) is present in the solid state. Also, heterocyclic amines such as 5,6-diaminoindazole could be reacted in the same manner and compounds such as 48 to 51 were described.



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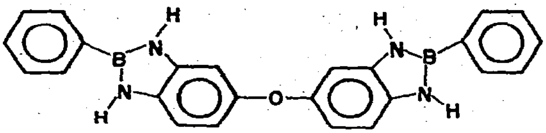

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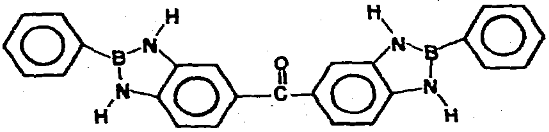

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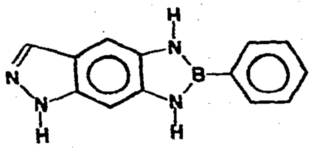
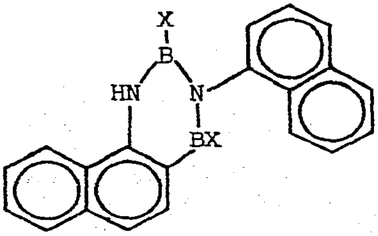


51

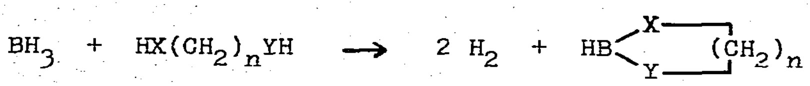
The reaction of α-naphthylamine with boron trichloride or boron tribromide was found to give 1:1 adducts, $L \cdot BX_3$, as well as (α-naphthylamino)dihaloboranes (113). However, the reaction can also be directed to give heterocyclic species of type 52.



52

Some theoretical studies on the yet unknown diboradiazabenzenes have been reported (260). Calculations on sigma charges, interatomic distances and description of the pi-electron distribution seem to indicate that the diboradiazabenzenes would be more stable than borazarobenzenes but less stable than borazine.

1,3-Dimethyl-2-chlorodiazaboracyclopentane, $ClB(NCH_3)_2(CH_2)_2$, reacts with trimethylstannyl lithium to yield 1,3-dimethyl-2-trimethylstannyldiazaboracyclopentane (57). The compound is not particularly oxygen sensitive suggesting that incorporation of a metal-bonded boron into a cyclic system increases the oxidative stability of the resultant material as compared to an acyclic system. Freshly generated borane reacts in boiling tetrahydrofuran with primary or secondary amines under formation of monoaminoboranes (161). Even in the presence of a large excess of the amine no additional boron-hydrogen bond of the borane is reactive under these conditions. In contrast, diamines, aminoalcohols, glycols or dithiols react with borane under these same conditions by reaction of two of the B-H bonds of the borane to yield heterocyclic materials according to the following equation:

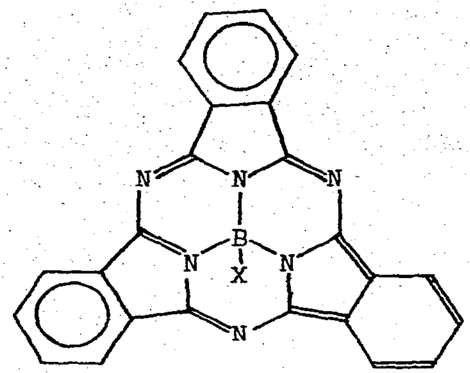


$$BH_3 + HX(CH_2)_nYH \longrightarrow 2\ H_2 + HB\langle{}^{X}_{Y}\rangle(CH_2)_n$$

$X = NR, O, S$
$Y = NR, O, S$
$n = 2, 3$

Proton and boron-11 magnetic resonance studies on 2-phenyl-1,3,2-diazaboracyclohexanes suggest that the N-C-C-C-N part of the compounds exists in rapidly inverting chair-type conformations (180).

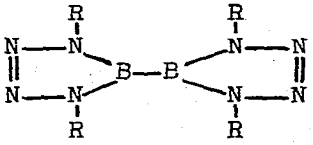
The interesting polycyclic system 53 was obtained by reaction of phthalodinitrile with boron trichloride or phenyldihaloboranes (21).



53

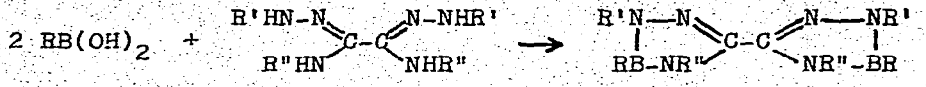
6.5 Compounds Containing the B-N-N Group

Tetrazaborolines which are halogen substituted at the boron have been prepared (130) by treatment of methylamine-trichloroborane with methyl azide in the presence of a tertiary amine and by bromination of 1,4-dimethyltetrazaborolin with N-bromosuccinimide. 1,4-Dimethyl-5-chlorotetrazaborolin can be reacted with silver pseudohalides to yield the corresponding 5-cyano, thiocyano and selenocyano derivatives; the vibrational spectra of the materials have been recorded. Coupling of the 5-chloro compound with sodium amalgam leads to the formation of the diborane(4) tetrazaborolin derivative 54.



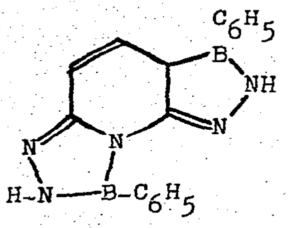
54

Bisboratriazaroles, 55, can be prepared in excellent yield by heating oximidrazones with dihydroxyboranes (19) as shown in the following scheme:



55

Similar products are obtained on treatment of dihydroxyphenylborane with 2,4-bis(hydrazino)pyrimidine (56) or 2,3-bis(hydrazino)quinoxaline (57).



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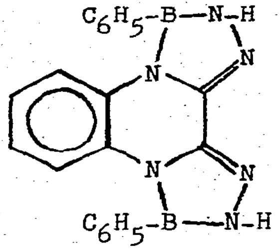
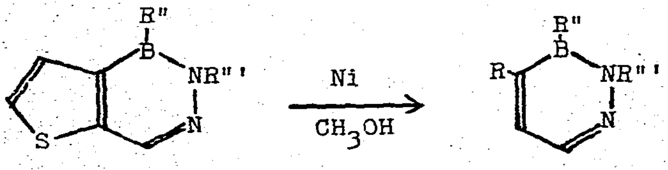


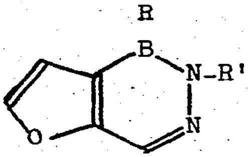
57

Raney-nickel desulfurization of borazarothienopyridines, 58, yields the novel monocyclic heteroaromatic 3,2-borazaropyridine system, 59, which is isoelectronic with pyridine. Compounds of type 59 are extremely resistant towards hydrolytic ring cleavage; the structure was confirmed by nuclear magnetic resonance data and the ultraviolet spectra of compounds of type 59 are extremely similar to those of their isoelectronic analogs (274).



58 59

2-Formyl-3-furanboronic acid and 3-formyl-2-furanboronic acid react with hydrazines to yield the borazarofuropyridines, 4,5-borazaro[2.3-c]pyridine, 60, and 7,6-borazaro[3.2-c]pyridine, 61, respectively (266). No aromatic substitution may be performed on these compounds, which is at least partially due to the instability of the furan ring.



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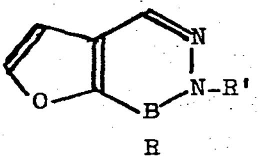


61

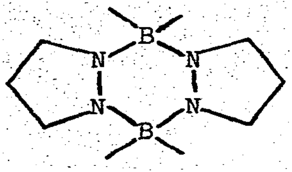
The reaction of hydrazine-1,2-bis(diphenylborane) with nitriles yields azines of borylamine ketones by addition of each boron-nitrogen bond of the hydrazinoborane across the carbon-nitrogen triple bond of a nitrile (16). The reaction can be depicted by the following equation:

$$2\ RCN + R'_2B\text{-}NH\text{-}NH\text{-}BR'_2 \longrightarrow R'_2B\text{-}NH\text{-}CR{=}N\text{-}N{=}CR\text{-}NH\text{-}BR'_2$$

R = alkyl, aryl
$R' = C_6H_5$

The resultant products appear to have a coordinated cyclic structure, by back-coordination of the boron atoms to the nitrogen atoms of the hydrazine grouping. In analogous reactions of the same hydrazinoborane with carbonyl compounds (aldehydes, ketones), the same basic reaction path seems to prevail. However, due to the great affinity between boron and oxygen, derivatives of a C_6H_5BO species and the azines of the original carbonyl compound are formed.

The chemistry of the pyrazoboles, 62, and the unique role of the pyrazolylborates, $R_{2-n}B(pz)_{n+2}^{-1}$ (pz = 1-pyrazolyl), were reviewed last year (277) and continue to receive considerable attention.



62

Infrared and nuclear magnetic resonance studies on $[B(pz)_4](C_5H_5)(CO)_2Mo$ indicate that the tetrakis(pyrazolyl)borate ligand is bidentate while the cyclopentadienyl group is pentahapto (117). Similar studies on [hydridotris(1-pyrazolyl)borate](h^5-cyclopentadienyl)dicarbonylmolybdenum, $[HB(pz)_3](C_5H_5)(CO)_2Mo$, and on $[(C_2H_5)_2B(pz)_2](C_5H_5)(CO)_2Mo$ support these findings (136). The bidentate pyrazolyl groups coordinate to form six-membered rings which exist in two conformers which interconvert in solution. Also, the temperature dependence of the proton magnetic resonance spectra of some poly(1-pyrazolyl)boratodicarbonylmolybdenum-π-allyls, $[RB(pz)_3](CO)_2Mo$-π-allyl, has been studied (123). Fluxional behavior was observed involving an internal rotation of the tridentate $RB(pz)_3^-$ group around the boron-molybdenum axis. Further infrared and proton magnetic resonance studies on $[H_2B(3,5-(CH_3)_2pz)_2](C_7H_7)(CO)_2Mo$ and $[(C_2H_5)_2B(pz)_2](C_7H_7)(CO)_2Mo$ indicate that the C_7H_7 groups are trihapto and the pyrazolylborate groups are bidentate (213).

7. ADDUCTS AND SALTS

7.1 Borane Adducts

Amine hydrochlorides, LHX, react with $Li(CH_3)_2P(BH_3)_2$ to yield compounds of the type $L-BH_2-P(CH_3)_2-BH_3$ (176). Pyrolysis of the latter products results in the formation of $[(CH_3)_2P-BH_2]_3$ and materials which are characteristic for the thermal decomposition of the corresponding amine-boranes, L·BH_3. The Lewis basicity of some difluorophosphines towards borane has been evaluated (229). The base strengths were found to decrease in the series CH_3PF_2, $(CH_3)_2NPF_2$, CH_3OPF_2, CH_3SPF_2. Dialkylamino-fluorophosphines, $F_nP(NR_2)_{3-n}$, react with various boranes to form relatively stable adducts (12). For example, diborane was found to give 1:1 adducts of the type $H_3B{\cdot}F_nP(NR_2)_{3-n}$ and similar materials were obtained from the interaction of dialkylaminofluorophosphospines with trimethylborane and also higher boranes such as tetraborane. In the latter case, the boron hydride forms a BH_3 and a B_3H_7 fragment, each of which coordinates with the phosphine. In all of these adducts the boron is presumably coordinated with the phosphorus atom. In contrast, boron trifluoride interacts with dialkylaminofluorophosphines by coordination between boron and nitrogen and the resultant complexes decompose by fluorine migration to produce phosphorus(III) fluoride and dimeric (dimethylamino)difluoroborane.

The reaction of borane with substituted piperidines is similar in energetics to the quaternary salt formation of the amine with methyl halides or tosylates, giving preferential axial B-N bond formation (70). In the cited reaction a mixture of diastereomeric amine-boranes is obtained and the composition could be determined by nuclear magnetic resonance spectroscopy.

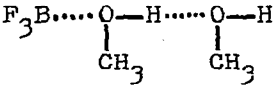
Near 120° pyridine-borane, $C_5H_5N{\cdot}BH_3$, undergoes a rearrangement by migration of boron-bonded hydrogen to the ring; the latter is partially saturated and a chain polymer containing boron-boron bonds is formed (252). The reaction of borane with acetone gives a 1:1 adduct rather than an alkoxyborane (7). At 450°K and low partial pressures of the reagents, the absolute bimolecular rate constant for this reaction is 3×10^8 / mole sec.

The microwave spectra of four isotopic species of $(CH_3)_3P{\cdot}BH_3$ and nine isotopic species of $CH_3PH_2{\cdot}BH_3$ have been assigned (62). Infrared, Raman and nuclear magnetic resonance data suggest that in 1,1-dimethylhydrazine-borane the BH_3 group is attached to the nitrogen atom which is substituted with hydrogen (198). The standard enthalpies of formation of hydrazine-borane and hydrazine-bisborane have been determined by pyrolysis (38). The reaction leads to quantitative formation of boron nitride and hydrogen and, in the case of the bisborane adduct, nitrogen and ammonia as well. The molecular structure and crystal structure of ethylenediamine-bisborane has been studied by X-ray spectroscopy (11). In the solid state the compound exists as an open-chain molecule in <u>trans</u> conformation with a boron-nitrogen distance of 1.60 Å.

Hydrogen fluoride was found to react with trimethylamine-borane by stepwise exchange of boron-bonded hydrogen with fluorine (121); trimethylammonium tetrafluoroborate was obtained as a side-product. In a study of displacement reactions by nuclear magnetic resonance techniques it was shown (214) that, using trimethylamine as a reference base, boron trifluoride is the stronger acid than either BH_2F, BHF_2 or diborane.

The vacuum ultraviolet spectra of trimethylamine-borane and trimethylamine-trideuterioborane exhibit two electronic transitions (253). Also, the barrier to internal rotation in ammonia-borane, $H_3N{\cdot}BH_3$, was analyzed in terms of the localized charge distributions and was found to be <u>ca.</u> 1.9 - 2.0 kcal/mole (262), and the reader's attention is called to a detailed proton magnetic resonance study on trimethylamine-trimethylborane (275).

The infrared spectra of some complexes of boron trifluoride with aldehydes have been recorded (66). Complexing of the aldehydes with the BF_3 causes a shift of the carbonyl stretching frequency of ca. 70 cm^{-1} to lower frequencies whereas the CH stretch of the aldehyde group shifts about 150 cm^{-1} to higher frequencies. As elucidated from their infrared spectra (67) complexes formed from two molecules methyl alcohol or acetic acid and one molecule of boron trifluoride have an open structure, 63. The dimethyl etherate



$F_3B\cdots\underset{CH_3}{O}-H\cdots\underset{CH_3}{O}-H$

63

of boron trifluoride was found to act as a selective methylating agent of (di)thiohydantoin derivatives (6), and the curing of epoxy resins with amine complexes of boron trifluoride has been described (47, 86).

Boron trifluoride forms solid 1:1 complexes with aromatic aldehydes (122); the $-CHO{\cdot}BF_3$ pseudo substituent is an extremely strong electron-withdrawing group.

The kinetics of the hydrolysis of pyridine-trichloroborane and trimethylamine-trichloroborane has been studied (48). Magnetic resonance spectra of boron trihalide complexes with heterocyclic organic nitrogen bases such as pyrazine, imidazole and pyridine derivatives have been investigated (14). Chemical shift differences were interpreted in terms of an electrostatic effect and possible pi-participation in the complexing process.

The infrared spectra of $HCN{\cdot}BBr_3$ and isotopically labeled derivatives thereof have been recorded (185). Fundamentals of the molecule were assigned and some force constants have been calculated.

Fairly stable trialkyl phosphite complexes with boron tribromide can be obtained by bromination of the corresponding borane complexes (63) as shown in the following equation:

$$(RO)_3P{\cdot}BH_3 \ + \ 3\ Br_2 \ \longrightarrow \ (RO)_3P{\cdot}BBr_3 \ + \ 3\ HBr$$

The rate of decomposition of the halide complexes in dioxane solution decreases with increasing size of the alkyl substituent, probably due to steric reasons.

Tris(o-alkoxyphenyl)boranes form 2:1 complexes with diamines such as ethylenediamine, m-phenylenediamine or toluene-2,4-diamine (197). Only in the case of 1,6-hexanediamine when it was reacted with tris(o-ethoxyphenyl)borane was a 1:1 adduct obtained, apparently due to the low solubility of the material in ethers. As a rule, the complexes of aliphatic diamines appear to be chemically more stable than those of aromatic amines.

7.2 Boronium Cations

Iodine displacement from trimethylamine-iodoborane with amides yields cations of the type $[(CH_3)_3N{\cdot}BH_2(\text{amide})]^+$, which can be isolated as hexafluorophosphates (92). Similar ions with cyanides in place of the amides and even such containing cyanide bridges between two boron moieties have been described in the same work.

The reaction of diborane with ammonia in n-hexane or in liquid ammonia at -83° leads to both symmetrical and unsymmetrical cleavage products, i.e., ammonia-borane and bisammineboronium tetrahydridoborate (93). However, the former is obtained in low yield only, independent of the ammonia concentration. On the other hand, increasing the temperature favors formation of the ammonia-borane as does increasing base strength of ether if the reaction is carried out in such latter solvents. A preliminary report on the reaction of methyldiboranes with ammonia or methylamines notes a tendency for unsymmetrical cleavage of the borane to decrease with the methyl substitution of the ligand (44). In the boronium salts boron-bonded methyl groups seem to reside exclusively on the boronium ion rather than on the borate ion.

7.3 Borates

A kinetic study of the intermediates formed in the hydrolysis of the tetrahydridoborate ion, BH_4^-, has been reported (177); recent studies (215) suggest the existence of an intermediate BH_5 species in that process.

The synthesis of tetraalkylammonium tetrahydridoborate has been described in a recent note (186); however, all attempts to isolate $HMgBH_4$ have failed (123). Indeed, if the latter compounds is formed, it apparently readily disproportionates to yield MgH_2 and $MgBH_4$. The crystal structure of a homolog of the latter, <u>e.g.</u>, beryllium hydridoborate, is that of a helical polymer of BH_4Be and BH_4 units (90).

Diborane(6) adds to trimethylamine-alane, $(CH_3)_3N{\cdot}AlH_3$, to yield $(CH_3)_3N{\cdot}Al(BH_4)_3$ (8). Excess diborane(6) is reflected in an equilibrium competition between aluminum tetrahydridoborate and diborane(6) for the trimethylamine. Upon addition of diborane(6) to solutions of dimethylaminoalane, $(CH_3)_2HN{\cdot}Al(BH_4)_3$ is formed. In this case, excess diborane(6) provides μ-dimethylaminodiborane and aluminum tetrahydridoborate.

A low temperature study of the interaction between water or alcohol and diborane(6) has provided evidence indicating asymmetric cleavage of the latter with both of the agents (178). The reaction of tri-sec.- butylborane with lithium trimethoxyaluminohydride affords lithium tri-sec.-butylhydridoborate in quantitative yield (232).

The vibrational spectra of borane adducts presumably containing anions such as BH_3CN^-, BD_3CN^-, BH_3NC^- or BH_3F^- have been recorded and the hybrid orbital force field model was found to be applicable to these ions (124). A rough correlation seems to exist between donor strength, boron hybridization and the BH_3 stretching force constant for the A_1 symmetric coordinate and the BX force constants were found to decrease in the series F, CN, NC, H, CC, PF_3, PH_3.

The compound $[NF_4]^+[BF_4]^-$ has been prepared by irradiation of a mixture of NF_3, BF_3 and elemental fluorine (143). The crystalline material is stable at room temperature in dry air; it readily reacts with moisture or organic matter. A complete vibrational assignment for NH_4BF_4 has been suggested (68).

Triphenylphosphine oxide complexes of metal(II) tetrafluoroborates have been reported (89) and the tetrafluoroborate anion is still a favored anion for the preparation and isolation of many unusual ionic species. For example, several new iron(IV) complexes of N,N-disubstituted dithiocarbamates (9) and 1,1-heterosubstituted phosphorinyl-4-carbonium derivatives (112) could be isolated as tetrafluoroborates. Also, o-methyldibenzofuranium tetrafluoroborate, a new Meerwein reagent, has been described (102) and the crystal structure of dicarbonyl-2,2'-bipyridine-pyridine-π-allylmolybdenum was studied on its tetrafluoroborate (116). The use of aryldiazonium tetrafluoroborates to synthesize aromatic tellurium compounds may also be noted in this context (243).

The tetrafluoroborate ion causes characteristic shifts in the visible absorption spectra of lanthanum(III)-alizarin complexon chelate (33). This observation seems of significance for the colorimetric determination of fluorine by the ALC method in the presence of boron.

The tetrahaloborate ions undergo halogen exchange in methylene chloride solution to form mixed tetrahaloborate ions (125). Only in the BF_4^-/BI_4^- system, exchange is so rapid that nuclear magnetic resonance signals cannot be observed for mixed species. In all other cases the latter can be detected by boron-11 and fluorine-19 resonance and the nmr parameters of such mixed tetrahaloborate anions show trends resembling those of the mixed boron trihalides.

The joint interaction of boron trichloride and phosphorus pentachloride with ammonium chloride leads to the formation of chlorophosphazonium tetrachloroborates, $[Cl(Cl_2P{=}N)_nPCl_3][BCl_4]$ (267). The degree of condensation of the cation is primarily dependent on the reaction temperature. Pyrolysis of these salts occurs according to the following equation:

$$[Cl(Cl_2P{=}N)_3PCl_3][BCl_4] \longrightarrow (-PCl_2{=}N-)_3 + [PCl_4][BCl_4]$$

Alkali metal tetrachloroborates, $MBCl_4$ (M = K, Rb, Cs, NH_4), have been prepared by reaction of $(NO)(BCl_4)$ with the alkali metal chlorides in liquid nitrosyl chloride (36). All the tetrachloroborates are hygroscopic crystalline materials which react vigorously with water. Their thermal decomposition generally occurs according to:

$$MBCl_4 \longrightarrow MCl + BCl_3$$

The ammonium salt, however, begins to decompose even at room temperature and under vacuum; the salt affords an unidentified material in 20% yield.Rubidium and cesium tetrachloroborate react with N_2O_4 in liquid nitrosyl chloride to form tetranitratoborates (37) according to the following equation:

$$MBCl_4 + 4\ N_2O_4 \longrightarrow M[B(NO_3)_4] + 4\ NOCl$$

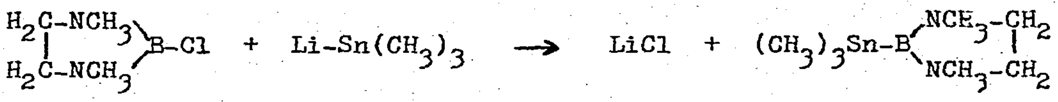
The alkali metal tetranitratoborates are crystalline materials which are insoluble in water and which gradually decompose at room temperature with release of nitrogen dioxide.

The existence of cyclic cyanoboranes of the composition $(BH_2CN)_n$ with n = 4 to 9 has been demonstrated (46, 233). Such species are obtained on interaction of the cyanotrihydridoborate anion with hydrogen chloride in media other than ethers.Several copper(I) and silver(I) cyanotrihydridoborates and cyanotriphenylborates have been prepared and their structure was elucidated by spectroscopic studies (13). Sodium cyanotriphenylborate in o-nitrotoluene was found to be an effective reagent for the solvent extraction of cesium and rubidium ion from aqueous solution (231).

In the reactions of sodium tetraphenylborate with acyl peroxides heterolytic cleavage of the peroxide link occurs with formation of the phenyl ester and the sodium salt of the corresponding acid (157). The triphenylborane reacts with the solvent and also undergoes oxidation.The absorption behavior of the tetraphenylborate anion at a mercury electrode has been studied (111). Strong absorption was noted in the potential value range of -0.15 to -1.00 Volt, whereas at more positive values the anion is oxidized.Finally, it may be noted that the bonding of molecular nitrogen in trans-hydrido(dinitrogen)bis(phosphine)iron(II) tetraphenylborate has been studied by Mössbauer spectroscopy (32).

8. METAL-BORON COMPOUNDS

On reaction of 1,3-dimethyl-2-chlorodiazaboracyclopentane with trimethylstannyl lithium a covalent boron-tin bond is formed as shown in the following equation (57):



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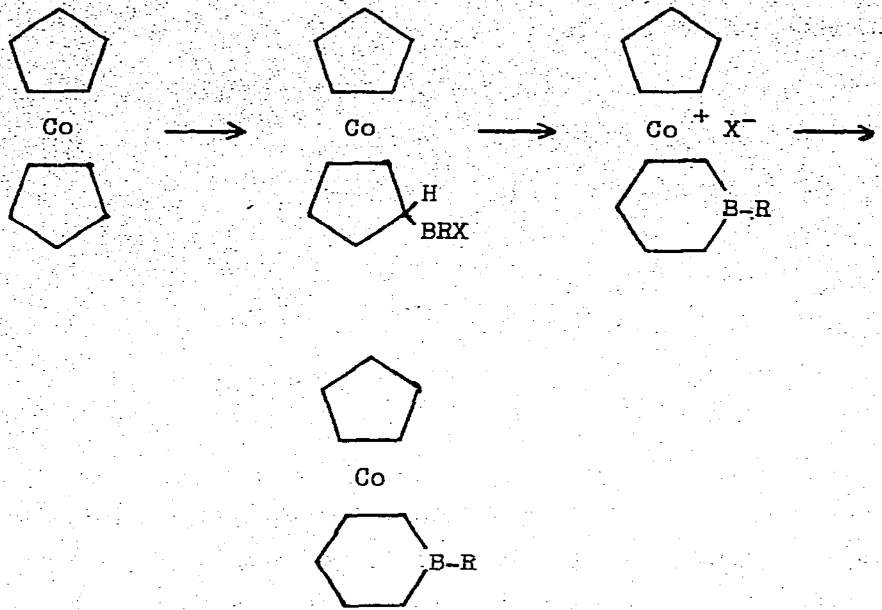
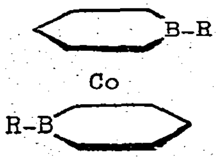
Surprisingly, 64 is not as oxygen sensitive as the quite similar acyclic $[(CH_3)_2N]_2B-Sn(CH_3)_3$ (58) suggesting that a stabilization of the boron-metal bond is brought about by incorporation of the boron into an annular system.

Other new metal derivatives of organoboron species include several paramagnetic cobalt complexes of "borabenzene". Though the parent compound, C_5H_5B, is unknown, derivatives of the borabenzene can be obtained by reaction of $Co(C_5H_5)_2$ with organoboron dihalides (41, 278). Preparative details for the synthesis of the paramagnetic species $Co(C_5H_5)(C_5H_5BR)$ and $Co(C_5H_5BR)_2$ as well as the diamagnetic cation $[Co(C_5H_5)(C_5H_5BR)]^+$ were described. In these materials, borinate ions, $(C_5H_5BR)^-$, are bonded to the metal as benzenoid hexahapto ligands. The synthesis is thought to proceed by the following mechanism:



The structure of bis(1-methoxyborinato)cobalt and bis(1-methylborinato)cobalt was studied by three-dimensional X-ray spectroscopy (174,279). Both molecules of type 65 are centrosymmetric and the very nearly planar rings are parallel to each other to form sandwich-type complexes with the metal.



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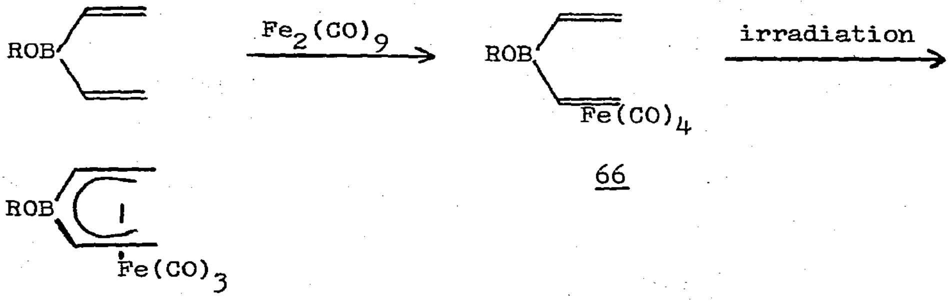
(R = CH_3, OCH_3)

In hexaethylborazinetricarbonylchromium the borazine ring is bonded centric to the $Cr(CO)_3$ moiety (268,271); the heterocycle has a very minute chair conformation and the nitrogen atoms are staggered with respect to the CO groups. The median boron-nitrogen bond distance is 1.44 Å , close to that of borazine.

Various metal complexes of 1-pyrazolylborates have been discussed in detail in section 6.5 of this article.However, closely related to the cobalt derivatives of the borabenzene cited above seem to be some iron complexes which were obtained on reaction of alkoxydivinylboranes with diiron enneacarbonyl (39). In this reaction a labile tetracarbonyl iron complex, 66, is formed initially. After removal of the byproduct iron pentacarbonyl the species can be irradiated to yield alkoxydivinylborane-tricarbonyliron, 67, which contains a boron-iron bond. On the basis of nuclear magnetic resonance data the divinylborane ligand of 67 acts as a pentadienyl species. The overall reaction is depicted in the following scheme:



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67

The reaction of dicobaltoctacarbonyl with the triethylamine adduct of boron trichloride or boron tribromide respectively leads to methylidynetricobalt nonacarbonyl cluster compounds, $Co_3(CO)_9COBX_2N(C_2H_5)_3$ (X = Cl, Br) (236). The mechanism of the reaction was discussed in terms of the initial formation of an adduct in which the boron is bonded to the oxygen of a CO bridge of the $Co_2(CO)_8$. Partial decomposition of the adduct supposedly yields transient $Co(CO)_4$ which reacts with the initial adduct and loss of carbon monoxide to yield the final product. Treatment of $[(C_6H_5)_3P]_3Pt$ with boron trichloride yields the adduct $[(C_6H_5)_3P]_3Pt \cdot 2BCl_3$, whereas $[(C_6H_5)_3P]_4Pt$ affords the same species besides triphenylphosphine-trichloroborane (126). Treatment of tris(triphenylphosphine)platinum(0)-bis(trichloroborane) with pyridine decomposes the complex with the formation of pyridine-trichloroborane. In this context it may be mentioned that the complex $[(C_6H_5)_3P]_3RuHCl$ reacts with triethylaluminum and nitrogen in ether to give dihydrido(dinitrogen)tris(triphenylphosphine)-ruthenium, $[(C_6H_5)_3P]_3Ru(N_2)H_2$. The nitrogen of this latter compound can be displaced with the inner diazonium salt $N_2B_{10}H_8S(CH_3)_2$ under formation of $[(C_6H_5)_3P]_3Ru(H_2)N_2B_{10}H_8S(CH_3)_2$, in which dinitrogen is bridging boron and ruthenium (10). The RuNNB moity is surprisingly stable as evidenced by its inertness to HCl, $NaBH_4$, hydrogenolysis or atmospheric oxidation. Interaction of boron trichloride with stannylphosphine-metal pentacarbonyl, $(CO)_5M \cdot P(C_6H_5)_2[Sn(CH_3)_3]$ (M = Cr, Mo, W) leads to chlorination of the tin atom (228).

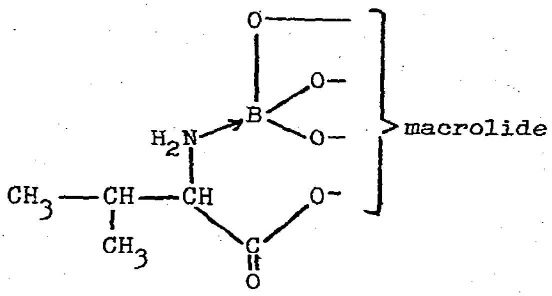
Finally, a study on the synthesis and an investigation of the electrophysical properties of polymers containing ferrocene and boron moieties might be mentioned (50).

9. MEDICINAL ASPECTS

The interest in the potential application of boron compounds for medicinal purposes seems to grow constantly; in the following section some data are compiled which may be of particular interest to the medicinal chemist.

A review article illustrating pharmaceutical aspects of inorganic and organic boron compounds has already been cited (87).

The crystal structure of the recently discovered boromycin, 68, has been studied by X-ray spectroscopy of the crystalline cesium salt, which was obtained by cleavage of D-valine from boromycin with cesium hydroxide (88). This investigation has led to a slightly revised empiricial formula, $C_{45}H_{74}BNO_{15}$, for the antibiotic and the anion was found to have roughly the shape of a sphere with a lipophilic surface and a cleft lined with oxygen atoms.



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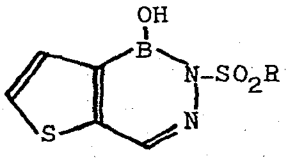
A number of heteroaromatic boron compounds containing B-N-N groups as annular units, e.g., 69 and 70, were found to exhibit interesting antibacterial activity (80). In particular, derivatives of the latter type 70 were found to be highly active against gram-negative bacteria. In order to elucidate the substituent effects on the antibacterial activity, a series of exocyclic substituted



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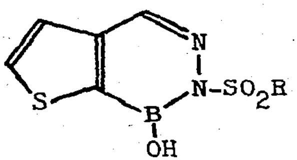

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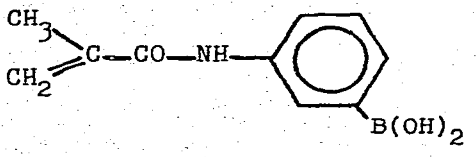
(2, 3, or 7-position of 69, 2, 3, or 4-position of 70) have been synthesized (79). It is interesting to note that methylation of the borazaromatic ring causes a distinct decrease in the antibacterial activity. More complex effects are observed with substitution of either ring with nitro groups or, in particular, with chlorine.

Several neutral polyhedral boranes containing a variety of functional groups have been prepared and are being evaluated as possible agents for neutron capture therapy (218). In this context it may also be noted that a diazonium salt of 1-(4-aminophenyl)-1,2-dicarba-closo-dodecaborane(12) has been incorporated into anti-bovine serum in the continuing search for tumor-specific boron compounds (148).

Preparative separation of ribo- and deoxyribonucleic acid components can be accomplished by column chromatography of dihydroxyboryl-substituted polymers (244). The boron monomer, 71 can be radical polymerized and the resultant material was found to be an effective agent for the cited purpose.



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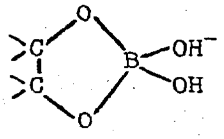
In studies concerning the reaction between sodium tetraphenylborate and alkaloids it was found that the ester function of ester-type alkaloids is readily hydrolized by the borate (208). Methylhomatropines and methyltropine were found to yield methyltropine tetraphenylborate quantitatively. Preliminary data indicate a substantial acceleration of ester hydrolysis by the sodium tetraphenylborate. Also, sodium tetraphenylborate has been utilized for the dissociation of hepatic cells (74) but it has been shown that cells thus treated show metabolic and ultrastructural alterations (75,76). The exposure of intact human erythrocytes to sodium tetraphenylborate results in inactivation of acetylcholinesterase (77). In contrast to other desactivation agents, sodium tetraphenylborate affects the activity of cytoplasmic enzymes of whole erythrocytes indicating that the reagent traverses biological membranes (73).

Thermal isomerization of steroidboranes has been studied (187, 222) and the mass spectra of some corticosteroid boronates give evidence for characteristic fragmentation which is virtually not affected by the boron substituent (49).

The diffusion of organoboron species into cerebrospinal fluid has been studied on pregnant rats (85) and an article on the toxicity of boron trifluoride may be of interest (194). Also, toxicological studies on borax and boric acid have been reported (254).

The electrophilic mobilities of various polyols such as aldoses, ketoses, glycosides, <u>etc.</u> in diphenylborate at pH 10 closely parallel those obtained in borate (273). The Raman spectra of aqueous solutions containing $B(OH)_4^-$ and various polyols have been studied (61). The experimental data were interpreted by assuming chelate formation as indicated in 72, and the observation of a boron-oxygen ring stretching seems to be a reliable way to establish the ring size of such chelates.



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