BORON

ANNUAL SURVEY COVERING THE YEAR 1971
PART II

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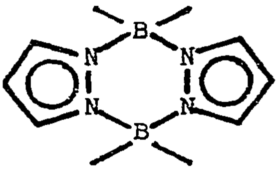
Contents

Reviews and Summaries

The chemistry of pyrazoboles, 1, and of the pyrazolylborates, $R_{2-n}B(pz)_{n+2}^{-1}$ (pz = 1-pyrazolyl) and, in particular, the unique role of the latter as ligands in organometallic chemistry has been reviewed by Trofimenko (1). Publications on

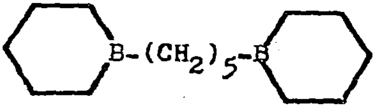


1

cationic boron complexes are compiled in an article (3) listing 189 references; it covers published work through the middle of 1969 thus demonstrating the rapid development of this area since Parry and his coworkers (4) elucidated the structure of the diammoniate of diborane. Atkinson and Currell (2) discuss in detail various aspects of polymers having a backbone of boron-nitrogen units. The polymer chemistry of boron cluster compounds has been summarized by Schroeder (5). Reviews on oxidation reactions with peroxytrifluoroacetic acid-boron trifluoride (6) and diene syntheses via boronate fragmentation (7) appear to be of interest to the organic chemist.

Triorganoboranes and Organohydridoboranes

Hydroboration of 1,4-pentadiene followed by isomerization for three hours at 170° is a convenient way to synthesize 1,5-bis(1-borinyl)pentane, 2. Interaction of the latter with diborane gives the bisborinane 3, which can be used very effectively for the hydroboration of various olefins to provide B-alkylborinanes in excellent yield (17).



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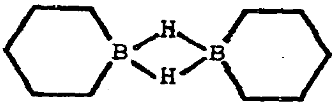

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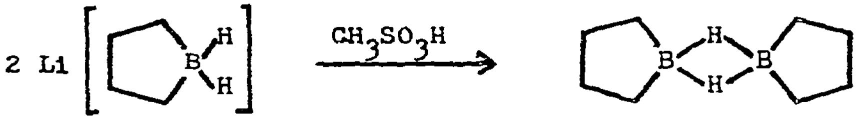
Similarly, hydroboration of 2,4-dimethyl-1,4-pentadiene yields bis(3,5-dimethyl)borinane; bis(3,5-dimethyl)borepane was also prepared in a similar manner (18). Both compounds can be utilized in reactions analogous to that of bisborinane for the hydroboration of olefins and are particularly advantageous in those reactions where the avoidance of disproportionation is desired. The basic bisborolane 4 is obtained by reacting lithium tetramethylenedihydridoborate with methanesulfonic acid as illustrated in the following scheme (191).



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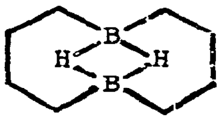
In the absence of trapping agents, bisborolane rapidly converts to 1,6-diboracyclodecane, 5, and a polymeric species.



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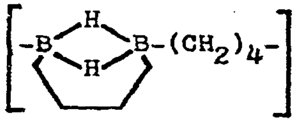
The hydroboration reaction of a 1:1 molar ratio of 1,3-butadiene and borane in tetrahydrofuran gives a polymeric material wherein the repeating unit is largely pseudocyclic 1,2-tetramethylenediborane, 6 (83). If the ratio of reactants is 3:4 or smaller,



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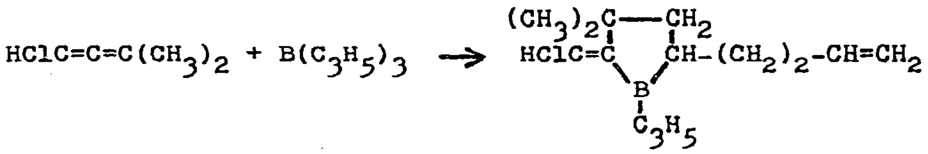
bis(1,2-tetramethylenediboryl)butanes are obtained as the primary product. These results have been considered in terms of sequential reactions and it was noted that, in the absence of a stabilizing double-hydrogen bridge, the borolane-containing structures are more stable than their open chain analogs.

The novel borolane derivative 7 was obtained from the reaction of triallylborane with 1-chloro-3-methyl-1,2-butadiene as shown in the following equation (44):



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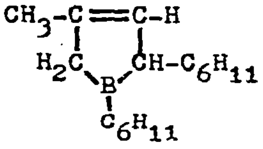
In somewhat similar manner dicyclohexyl-3-methyl-trans-1,3-butadienylborane, $(C_6H_{11})_2B\text{-}CH{=}CH\text{-}CCH_3{=}CH_2$, undergoes a cyclization upon ultraviolet irradiation to form the boracyclopent-3-ene derivative 8 (45).



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Several allylboranes have been prepared by monohydroboration of dienes such as 1,2-octadiene or phenylpropadiene (199). On protonolysis of these allylboranes allylic rearrangements were observed as is illustrated by the following scheme.

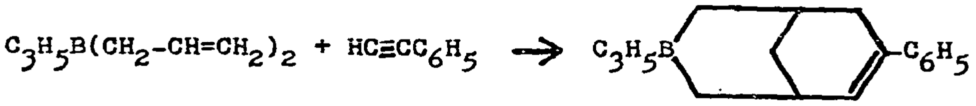
$$>C=C=CH_2 \xrightarrow{R_2BH} >C=CH-CH_2-BR_2 \xrightarrow{H^+} >CH-CH=CH_2$$

Addition of allylboranes to monosubstituted acetylene and followed by protonolysis has been found to be a general method for the synthesis of 1,4-substituted pentadienes (46). The initial reaction occurs at room temperature or below according to the following equation:

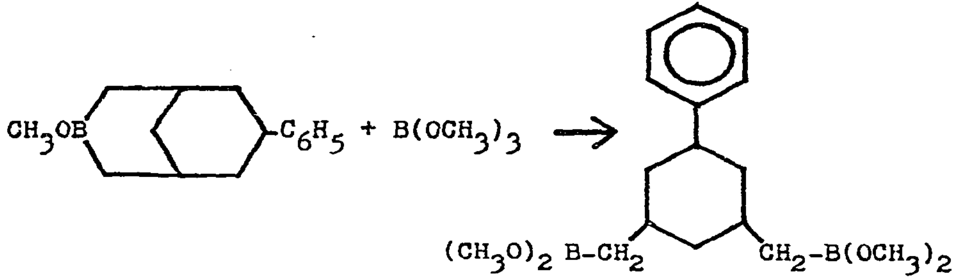
$$B(C_3H_5)_3 + RC{\equiv}CH \longrightarrow (C_3H_5)_2B-CH=CR-CH_2-CH=CH_2$$

However, all three boron-bonded allyl groups can react in the same manner and subsequent action of H^+ cleaves the $B-C_{vinyl}$ bond. The terminal carbon-carbón double bond of the boron-containing intermediate is readily hydrogenated and this reaction proceeds particularly well when alkoxyacetylenes are used; alkylacetylenes react much slower and, in this case, only one of the allyl groups of the triallylborane reacts in the indicated manner.

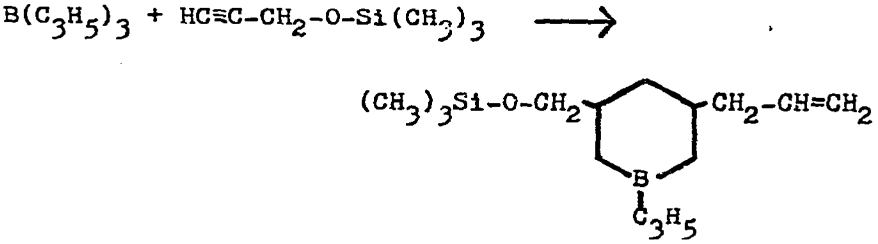
Triallylborane reacts with phenylacetylene at room temperature in an exothermic reaction under formation of a bicyclic system (203). The reaction is analogous to that of triallylborane with acetylene and alkylacetylenes and can be summarized by the following equation:



The bicyclic system is the product of a thermal transformation of materials initially formed on reaction of triallylborane with phenylacetylene. Proton magnetic resonance data indicate the initial formation of chain-type species such as $CH_2=CH-CH_2-CC_6H_5=CH-B(CH_2-CH=CH_2)_2$ and of a monocyclic intermediate. Cleavage of the boron-containing ring of the bicyclic system may be accomplished with trimethoxyborane as illustrated in the following equation:

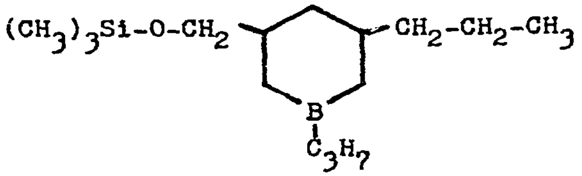


2-Propynyloxytrimethylsilane also reacts with triallylborane (211). However, even at room temperature, a monocyclic system is formed directly as depicted in the following scheme.

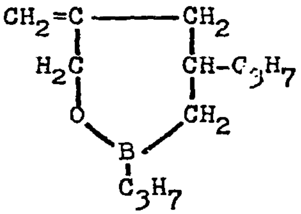


This monocyclic product cannot be isolated in pure state and converts on heating to a bicyclic compound. This reaction is analogous to that of other 3-substituted 1,5-dialkylboracyclohex-2-enes.

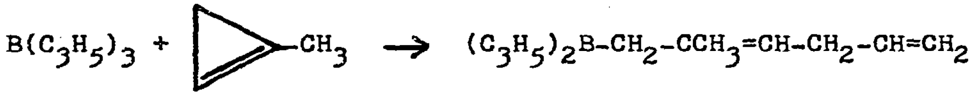
Hydrogenation of the monocyclic compound yields



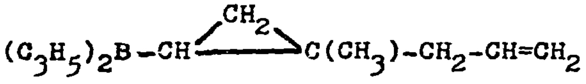
with retention of the B-vinyl bond. Heating this last compound with methyl alcohol provides 6-methylene-2,4-dipropyl-1,2-oxaborepane, a novel heterocyclic system.



Triallylborane reacts with 1-methylcyclopropene by two different reaction paths (155): Either cleavage of the C^2-C^3 bond of the cyclopropene ring occurs with addition of the triallylborane fragments as is illustrated in the following equation,



or these same triallylborane fragments may add in the cis configuration across the annular double bond to yield 9.



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In the presence of excess cyclopropene all three boron-carbon bonds of the triallylborane can participate in the reaction.

In the preparation of trialkylboranes by interaction of boron trifluoride-etherate with the appropriate alkylmagnesium halide, RMgX (R = n-, s-, or i-C_4H_9), no isomerization of the alkyl groups occurs (8).

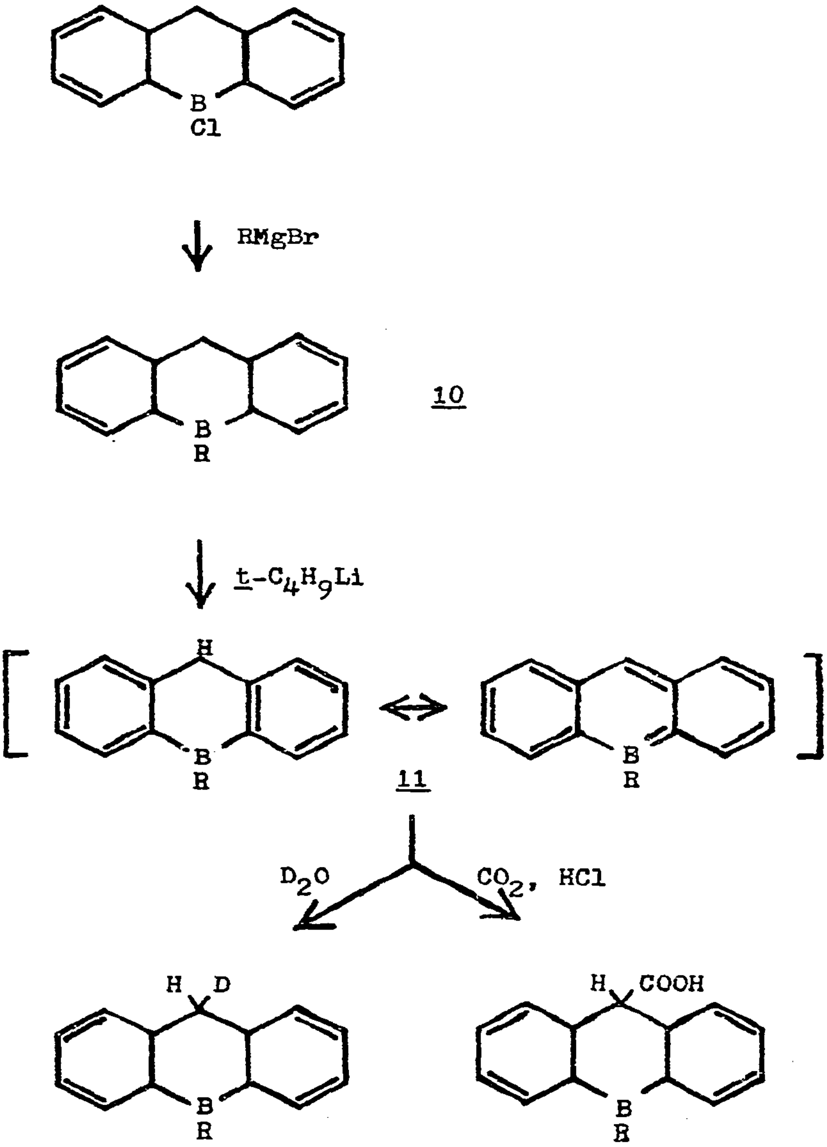
Cyclopentadienyl-diethylborane is obtained as an adduct with either pyridine or triethylamine when the corresponding amine adduct of diethylchloroborane is reacted with sodium cyclopentadienide in ether (19). Treatment of the resultant adduct with boron trifluoride-etherate provides the non-coordinated triorganoborane, the dienyl group of which can undergo Diels-Alder reactions at room temperature.

Methylene dilithium reacts with boranes, BR_3 [R = Cl, Br, CH_3, OCH_3, $N(CH_3)_2$] or RBR'_2 [R = CH_3, $N(CH_3)_2$; R' = Cl, Br], to yield a bisborylmethane intermediate, $H_2C(BR_2)_2$. In the case of R = $N(CH_3)_2$ small amounts of the intermediate could be isolated but, in general, it quickly rearranges to BR_3 and $(-CH_2-BR-)_n$ polymers (9).

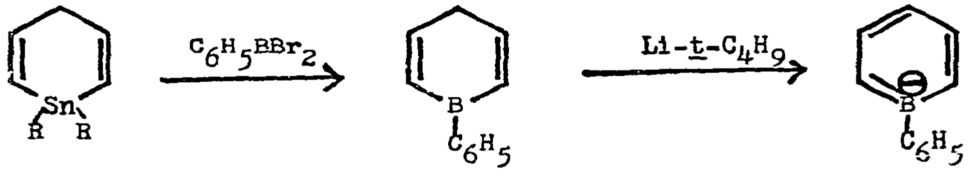
Aluminum trimethoxide forms relatively stable adducts with dialkylboranes of the type $(CH_3O)_3Al\cdot BR_2H$ (48). Reaction of such compounds with olefins has been used to prepare mixed organoboranes containing functional substituents. These adducts can also be used to synthesize pyridine-dialkylboranes and free dialkylboranes.

In the monohydroboration of terminal alkynes with dicyclohexylborane or 2,3-dimethyl-2-butylborane, the boron atom appears almost exclusively at the terminal position of the original triple bond (82).

9-Chloro-9,10-dihydro-9-boraanthracene reacts with mesitylmagnesium bromide to yield the corresponding 9-mesityl derivative 10 (10). If the latter is treated with t-butyllithium a deep red colored solution is obtained which may contain the anthracene-type chromophoric organoboron species 11. This intermediate which has not yet been isolated can react with D_2O or CO_2 as is illustrated in the reaction sequence outlined below:



Similarly, the 1-phenylborabenzene anion, 12, has been prepared by the interaction of 1,4-dihydro-1,1-dibutylstannobenzene with dibromphenylborane, $C_6H_5BBr_2$, and subsequent deprotonation of the 1-phenyl-1,4-dihydroborabenzene with t-butyllithium as illustrated in the following reaction sequence (11).



12

Trialkylboranes undergo a ligand exchange reaction with tris(aryloxy)boranes as illustrated in the following equation (13).

$$2\ BR_3 + B(OAr)_3 \longrightarrow 3\ R_2BOAr$$

The reaction is catalyzed by BH_3 and has been used to synthesize a variety of dialkylboronic acids (dialkylhydroxyboranes) and their esters (13). Reduction of aryloxydialkylboranes with lithium aluminum hydride in tetrahydrofuran provides dialkylboranes, R_2BH, in high yield and purity (14). Hence, when this method is used dialkylboranes are directly and simply available. Monoalkylboranes can be obtained by hydroboration of olefins with catecholboranes (15). This latter reaction provides B-alkylcatecholboranes; they, in turn, can be reduced with lithium aluminum hydride to give the monoalkylboranes in nearly quantitative yield (16).

It is worth noting that the gas phase reaction of borane with ethylene to yield ethylborane, $C_2H_5BH_2$, was studied by Fehlner (190) and several aspects of the hydroboration were discussed.

Trialkylboranes react with lithium or sodium tetrahydridoborate to form addition products according to the following equation (40, 210):

$$BR_3 + MBH_4 \rightleftharpoons M(H_3B\text{-}H\text{-}BR_3)$$

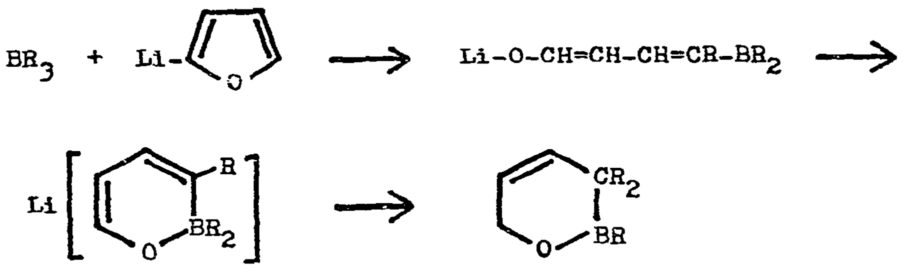
The structure of the resultant adduct was determined by nuclear magnetic resonance studies and the equilibrium reaction was found to be selvent dependant. Also, lower temperatures favor the formation of the trialkyltetrahydridodiborate (210).

Methyl radicals react in the gas phase with triethylborane in a homolytic substitution at boron (70). In the triplet state, ketones will react with trialkylboranes in a bimolecular homolytic substitution to give the radicals $R_2COBR'_2\cdot$ and $R'\cdot$ with the latter originating from the trialkylborane (42, 238). Trialkylboranes react with diazoketones or with methyl vinyl ketone to yield vinyloxyboranes, $R'CH{=}CR''\text{-}O\text{-}BR_2$ (26).

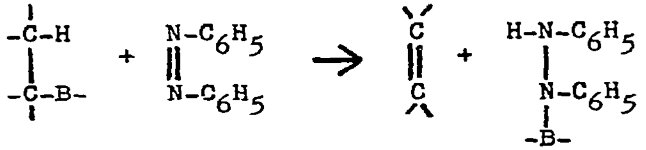
Tri-*n*-butylborane reacts with chlorodifluoromethane (with alkoxide induction) to give trialkylcarbinols (35). This reaction is similar to the "carbonylation-oxidation" developed by Brown and coworkers (73). Trialkylboranes will react with copper(II) bromide in the presence of water by conversion of a single alkyl group of the borane into the corresponding alkyl bromide (43).

The protonolysis of organoboranes has been studied by reacting trialkylboranes with propinoic acid (34). Little selectivity was observed in the removal of primary or secondary alkyl groups; however, trialkylboranes containing tertiary alkyl groups were found to react much slower apparently due to steric effects only.

The reaction of triorganoboranes with α-lithium furan was found to yield 1,2-boroxarocyclohex-4-enes as illustrated below (194).

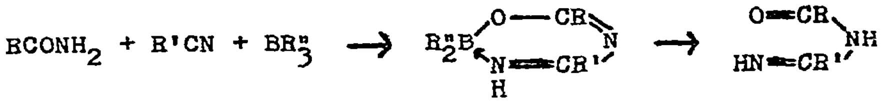


Trialkylboranes react with 2-methyl-2-nitrosopropane or *cis*-azobenzene even under mild conditions (at room temperature) with the elimination of one olefin group (152). The reaction is thought to occur *via* a cyclic transition state as indicated for the case of azobenzene by the following scheme.



The olefin and the hydroborated product are obtained in essentially quantitative yield.

Nitriles react with primary amides and trialkylboranes in tetrahydrofuran to give intermediates, 13, which can be decomposed in a manner such that the overall reaction provides a synthesis of N-acylamidines (33).



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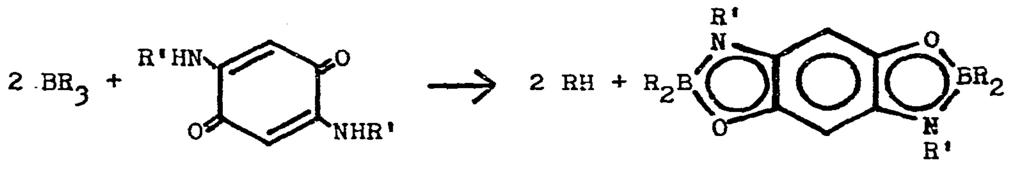
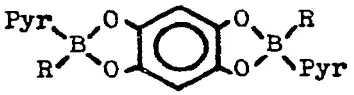
The reaction of trialkylboranes with 2,5-bis(ethylamino)-1,4-benzoquinone in refluxing xylene proceeds with the generation of alkane in accordance with the following equation (41):



Other 2,5-bis(alkylamino)-1,4-benzoquinones react in like manner; the substitution of a borylsulfonate, R_2BO_3SAr, (in the presence of sodium hydride) for the trialkylborane increases the yield substantially. 2,5-Dihydroxy-1,4,benzoquinones will also undergo the same basic reaction and the resultant materials can be stabilized as pyridine adducts, 14. The reaction of trialkylboranes with 1,4-naphthochinone in the presence of small amounts of oxygen yields (after hydrolysis of the intermediates) 2-alkyl-1,4-naphthalenediols (188).



14

Organoboranes derived from terminal olefins via hydroboration react rapidly and quantitatively with mercuric acetate in tetrahydrofuran (at room temperature) to yield alkylmercury(II) acetate as illustrated in the following sequence (12).

$$3\ RCH{=}CH_2 + BH_3 \rightarrow (RCH_2\text{-}CH_2)_3B \xrightarrow{3\ Hg(OAc)_2} B(OAc)_3 + 3\ RCH_2\text{-}CH_2\text{-}Hg\text{-}OAc$$

This reaction provides a new route for synthesizing organomercury derivatives. The mercuration of organoboranes containing secondary alkyl groups requires higher temperatures and several hours of reaction time. Moreover, not more than two of the three secondary alkyl groups will react in this latter case (32).

$$BR_3 + 2\ Hg(OAc)_2 \xrightarrow[heat]{THF} RB(OAc)_2 + 2\ RHgOAc$$

Organoboranes containing very bulky alkyl groups exhibit exceedingly slow rates of reaction and simultaneous decomposition of the resultant organomercurials limits the synthetic utility of the cited reaction. Arylmercury halides react with diborane in tetrahydrofuran to give intermediate organoboranes which can be oxidized with alkaline hydrogen peroxide to produce high yields of phenols (158). The intermediates were not isolated but are thought to be arylboranes.

The cleavage of the boron-carbon bond in 2-alkoxy-1,4-pentadienylboranes, $R_nB(CH=COR'-CH_2-CH=CH_2)_{3-n}$, by alcohols has been investigated and was discussed in terms of:

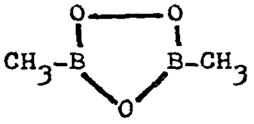
(a) attack of the free electron pair of oxygen of the alcohol at the $B-C_{vinyl}$ bond, and

(b) initial addition of alcohol at the vinylether C=C bond.

The experimental observations seem to support the former reaction path (48).

The reaction of organoboranes with oxygen under very mild condtions can be controlled to give an essentially quantitative conversion of all three boron-bonded alkyl groups to the corresponding alcohol (20); elemental iodine acts as exceptionally favorable inhibitor for the reaction of oxygen with trialkylboranes (22).

The reaction of trimethylborane with oxygen in the gas phase at 125° produces small amounts of an intermediate of the composition $(CH_3)_2B_2O_3$ as evidenced by mass spectroscopy (21). Though the material could not be isolated, a cyclic structure, 15 was suggested for the compound based on some infrared data including the tentative assignment of ring stretching modes at 1360 and 1167 cm^{-1} respectively. An antisymmetrical B-C stretch was assigned to a band observed at 928 cm^{-1}.

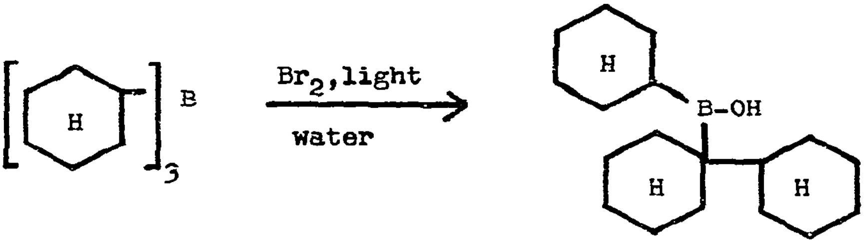


15

Trialkylboranes readily undergo an oxygen-induced reaction with organic iodides to produce the corresponding alkyl iodides (23). Moreover, benzylic and allylic iodides may readily be coupled under mild conditions via the air-induced abstraction of iodine using triethylborane as the reagent.

Irradiation of a mixture of triethylborane and iodine in cyclohexane leads to ethyl iodide as the only isolable product (24) and the thermal iodination of triethylborane in cyclohexane solution in the 100-140° temperature range (151) was also found to follow a free radical mechanism. When an excess of triethylborane was used in this reaction only ethyl iodide and diethyliodoborane were obtained.

Trialkylboranes react with bromine in the presence of light to produce α-bromo-organoboranes with the elimination of hydrogen bromide (25). If water is present in the reaction mixture, a facile rearrangement of alkyl groups from boron to carbon occurs. This procedure, therefore, constitutes a simple method for joining two or three alkyl groups to produce highly substituted alcohols as illustrated by the following scheme.



The photoelectron spectrum of trivinylborane has been recorded and was compared with that of triethylborane (77). The first ionization potentials of both compounds are close together with values of 9.6 and 9.7 eV respectively and the band is a broad envelope. Each compound exhibits similarities in its spectrum to that of ethylene and ethane respectively. On that basis it was concluded that the first bands represent ionization from essentially a boron-carbon sigma bond and that there is but little conjugation effect evidenced through the boron in trivinylborane.

The gas phase Raman spectrum of trimethylborane has been recorded and the observed data are consistent with those expected for a molecule with D_{3h} symmetry (76). The mass spectrum of trimethylborane at low source temperature (20-35°)

shows the absence of any associated species (162). The $(CH_3)_2B^+$ ion was found to be abundant; the amount observed increases slightly with the source temperature; no metastable peaks indicating ethane elimination from the cited ion were observed.

The Raman spectra of monomethyldiborane(6) and trimethyldiborane(6) were recorded at -70^o and at room temperature and an assignment for the fundamentals of the molecules has been suggested (71). In a discussion of the experimental data it was noted that the symmetric methyl deformation of these compounds appears to be considerably influenced by the attached atom and its hybridization.

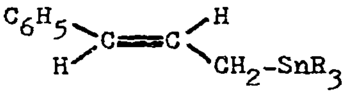
An indirect measurement of the ^{11}B-H coupling constants in organoboron compounds has been proposed (69). The method is based on the determination of line broadening in ^1H and ^{11}B spectra resulting from the ^{11}B quadrupole relaxation. The method was investigated using trimethoxyborane, alkoxyvinylboranes, and triallyl complexes with amines. In a first study on ^{11}B-^{13}C coupling constants of boron nuclei in a nonsymmetrical environment the ^{11}B-^{13}C coupling constant of 1-methylpentaborane(9) was found to be 72.6 Hz (192).

Based on ^1H nuclear magnetic resonance data, the existence of cis and trans isomers in tricrotylborane, $B(CH_2\text{-}CH{=}CH\text{-}CH_3)_3$, has been demonstrated (68). These species have been shown to isomerize via an allylic rearrangement.

Finally, it should be noted that the graft copolymerization of methyl methacrylate with hemoglobin can be initiated by trialkylboranes (160).

Organoboron Halides

The preparation of ethylhaloboranes by the interaction of triethylaluminum with boron trihalides has been studied in detail (36). The high alkylating power of triethylaluminum promotes transfer of all three organic groups from aluminum to boron even at ambient temperature. Furthermore, the reaction can be made to yield either R_2BX or RBX_2. The power of the organic aluminum derivatives to alkylate decreases in the series $BF_3 > BCl_3 > BBr_3 > BI_3$ and the tendency to form BR_3 rather than organohaloboranes (even in the presence of excess BX_3) decreases in the order $BF_3 > BBr_3 > BI_3 > BCl_3$. Th alkylation of boron halides with AlR_3 is a stepwise process and is not suitable for the preparation of organofluoroboranes. However, this method provides an attractive alternative to the organotin process (37). In order to study the mechanism of the latter procedure, the reaction of <u>trans</u>-cinnamyl-triethyltin and triphenyltin, <u>16</u>, with boron tribromide has been studied (38).



$R = C_2H_5, C_6H_5$

<u>16</u>

The <u>trans</u>-cinnamyl group was preferentially transferred from the tetraorganotin to boron to yield the organodibromoborane and cyclic transition states were formulated. It is noteworthy that the carbon-carbon double bond of the <u>trans</u>-cinnamyldibromoborane is attacked by excess boron tribromide to yield 1-phenyl-2-bromo-1,3-bis(dibromoboryl)propane.

Interaction of tetrachlorodiborane(4), B_2Cl_4, with cyclohexene yields cis-1,2-bis(dichloroboryl)cyclohexane (178). On treatment of the latter with antimony trifluoride, the corresponding fluorine derivative is obtained and reaction with boron tribromide results in the displacement of chlorine by bromine. Also, interaction between this same compound and lithium tetrahydridoborate yields cis-1,2-bis(dihydridoboryl)cyclohexane. Reacting either compound with dimethyl ether provides 1:1 adducts, but the fluorine and chlorine derivatives also form 1:2 adducts with the same ether. Quantitative displacement of ether can be effected with trimethylamine.

Several cyclicolefins were reacted with tetrachlorodiborane(4) affording the cis addition product in all cases (179). Tetrachlorodiborane(4) reacts with fluoroethylenes to yield chloroolefins and fluorinated diborane(4) derivatives or halovinylboron halides as the principal products (180). When tetrachlorodiborane(4) and vinyl chloride react in a 2:1 molar ratio, 1,1,2-tris(dichloroboryl)ethane is obtained along with boron trichloride. Both B_2Cl_4 and B_2F_4 react similarly with haloethylenes that contain a halogen heavier than that in the diborane(4) species. The reaction probably proceeds by the initial addition of B_2X_4 to the haloolefin, elimination of BX_3, and further addition of the tetrahalodiborane(4) to the resulting vinyldihaloborane (181).

Reacting trivinylborane with tetrachlorodiborane(4) gives a 1:1 product, $(CH_2{=}CH)_2B\text{-}CHBCl_2\text{-}CH_2\text{-}BCl_2$ (182). The latter reacts with BX_3 [$X = Cl, N(CH_3)_2$] to form a triborylalkane, $X_2B\text{-}CHBCl_2\text{-}CH_2\text{-}BCl_2$. Pyrolysis of $(CH_2{=}CH)_2B\text{-}CHBCl_2\text{-}$

CH_2-BCl_2 yields 1,2-bis(dichloroboryl)ethylene, but in the presence of methylamine the pyrolysis led to trimethylamine-divinylborane. Interaction between trivinylborane and tetrachlorodiborane(4) in a 1:2 molar ratio affords the unstable (above -78°) $CH_2{=}CH\text{-}B(\text{-}CHBCl_2\text{-}CH_2\text{-}BCl_2)_2$; no 1:3 reaction product was observed.

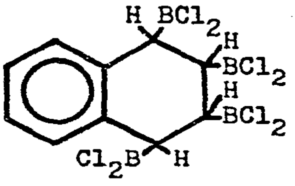
Tetrachlorodiborane(4) and dimethylmercury interact according to the following equation (183):

$$B_2Cl_4 + Hg(CH_3)_2 \longrightarrow B_2Cl_3CH_3 + ClHgCH_3$$

However, this reaction is potentially hazardous and explosions can occur during the preparation.

In view of the use of tetrachlorodiborane(4) as reagent in organoboron chemistry, it should be noted that the vibrational spectrum of isotopically labeled B_2Cl_4 has been recorded and revised assignments for some of the fundamental vibrations of the molecule have been suggested (78). From these spectroscopic data, a series of valence force constants was calculated for the molecule. The force constant of the boron-boron bond of 3.4 mdyn/Å is very close to that of a B_2 molecule (3.58 mdyn/Å) and is considerably greater than that found in polyhedral boron hydride ions.

1,2,3,4-Tetrakis(dichloroboryl)-1,2,3,4-tetrahydronaphthalene, 17, reacts with trimethylamine or triethylamine to form stable 1:3 complexes (184). Other bases, however, produced unstable 1:2 adducts with 17.



17

The reaction of some substituted aromatic amines with phenyldichloroborane in boiling benzene did not produce the expected borazine derivatives (89). Only between one and two of the theoretical number of moles of hydrogen chloride evolve. The interaction between phenyldichloroborane and dimethylaniline appears to proceed by substitution of boron in the arylamine ring.

The barrier to internal rotation in CD_3BF_2 has been calculated (174) and the high-resolution photoelectron spectra of the boron trihalides have been reported (161); they were interpreted on the basis of band splitting, fine structure, and their correlation with theoretical data. From the orbital energies it was deduced that the molecular stabilization energy follows the sequence $BF_3 > BCl_3 > BBr_3 \gtrsim BI_3$ which still appears to be consistent with the opposite sequence of π-electron delocalization.

The asymmetry parameters of the ^{35}Cl nuclear quadrupole resonance spectra of boron trichloride and phenyldichloroborane have been measured on polycrystalline samples of the compounds (185). The value of 0.54 ± 0.02 for boron trichloride is consistent with recent molecular orbital calculations on boron trihalides and a boron-halogen π-bond order of $BI_3 >$

$BBr_3 \approx BCl_3$. This work was extended further to a survey of the ^{35}Cl nuclear quadrupole frequencies of a variety of organoboron chlorides and adducts of boron trichloride (186). The data were discussed in terms of π-character and charge distribution in the boron-chlorine bond.

Mass spectrometric data indicate that the boron-fluorine bond dissociation energy is reduced if boron trifluoride is coordinated with diethyl ether (201).

Acids, Esters, and Sulfur Derivatives

A variety of dialkylboronic acids (*i.e.*, dialkylhydroxyboranes) and their esters have been prepared by a ligand exchange reaction between trialkylboranes and tris(aryloxy)-boranes (13).

$$2\ BR_3 + B(OAr)_3 \longrightarrow 3\ R_2BOAr$$

Dialkylvinyloxyboranes, $R_2B{-}O{-}CR'{=}CHR''$, are formed by the reaction of trialkylboranes with diazoketones or by radical addition of trialkylboranes to methyl vinyl ketone (26).

Hexafluoroacetone and other polyfluorinated ketones react with boron halides, organoboron halides, or alkylthioboranes to form perhalogenated organooxyboranes and related materials (163) as illustrated in the following equation:

$$>B{-}X + OC(CF_3)_2 \longrightarrow\ >B{-}O{-}C(CF_3)_2X$$

$$X = Cl,\ Br,\ I,\ SCH_3$$

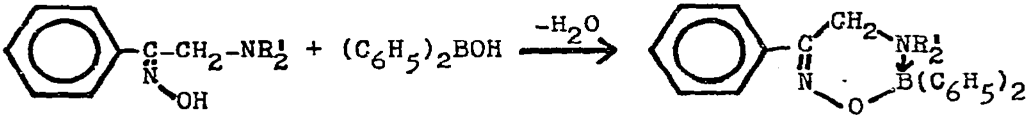
All three B-X bonds of boron trihalides are reactive in such a reaction. It should be noted that the unsymmetrical perhaloketone $CF_2Cl-CO-CFCl_2$ reacts with boron trichloride metathetically to afford boron trifluoride as the only boron-containing product. Hence, it is not surprising that boron trifluoride cannot be utilized in a reaction according to the preceding equation.

Various monofunctional boranes combine with acid anhydrides as depicted in the following equation (120):

$$R_2B-X + (R'CO)_2O \longrightarrow R_2B-O-CO-R' + R'COX$$

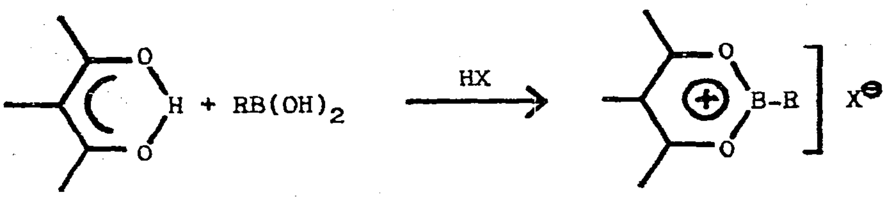
$$X = SR,\ NHR,\ NR_2$$

The reaction of some _Z_- and _E_-oximes with diphenylhydroxyborane (diphenylborinic acid) has been studied (29); it was found to give crystalline materials. The respective derivatives of the _Z_-oximes are reported to have the structure of the (ω-aminoacetophenone)oximato-diphenylboron complex depicted in the following scheme.



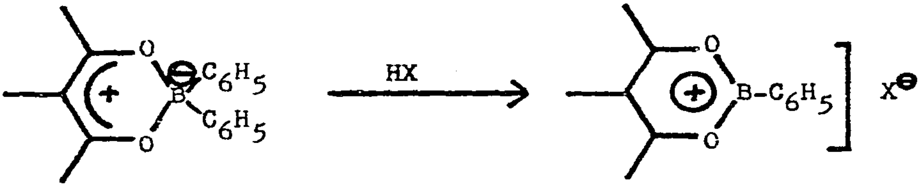
Phenylborates have also been used in carbohydrate synthesis; _e.g._, the halogenation of _D_-glucose phenylborate was studied and pointed the way to a synthesis of halo-desoxysugars (170).

The reaction of 1,3-diketones with dihydroxyphenylborane, $C_6H_5B(OH)_2$, in the presence of strong acids leads to the formation of 1,3,2-dioxaboronium salts, _18_ (213).



18

The same compounds can be prepared by photodeboronation of 1,3-diketonates of diphenylhydroxyborane.



The reaction between β-aminoethoxydiphenylborane and bis(1,3-diketones) such as 1,1,2,2-tetraacetylethane yields bichelated complexes of the following type 19 (214).

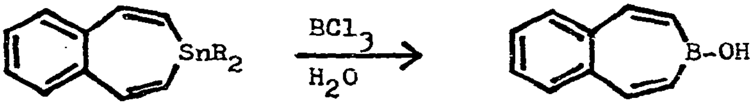
These dichelates exhibit fairly high thermal and hydrolytic stability.

A variety of dibutoxyboranes of the type

$$Y(CH_2)_n\text{-}B(OC_4H_9)_2$$

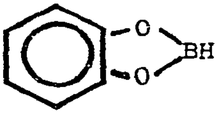
$$n = 3\text{-}6;\ Y = Cl,\ Br,\ I,\ OH,\ CN,\ N(C_2H_5)_2,\ COCH_3$$

have been prepared by conventional organometallic synthesis (28). Also, 1,1-di-n-butyl-3-benzostannepin was found to react with boron trichloride by exchange of the tin with boron (39). Subsequent hydrolysis of the product leads to the isolation of 3(3H)-benzoborepin-3-ol, 20.



20

A very convenient synthesis of alkyldihydroxyboranes results from the fact that 1,3,2-benzodioxaborole, 21, is



21

readily prepared from catechol and BH_3 (27). The dioxaborole reacts with olefins at 100° affording B-alkylation; subsequent hydrolysis leads to $RB(OH)_2$.

As noted above, 2,5-dihydroxy-1,4-benzoquinone reacts with trialkylboranes to form boron-oxygen bonds (41); the resultant materials can be isolated as pyridine adducts, 14.

Perfluoroalkoxyboranes can be prepared by reacting perfluoroalkyl hypochlorites with boron trichloride through oxidative displacement of chlorine from boron (30, 187).

$$3\ R_fOCl + BCl_3 \longrightarrow (R_fO)_3B + Cl_2$$

In the case of $R_f = CF_3$ or i-C_3F_7, a facile α-fluorine shift is observed to vacant boron p-orbitals; decomposition of the compounds leads to boron trifluoride and certain carbonyl derivatives as final products.

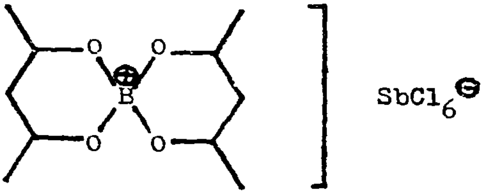
$$(\underline{i}\text{-}C_3F_7O)_3B \longrightarrow BF_3 + 3\ (CF_3)_2CO$$

If $R_f = \underline{t}\text{-}C_4F_9$, the perfluoroalkoxyborane is thermally fairly stable although the compound hydrolyzes readily; all of the perfluoroalkoxyboranes appear to be strong boron Lewis acids.

The crystal structure of triethanolamine borate, $N(CH_2CH_2O)_3B$, was examined by X-ray diffraction (168). The molecular structure was found to be of the triptych type suggested by Brown and Fletcher (169); it has a transannular boron-nitrogen bond length of 1.65 Å.

The limiting equivalent conductivity of the acid $HB(OOCCF_3)_4$ was measured and was found to be 22.34 $ohm^{-1}cm^2eq^{-1}$. Though the salt $CsB(OOCCF_3)_4$ is readily prepared the parent acid could not be isolated (217).

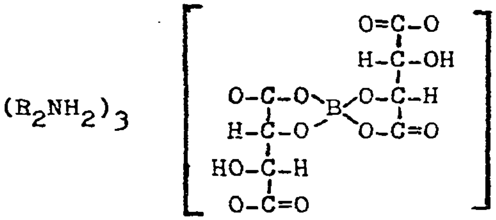
Action of chlorine in bis(1,3-diketonato)boronium hexachloroantimonates of acetylacetone or benzoylacetone, 22,



22

affords monochlorination of the diketone in the 2-position (213).

Aqueous solutions of 1:2 molar mixtures of boric and tartaric acid or boric and citric acid react with amines such as dihexylamine, diheptylamine, etc., to yield the corresponding crystalline boroditartrates (borodicitrates) (228). Infrared spectral data indicate that the boron atom is linked with the oxygen atoms of the hydroxy and carboxy groups of the organic acid as illustrated in 23.



23

Peroxyboron derivatives are exceedingly rare. However, dibutoxychloroborane was found to react with s-butyl peroxide yielding dibutoxy(s-butylperoxy)borane according to the following equation (31):

$$(RO)_2BCl + HOOR \longrightarrow (RO)_2B\text{-}O\text{-}O\text{-}R + HCl$$

Thermal decomposition of the compound in nonane solution follows first order kinetics. Peroxyboron derivatives such as dimethoxybutylperoxyborane, $(CH_3O)_2B\text{-}O\text{-}O\text{-}C_4H_9$, are thermally stable up to 120° (173,175) and tris(t-butylperoxy)borane was found to decompose rapidly in hydrocarbon solution at temperatures above 130° (171). The nature of the pyrolysis products and the kinetic features of the reaction seem to substantiate a free radical mechanism (206). The rate constants of spontaneous and induced decomposition of the cited peroxyboron derivative were found to be similar to those of normal organic peroxides such as benzene peroxide (171).

An organoboron peroxide with a cumyl group bonded to the peroxide oxygen was obtained from the reaction of di(n-butoxy)chloroborane with the sodium salt of cumyl hydroperoxide (172). This compound hydrolyzes readily in air and thermal decomposition in n-nonane solution also appears to proceed by a radical mechanism.

The effect of alkyl group structure and substitution on boron in radical reactions has been studied by reacting several alkoxyboranes with bromine (49). The results indicate that the radical reactivity of organoboron derivatives is a sensitive structural function of the organic functional group(s) bonded to the boron atom and the nature of the substituents bonded to boron and that of the attacking species. The preferred attack by an oxygen radical at boron is apparently controlled by the thermodynamics involved and the preferred attack by bromine at the hydrogen atoms of the organic group(s) appears to be a reflection of the low energy content of the boron-bromine bond.

A number of phenylboron derivatives such as

$$C_6H_5B(OC_2H_5)_2$$
$$C_6H_5B(OC_4H_9)_2$$
$$C_6H_5B(N(CH_3)_2)_2$$
$$C_6H_5B(NCH_3\text{-}CH_2\text{-})_2$$

were found to exhibit prominent peaks in their mass spectra which were assigned to the tropylium ion, $C_7H_7^+$ (193). In contrast, bis(dimethylamino)phenylmethylaminoborane, $[(CH_3)_2N]_2B\text{-}NCH_3\text{-}C_6H_5$, does not form this ion on electron impact.

Aromatic o-dithiols react with boron trichloride to form 2-chloro-1,3,2-benzodithiaborolanes (146). On treatment of the latter with 2,2'-bipyridine, the corresponding boronium chloride salts were obtained; these can be reduced to give the neutral spiro compounds.

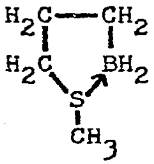
The preparation of a variety of thiodimethylboranes, $R\text{-}S\text{-}B(CH_3)_2$, with $R = H$, CH_3, C_6H_5, $B(CH_3)_2$, $Sn(CH_3)_3$, $P(C_6H_5)_2$, $As(CH_3)_2$, or $Mn(CO)_4$, has been described (144). The general Lewis acidity of the thiodimethylboranes is illustrated by their proclivity to form adducts with Lewis bases, but no sulfonium salts were obtained. The strong Lewis acidity of the sulfur atom in $(CH_3)_2B\text{-}S\text{-}B(CH_3)_2$ and $(CH_3)_3Sn\text{-}S\text{-}B(CH_3)_2$ leads to slow decomposition of the compounds. The vibrational spectra of some thiodimethylboranes, $RSB(CH_3)_2$ ($R = CH_3$, C_6H_5, $B(CH_3)_2$) and of some related materials have been studied (142). On the basis of force constant calculations, no π-bonding appears to occur between boron and sulfur in these compounds.

The equilibrium

$$>B\text{-}S\text{-}R' \quad + \quad HNR_2 \quad \rightleftharpoons \quad >B\text{-}NR_2 \quad + \quad R'SH$$

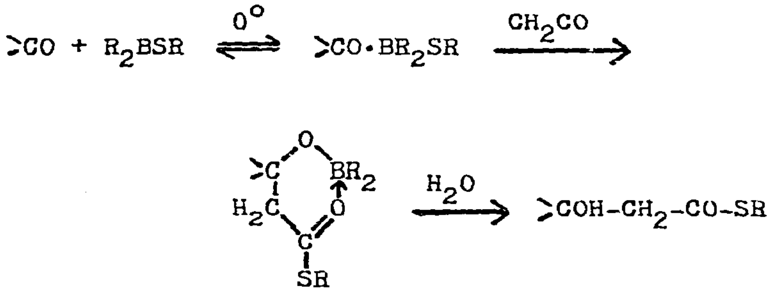
can be shifted in favor of the boron-nitrogen derivative (122). This observation has motivated the preparation of several hydrazinoboranes. Similarly, alkylthiodialkylboranes were found to react with acetamide with the formation of dimeric acetamidodialkylboranes, $(R_2B\text{-}NH\text{-}CO\text{-}CH_3)_2$, and release of an alkylthiol (127).

3-Methylthiopropylborane was obtained from the reaction of dimethyl sulfide-borane with allylmethyl sulfide (140). The compound is stable in the monomeric form and can be distilled without disproportionation. These observations seem to indicate backbonding from sulfur to boron as depicted in structure 24.

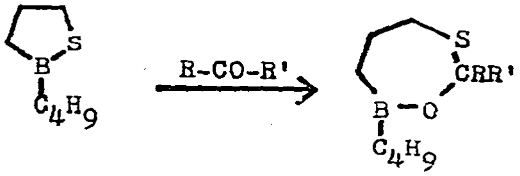


24

Alkylthiodialkylboranes react with carbonyl compounds and ketene according to the following scheme (205).



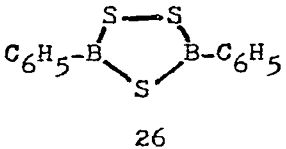
A new type of heterocyclic system, 1,3,4-thiaoxaborepane, 25, has been prepared by Mikhailov and coworkers (139). Addition of 2-*n*-butyl-1,2-thiaborolanes to aldehydes or ketones was found to proceed by addition of the borane to the carbonyl group resulting in the formation of this novel heterocyclic system.



25

The reaction proceeds best with aldehydes; in the case of ketones it may be reversed.

Phenyldihaloboranes react with sodium sulfide under formation of B-triphenylborothiin, $(-BC_6H_5-S-)_3$ (237); however, the reaction of phenyldihaloboranes with sodium disulfide yields the five-membered heterocycle 26.



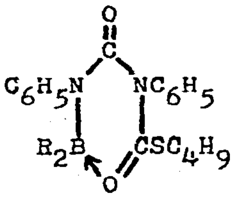
26

Several redox reactions of iodoboranes with bromine, sulfur, and dimethyl sulfoxide have been described to yield this same heterocycle 26 as well as bromoboranes, borothiins, and boroxines besides elemental iodine (236).

Tris(alkylthio)boranes and ethylisopropyl ketone react to form a thienol ether as illustrated below:

$$3\ C_2H_5\text{-CO-CH}(CH_3)_2 + 2\ B(SR)_3 \longrightarrow B_2O_3 + C_2H_5\text{-C}(SR)_2\text{-CH}(CH_3)_2$$

The driving force for the reaction is thought to be the high affinity of boron for oxygen (141). Tris(ethylthio)borane thioalkylates phenyl isocyante in refluxing benzene to yield N-ethylthiocarbonyl-N,N'-diphenylurea, $C_6H_5\text{-NH-CO-NC}_6H_5\text{-CO-SR}$ (147). However, (n-butylthio)di-n-butylborane gives a coordinated cyclic species by reaction with two molecules of the isocyanate. The resultant compound, 27, hydrolyzes readily by cleavage of the boron-nitrogen bond. Similar



27

reactions occur with phenyl isothiocyanate and dicyclohexylcarbodiimide, various nitriles, and diphenyl ketone.

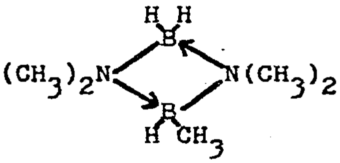
Hexamethyldisilselenane, $Se(Si(CH_3)_3)_2$, reacts with phenyldibromoborane to yield a novel heterocyclic system comprised of alternating boron and selenium atoms (230).

$$3\ RBBr_2 + 3\ Se(SiR'_3)_2 \longrightarrow (\text{-BR-Se-})_3 + 6\ R'_3SiBr$$

The heterocycle polymerizes irreversibly in benzene solution.

Boron-Nitrogen Compounds

The interaction of carbon vapor (from a carbon arc) with dimethylaminoborane yields dimethylaminomethylborane as an initial reaction product (133). The latter reacts with excess starting material to form the four-membered coordinated ring system 27. Other byproducts of this reaction are dimethylaminodimethylborane, dimethylamine-borane, and the



27

previously unknown diboryl oxide $(CH_3)_2N\text{-}BH\text{-}O\text{-}BH\text{-}N(CH_3)_2$.

$Na(CH_3)_2NBH_3$ reacts with BH_3 by two different reaction paths (134):

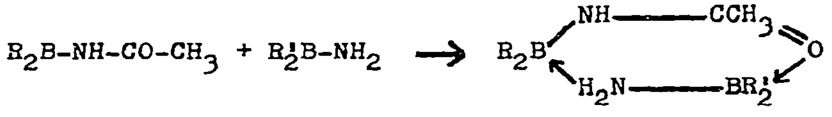
(a) Addition of a borane group according to the following equation:

$$Na(CH_3)_2NBH_3 + BH_3 \longrightarrow Na(CH_3)_2N(BH_3)_2$$

(b) Decomposition by a borane group probably <u>via</u> simple hydride transfer:

$$Na(CH_3)_2NBH_3 + BH_3 \longrightarrow (CH_3)_2N\text{-}BH_2 + NaBH_4.$$

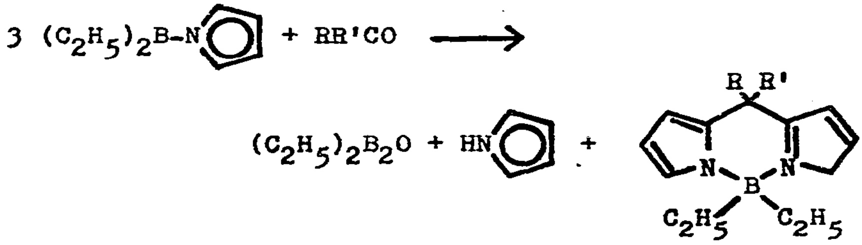
Dimeric acetamidodialkylboranes, $(R_2B\text{-}NH\text{-}CO\text{-}CH_3)_2$, have been synthesized by the reaction of alkylthiodialkylboranes with acetamide (127). Though they are normally dimeric, the acetamidodialkylboranes react as monomeric species. For example, with aminoboranes or 1,2-azaborolidines they react to yield coordinated heterocycles, <u>28</u>.



<u>28</u>

The structure of the latter was determined by nuclear magnetic resonance spectroscopy.

Diethyl-1-pyrrolylborane reacts with dialkyl ketones according to the following equation (129):



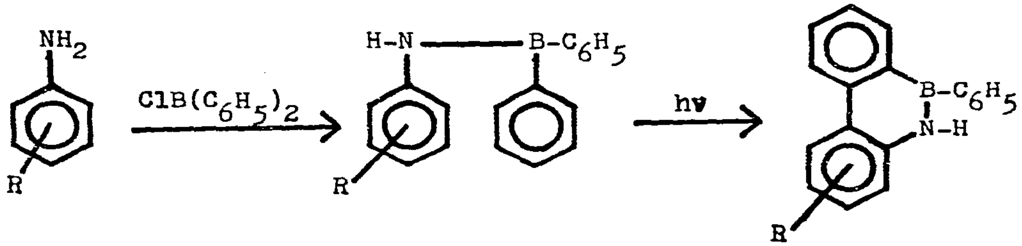
<u>29</u>

The indacene derivative 29 can also be obtained from triethylborane, pyrrole, and a ketone with the elimination of ethane. Compounds of type 29 are remarkably stable towards hydrolysis but can form ionic species either with base (anionic boron derivative) or acid (cationic boron species) and characteristic changes in the ultraviolet and proton magnetic resonance spectra accompany formation of the salts.

Tris(phenoxy)borane, $B(OC_6H_5)_3$, was found to react with aluminum and hydrogen and, in the presence of amines, to provide a novel synthesis of aminoboranes (130). In this reaction, the nature of the product is a function of the molar ratio of the borane to the amine. In diethylamine as solvent, tris(diethylamino)borane is obtained in 81% yield. Employing a ratio of one mole of tris(phenoxy)borane to two moles of amine, bis(diethylamino)borane is obtained in 80% yield. However, if the reaction is effected in a 1:1 molar ratio, diethylaminophenoxyborane, $(C_2H_5)_2N\text{-}BH\text{-}OC_6H_5$, and bis(phenoxy)diethylaminoborane, $(C_2H_5)_2N\text{-}B(OC_6H_5)_2$, are obtained in nearly equimolar quantities. This reaction was found to be insensitive to changes in reaction time or temperature. It should be noted that the reaction of aminoalanes with tris(pheoxy)borane was studied independently and provided strong evidence that the aluminum/hydrogen reduction of tris(pheoxy)borane proceeds through aminoalane intermediates.

Hexamethyldisilazane reacts with the trimethylamine adduct of dimethylaminodichloroborane in a dehydrohalogenation reaction to yield bis(trimethylsilyl)aminochlorodimethylaminoborane, $[(CH_3)_3Si]_2N\text{-}BCl\text{-}N(CH_3)_2$; bis(dimethylamino)chloroborane and bis(dimethylamino)-bis(trimethylsilyl)aminoborane were observed as byproducts (136). The rotational barrier about the $B\text{-}N(CH_3)_2$ bond in bis(trimethylsilyl)aminochlorodimethylaminoborane was found to be in the order of 18-21 Kcal/mole depending on the solvent (166).

Substituted anilines react with diphenylhaloboranes to yield aminoboranes which can then be oxidatively photocyclized to provide 10,9-borazarophenanthrenes according to the following reaction sequence (196); this process provides a simple entry to substituted borazarophenanthrenes (which are difficult to obtain by other preparative methods) and may well offer an attractive route to other condensed borazarohydrocarbons.



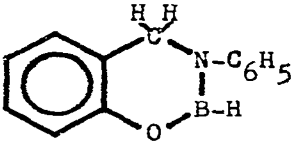
The hydroboration of Schiff bases (226) can be illustrated by the following equation:

$$C_6H_5N\text{=}CHC_6H_5 + BH_3 \longrightarrow (C_6H_5)(C_6H_5CH_2)N\text{-}BH_2$$

The resultant benzylphenylaminoborane is monomeric but slowly dimerizes on prolonged standing. On distillation, of the compound a rearrangement occurs leading to the formation of bis(benzylphenylamino)borane.

$$2\ (C_6H_5)(C_6H_5CH_2)N\text{-}BH_2 \longrightarrow BH_3 + [(C_6H_5)(C_6H_5CH_2)N]_2BH$$

Analogous reactions were observed on hydroboration of other Schiff bases such as N-benzylidene-2-naphthylamine. Schiff bases containing hydroxy groups offer two reactive centers for hydroboration and different reaction paths can occur. However, on hydroboration of salicylidene anils, the ultimate product of either reaction path was found to be compound 30.



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Aniline and diphenylamine (but not triphenylamine) form 1:1 adducts with boron trifluoride and the thermal dehydrohalogenation of the adducts has been studied (149). On heating aniline-trifluoroborane in the presence of aluminum poweder to 280°, B-trifluoro-N-triphenylborazine, $(\text{-BF-NC}_6H_5\text{-})_3$, is obtained. Similarly, diphenylamine-trifluoroborane can be dehydrohalogenated to give diphenylaminodifluoroborane though major side reactions occur.

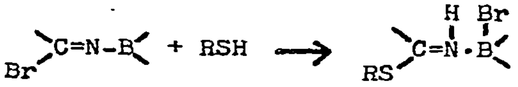
Lithium amides react with diborane to form lithium tetrahydridoborate and trisaminoboranes as depicted in the following equation (177):

$$3\ LiNR_3 + 2\ B_2H_6 \longrightarrow 2\ LiBH_4 + B(NR_2)_3$$

Boron trihalides (X = F, Cl) were found to react with N-lithiohexafluoroisopropylidenimine as shown in the following equation (139):

$$BX_3 + 2\ Li\text{-}N{=}C(CF_3)_2 \longrightarrow B[NC(CF_3)_2]_3 + 3\ LiX$$

An X-ray crystallographic study of (diphenylketimino)-dimesitylborane, $(C_6H_5)_2C{=}N\text{-}B(mes)_2$ (mes = mesityl), has established an allene-like geometry for the molecule (126). The B-N=C link is very nearly linear and both distances - BN with 1.40 Å and NC with 1.31 Å - are very short as is required for double bonding and allene-like structure of the BNC grouping. Additional studies in iminoborane chemistry describe the interaction of bromine-substituted monomeric iminoboranes with alkylthiols to yield alkylthioiminoborane hydrobromides, 31, which can be considered as adducts of the amine-borane type (135).



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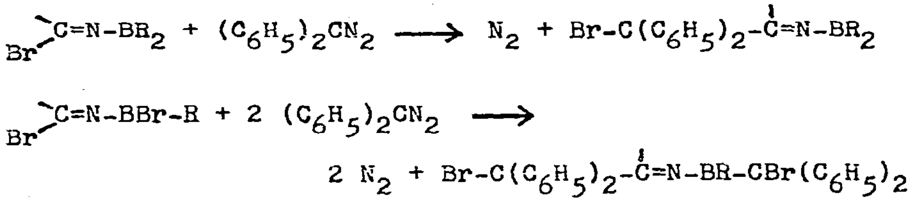
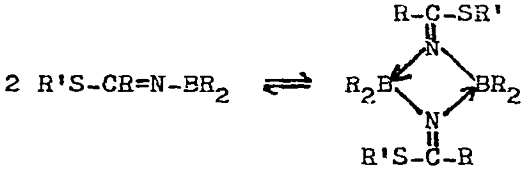
The latter lose hydrogen bromide on distillation in high vacuum and convert to iminoboranes, whereas on reaction with trialkylamine, the imine of the adduct is readily displaced by the trialkylamine. If thiophenols are used in the cited reaction rather than alkylthiols, boron-bonded bromine is also displaced in a reaction similar to the one above. The bromine substituted iminoboranes react readily with diphenyldiazomethane (132) and bromine bonded to either carbon or boron can react as is illustrated in the following equations:



Trialkylboranes or boron trihalides react with thiocyanates to produce sulfur-containing iminoboranes according to the following equation (137):

$$BR_3 + R'SCN \longrightarrow R'S-CR=N-BR_2$$

The iminoboranes formed in this reaction are normally dimers or are in equilibrium with a monomeric species:



Analogous products are obtained from the action of nitriles on organothioboranes or from the reaction of dimeric haloiminoboranes with alkylthiols.

$$RSBX_2 + R'CN \longrightarrow RS-CR'=N-BX_2$$

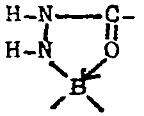
$$R''SH + X-CR=N-BR'_2 \longrightarrow HX + R''S-CR=N-BR'_2$$

The effect of non-bonding interactions on the boron-11 chemical shift has been studied with a series of alkylamino-boranes and alkoxyboranes (143). The non-bonded interactions may reduce the coplanarity about the boron atom and thus result in a decreased shielding of the boron; the data indicate that inductive effects and conformation of groups attached to the boron have a measurable effect on the boron-11 chemical shift.

The photoelectron spectra of a series of aminoboranes have been recorded (121). On the basis of qualitative molecular orbital considerations, the low energy PE bands are assigned to π-ionizations.

Compounds containing the grouping B-N-N as a structural unit can be considered as a special group of aminoboranes; this group comprises a variety of linear, cyclic, and some saltlike materials.

Several hydrazinoboranes of the type $(C_6H_5)_2B\text{-}NH\text{-}NHR$ have been prepared (131) and were found to be monomeric in solution. However, if R is a polar group such as C_6H_5CO, CH_3CO, or $(C_6H_5)_2PO$, the boron atom assumes four-coordination by forming a coordinated cyclic species, 32.



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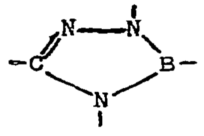
Nitrogen-bonded hydrogen of $(C_6H_5)_2B\text{-}NH\text{-}N(CH_3)_2$ can be displaced by reacting the hydrazinoborane with methyllithium (131). Subsequent reactions of the N-metal derivative affords compounds such as $(C_6H_5)_2B\text{-}NSi(CH_3)_3\text{-}N(CH_3)_2$.

The tris(hydrazino)borane $B(NH\text{-}N(CH_3)_2)_3$ adds boron trichloride, diborane, or methyl iodide (128). Apparently, initial addition occurs at the dimethylamino sites of the molecule with the formation of 1:3 adducts; but with an excess of agents, some addition at the NH sites of the molecule may also occur producing species such as the 1:5 adduct $B(NH\text{-}N(CH_3)_2)_3 \cdot 5BH_3$.

Nuclear magnetic resonance studies (125) on 2,2-dimethylhydrazinoboranes such as $B[NH\text{-}N(CH_3)_2]_3$, the bis(2,2-dimethylhydrazino)borane $HB[NH\text{-}N(CH_3)_2]_2$, and $[(CH_3)_2N\text{-}NH\text{-}]_2B\text{-}B[NH\text{-}N(CH_3)_2]_2$, indicate the existence of intramolecular hydrogen bonding in these compounds; the hydrogen bond energy was calculated to be about 2.5 kcal/mole. However, based on boron-11 nuclear magnetic resonance data, the boron is three-coordinated in all cases.

Boronic acid derivatives condense readily in boiling benzene with acid amidrazones to form derivatives of 5,1,3,4-boratriazaroles, 33 (123). The resultant compounds



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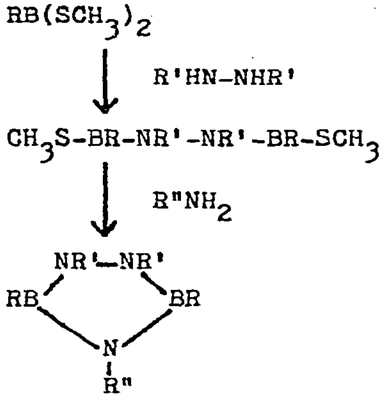
are stable to hydrolysis under mild conditions and show "aromatic" properties.

Various 1,3,4-triaza-2,5-diborolidines have been obtained through the following reaction sequence (122).



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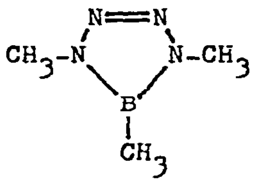
The intermediate 34 equilibrates according to the following equation:

$$2\ CH_3S\text{-}BR\text{-}NR'\text{-}NR'\text{-}BR\text{-}SCH_3 \rightleftharpoons RB(\text{-}NR'\text{-}NR'\text{-})_2BR + 2\ RB(SCH_3)_2$$

1,4,5-Trimethyltetrazaboroline, 35, reacts with Lewis acids such as BF_3, $SnCl_4$, or $SbCl_5$ to form stable complexes (124).



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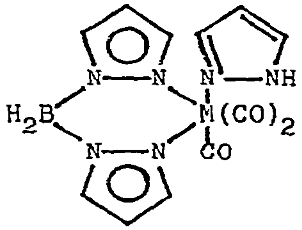
In these materials the tetrazaboroline ring acts as a monodentate ligand; only when $TiCl_4$ acts as the Lewis acid are bridged complexes probably formed. Titanium tetrachloride, 1,4,5-trimethyltetrazaboroline, and aromatic hydrocarbons react to form two series of complexes (165) of the general composition

4 $TiCl_4 \cdot 2(CH_3)_2N_4BCH_3 \cdot 2L$ (L = toluene, o-xylene), and

4 $TiCl_4 \cdot 2(CH_3)_2N_4BCH_3 \cdot L$ (L = benzene, p-xylene, naphthalene).

Interaction in mesitylene and m-xylene (and cyclohexane) resulted in the formation of $4TiCl_4 \cdot 3(CH_3)_2N_4BCH_3$ alone.

The ruthenium derivative $HB(pz)_3Ru(CO)_2X$ (pz = pyrazolyl, X = Cl, Br, I) has been prepared by reacting $Ru_3(CO)_{12}$ with $KHB(pz)_3$ and subsequently treating the dep red solution with halogen (84). Similarly, the reaction of $BrM(CO)_5$ or $M_2(CO)_{10}$ (M = Mn, Re) with potassium dihydrobis(pyrazolylato)borate afforded the crystalline complexes $\{[H_2B(N_2C_3H_3)_2]M(CO)_3(pyrazole)\}$, 36 (85). Reaction of the latter with phosphines or phosphites (L) yields derivatives of type 37.



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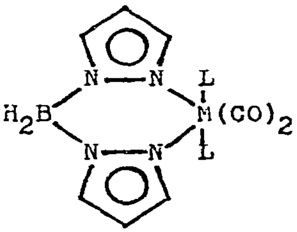

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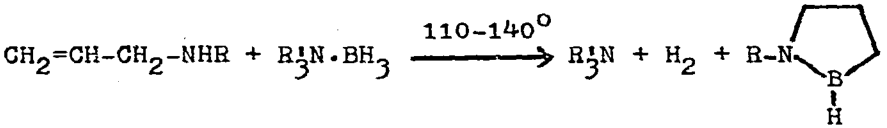
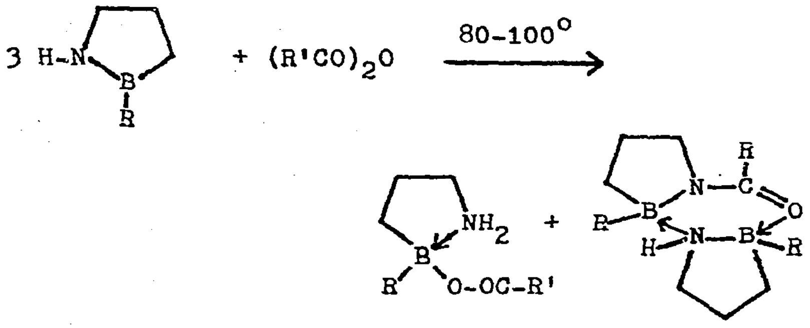
Hydroboration of secondary allylamines with triethylamine-borane yields 1,2-azaborolidines according to the following procedure (118):



R = n-C_3H_7, n-C_4H_9; R' = C_2H_5

Similarly, allylimines (obtained by condensation of aromatic aldehydes with allylamine) can be hydroborated with the same reagent to yield 1,2-azaborolidines in which R = $CH_2C_6H_5$, and a mixture of N-alkylallylamine, trialkylborane, and triethylamine-borane can interact to yield 1,2-dialkylazaborolidines (119). The 1,2-azaborolidines are dimeric in benzene solution and their tendency to dimerize seems to be governed by inductive effects of the boron substituents and also by steric factors. Dimerization increases in the order -BR-NR'- $<$ -BR-NH- $<$ -BH-NR- (119). A detailed nuclear magnetic resonance and infrared spectroscopic study of the monomer - dimer equilibrium of 2-butyl-1,2-azaborolidine revealed (227) that the equilibrium is only concentration depending and the nature of the solvent has virtually no effect.

1,2-Azaborolidines do not react with alcohol or water at room temperature. However, at elevated temperatures boron-bonded hydrogen is readily displaced by alkoxy or alkylthio groups (118). 1,2-Dialkylazaborolidines react with boron trichloride by displacement of the boron-bonded alkyl group by halogen (119). It is likely that intermediate cleavage of the annular boron-nitrogen bond occurs during this process. 2-Alkyl-1,2-azaborolidines can be acylated with acid anhydrides (120) to yield a novel type of organoboron heterocycle, 38, as is illustrated in the following equation:



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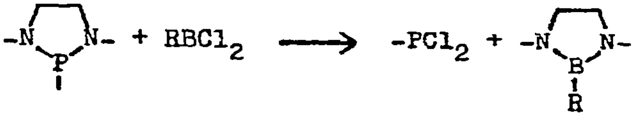
The structure of the latter compound is substantiated by the fact that an analogous product is obtained on interaction of dimeric acetamidodialkylboranes with 1,2-azaborolidines (127).

On hydroboration of diallylamine with triethylamine-borane (121), the bicyclic compound 39, 1-aza-5-borabi-

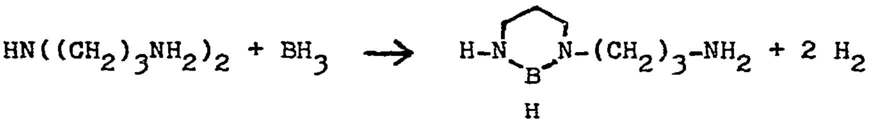
39

cyclo(3.3.0)octane, m.p. 138-139°, b.p. 145-155°, has been obtained.

Phenyldichloroborane reacts exothermally with 1,3,2-diazaphospholidines according to the following equation (113):



Several 1,3,2-diazaboracycloalkanes which are hydrogen substituted at the boron site can be obtained by reacting aliphatic diamines with sodium tetrahydridoborate and iodine (to generate BH_3 in situ) in refluxing tetrahydrofuran (114). In an analogous procedure it was found that the reaction of 3,3'-diaminodipropylamine with BH_3 proceeds in stepwise fashion (115). In refluxing tetrahydrofuran 40 is obtained in high yield according to the following equation:



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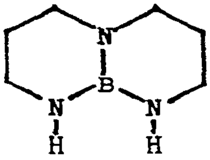
At 150°, 40 loses additional hydrogen on forming the bicyclic system 41. Similarly, 1,7,8,9-triazaborahydrindane, 42, and its monocyclic precursor 43 were obtained by using N(ω-aminoethyl)-1,3-diaminopropane as starting amine (114).



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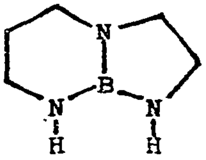

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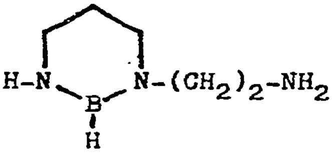

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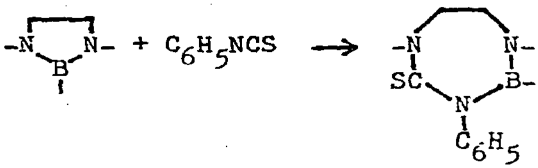
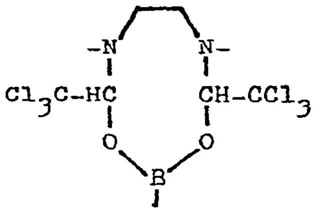
In analogy to previous work (116), 1,3,2-diazaborolidines were found to react with phenyl isothiocyanate in a 1:1 molar ratio in a ring expansion reaction (117) as is illustrated by the following equation:



However, with chloral the reaction occurs in a 1:2 molar ratio and yields a nine-membered heterocycle, <u>44</u>.



<u>44</u>

Ammonium chloride and sodium tetrahydridoborate can be interacted in the absence of solvent to afford borazine in 10-20% yield (50). A novel borazine synthesis involves the hydrogenation of tris(phenoxy)borane in the presence of aluminum and primary amines; this reaction provides a fairly convenient route to N-organosubstituted borazines (51) according to the following equation:

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow{H_2} 1/3\ (\text{-BH-NR-})_3 + Al(OC_6H_5)_3$$

Also, ligand displacement with simultaneous condensation of dialkylthioorganoboranes with primary amines yields borazines as depicted in the following equation (122):

$$3\ RB(SCH_3)_2 + 3\ R'NH_2 \longrightarrow (\text{-}BR\text{-}NR'\text{-})_3 + 6\ CH_3SH$$

The reaction of boron trichloride with methylamine can be directed to yield B-tris(methylamino)-N-trimethylborazine, $(\text{-}BNHCH_3\text{-}NCH_3\text{-})_3$, in good yield (52). Subsequent treatment of the aminoborazine with boron trichloride yields B-trichloro-N-trimethylborazine; this procedure provides a very convenient and fairly rapid method for synthesizing the latter compound.

The boron trifluoride adducts of methyl glycinate and of methyl β-alaninate have been dehydrohalogenated with a bulky tertiary amine to yield the corresponding N-substituted borazines (54).

Ferrocenyldichloroborane reacts with ammonia in toluene to yield B-trisferrocenylborazine (53). Remarkably, the 70 eV mass spectrum of the compound shows no fragmentation; only the molecular ion and the doubly charged molecular ion were observed!

Several reactions of B-trichloroborazines with metal-organic derivatives have been investigated. For example, B-trichloroborazines were found to react with sodium cyclopentadienide and the infrared data of the resultant product seem to indicate formation of boron-carbon sigma bonds in this process (55). However, no defined materials could be isolated. This latter observation is surprising since in previous work (56) N-substituted B-tris(cyclopentadienyl)-borazines were isolated and characterized. Also, B-trichloroborazines appear to react with sodium pentacarbonylmanganese with initial formation of boron-manganese bonds (55).

However, no metal-boron derivative was actually isolated and it is likely that the B-metalated borazine readily decomposes with the formation of polymeric borazines and $Mn_2(CO)_{10}$.

N-Trimethylborazine reacts with heavy metal halides such as TiX_4, SnX_4, HgX_2 (57), or AgX (58) by halogenation of the boron sites of the heterocycle. This approach can be used for the preparation of unsymmetrically substituted borazines.

Of great interest to the preparative chemist should be the finding that organic substituents bonded to the boron atoms of a borazine ring can be displaced by the action of Grignard reagent on the borazine (167). For example, methyl groups bonded to boron exchange with phenylmagnesium halide and *vice versa*. Apparently, equilibrium mixtures are obtained and it seems that virtually any B-substituted borazine can be made to react with an appropriate organometallic reagent thus offering interesting preparative possibilities.

The crystal structure of B-tris(dimethylamino)borazine has been investigated by X-ray spectroscopy (63). Endocyclic and exocyclic boron-nitrogen bonds were found to be equally long with a value of 1.43 Å thus conflicting with some previous molecular orbital calculations (64) which had indicated that exocyclic substitution of the boron atoms with amino groups would weaken the annular B-N bonds. An X-ray analysis of tricarbonyl(hexaethylborazine)chromium(0) indicates (65) that the mean of the B-N separations of the borazine ring in this compound is 1.44 Å and is virtually identical to that of the parent borazine. However, one of the boron-nitrogen distances deviates remarkably from the mean value with an experimentally determined distance of only 1.36 Å; there is no immediate explanation for this observation. Differences in the Cr-N distance (2.22 Å) and Cr-B separation (2.31 Å) lead to puckering of the borazine skeleton in the cited compound.

Proton magnetic resonance spectra of some B-aminoborazines such as $(-BNHCH_3-NCH_3-)_3$ have been recorded and were evaluated in terms of the aromatic character of the borazine ring. In this respect the aminoborazines seem comparable to the alcoylborazines (216). Also, some new molecular orbital considerations on the parent borazine were briefly described (67).

A vibrational analysis of borazine based on the infrared spectra of matrix-isolated species and the gaseous Raman spectrum of borazine has been reported (59). Suggested assignments of the fundamentals are in essential agreement with the calculated frequencies resulting from a normal-mode treatment published recently (60). The vibrational spectra of B-trihaloborazines, $(-BX-NH-)_3$ with X = Cl or Br (61) and F (62), and isotopically labeled derivatives thereof have been examined in detail. An assignment of fundamentals was suggested and it was noted that spectral changes affected by boron-bonded halogen are due mainly to a simple mass effect (or coupling of modes) rather than to changes in the electronic structure of the borazine ring. Particular strong coupling of B-F and B-N modes was observed (62).

The absorption spectrum of borazine in the 2000-1500 Å region has been investigated and three electronic transitions were observed (176). The spectrum is generally diffuse and some decomposition of the compound occurs quite readily; this event was interpreted to suggest predissociation of the molecule.

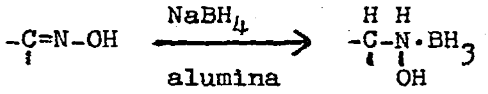
The mass spectra of some N-trialkylborazines, $(\text{-BH-NR-})_3$, have been recorded (156). The dominant feature of all spectra is a group of ions which apparently arises from cleavage of an alkyl radical from the α-carbon atom of a nitrogen-bonded group in the molecular ion.

The He(I) photoelectron spectra of B-trimethylborazine and N-trimethylborazine were recorded and were compared with that of borazine (66). The resultant data indicate that the highest occupied orbital in all three compounds is of the π type.

Adducts and Salts

Nitrosylborane has been detected by mass spectroscopy as an intermediate in the reaction of H_3BCO with nitrogen monoxide; the reaction ultimately leads to carbon dioxide, N_2O and boric acid (233).

Amino acid esters react with boranes BX_3 (X = H, F, Cl) to form 1:1 adducts of the type $ROOC\text{-}R'\text{-}NH_2 \cdot BX_3$ containing a boron-nitrogen coordinate linkage (54). Similarly, sodium tetrahydridoborate on alumina reacts with oximes at room temperature in benzene solution with the formation of hydroxylamine-boranes in which the boron is coordinated to the nitrogen atom (154).



$$-\underset{|}{C}{=}N{-}OH \xrightarrow[\text{alumina}]{NaBH_4} -\overset{H}{\underset{|}{C}}-\overset{H}{\underset{\underset{OH}{|}}{N}}\cdot BH_3$$

In like manner, excess diborane was found to react with indoles to form stable adducts of the amine-borane type in which the boron is coordinated at the NH site of the indole (90). Treatment of the latter adducts with sodium methoxide in methanol solution results in reduction to the indolines.

The rate constant for the reaction of free borane, BH_3, with trimethylamine to give trimethylamine-borane was found to be 1.1 x 10^9 l/mol sec at 500°K and a total pressure of 6 Torr (222). The data were briefly discussed in terms of general donor - acceptor reactions in the borane series. Nuclear magnetic resonance studies (225) reveal that the complexing power of triallylborane towards amines rises in the order 2-picoline $<$ trimethylamine $<$ pyridine $<$ 3-picoline.

In general, reaction of a borane (BX_3, $X = CH_3$, F, Cl) with methylhydrazines yields simple 1:1 adducts (221). However, trimethylborane and tetramethylhydrazine do not interact, and hydrazines of the type $N_2H_{1+n}(CH_3)_{3-n}$ cleave the boron-chlorine bond. On the basis of nuclear magnetic resonance studies it was concluded that adduct formation occurs at the more highly methylated nitrogen atom though isomeric products were obtained from monomethylhydrazine and boron trifluoride.

The first examples of amine-boryl tosylates have been prepared and isolated (91). In these compounds, a borane unit carrying a p-toluenesulfonate substituent is coordinated with a tertiary amine. Their synthesis is depicted by the following scheme.

$$R_3N\cdot BH_3 + (p)R\text{-}C_6H_4\text{-}SO_3H \xrightarrow[\text{benzene}]{\text{room t.}} H_2 + R_3N\cdot BH_2[O_3SC_6H_4R(p)]$$

$$R = CH_3$$

At reflux temperatures and in the presence of a second mole of the acid, further reaction occurs yielding the trimethylamine adduct of $HB[O_3S\text{-}C_6H_4\text{-}R(p)]_2$. Both amine-boryl tosylates are fairly inert towards moisture and oxygen but the boron-bonded hydrogen can be displaced by bromine when reacted with the elemental halogen. The monotosylate reacts with 4-methylpyridine by forming a bisamine-boronium cation.

Several p-substituted methylamine-diarylboranes have been prepared from the corresponding diarylhydroxyboranes by reduction with lithium aluminum hydride (81) and amine-borane type adducts have been the subject of several spectroscopic studies. For example, the vibrational spectra of acetonitrile adducts with boron trihalides, $CH_3CN\cdot BX_3$, have been investigated (93) and the results of a normal coordinate analysis indicate an increase in the B-N stretching force constant from 2.5 mdyn/Å (X = F) to 3.4 (X = Cl) and 3.5 (X = Br) mdyn/Å respectively. These findings are in consonance with theassumption that boron trichloride is a stronger acid in relation to acetonitrile than is boron trifluoride. Boron trifluoride forms 1:1 adducts with a variety of cyclic ketones (215). Evaluation of the obtained enthalpy data indicates that the adduct formation is particularly sensitive to steric factors.

Nonequivalence of hydrogen in the t-butyl group of t-butyldimethylamine-borane, $(CH_3)_3C-N(CH_3)_2 \cdot BH_3$, permitted determination of the activation parameters for t-butyl rotation using total nuclear magnetic resonance line-shape analysis (195).

The mass spectra of trimethylamine adducts of BX_3 (X = H, F, Cl, Br, I) and of bromofluoroboranes indicate that the trend in the proportion of the total positive current carried by ions containing boron and nitrogen is identical to that observed for the proton magnetic resonance shifts and other physicochemical data of the adducts with $I > Br > Cl > H > F$ (98). These results tend to support the assumption that B-X π-bonding exists in such donor-acceptor complexes, particularly if X = F.

The photoelectron spectra of complexes of boron trifluoride with dimethylamine and trimethylamine have been investigated (96). The marked increase of more than 3 eV in the ionization potentials of the amines upon coordination with the boron trifluoride suggests that the amine site of the amine-borane acquires an appreciable positive charge resulting in a tighter bonding of its electrons.

Fluorine-19 nuclear magnetic resonance studies of boron trifluoride adducts with pyridine 1-oxides and quinoline N-oxides illustrate that the $^{11}B-^{19}F$ coupling constant in acetonitrile is negative. Variations in the chemical shift values are purportedly due primarily to steric factors (95).

No halogen exchange is observed in dichloromethane solution between boron trifluoride and trimethylamine-trichloroborane (165). However, nuclear magnetic resonance studies indicate that the systems $BCl_3/(CH_3)_3N\cdot BBr_3$ and $C_6H_5N(CH_3)_2\cdot BF_3/C_6H_5N(CH_3)_2\cdot BCl_3$ may be suitable for obtaining kinetic parameters for the exchange of halogens on four-coordinate boron. In this conetxt, it is of interest to note that ^{35}Cl nuclear quadrupole frequencies of several complexes of boron trichloride show a remarkable constancy (between 21-22 MHz) for a wide variety of adducts with organic donor molecules (97).

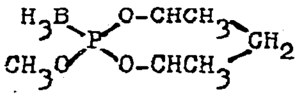
Boron trifluoride forms solid 1:1 adducts with aromatic aldehydes. Spectroscopic data (UV, IR, NMR) infer that the oxygen-boron bonding is not of a simple charge-transfer type (94) and the group $-CHO\cdots BF_3$ is a strong electron-withdrawing (pseudo) substituent. p-Dimethyl(or diethyl)aminobenzaldehyde forms three different types of complexes with boron trifluoride (189). If the two reactants are combined in a solvent a 1:1 adduct is obtained in which the BF_3 is bonded to the carbonyl oxygen. After the solution stands for several days and the solvent evaporates, a new material is formed in which the boron is coordinated to the nitrogen of the amino group. Finally, addition of an excess of boron trifluoride to a solution of the free aldehyde yields a 2:1 adduct in which both donor sites are complexed with boron trifluoride; these results were confirmed by spectroscopic data.

In this context it should also be noted that the new reagent boron trifluoride-trifluoroacetic anhydride may become a useful tool for the preparative chemist; so far it has been used successfully in some cyclization reactions (153). Also, some boron trifluoride-catalyzed rearrangements of neotriterpene epoxides have been described (197,198).

Boron trichloride and boron tribromide form 4:1 adducts with tetradentate ligands such as tetrakis(diphenylphosphinomethyl)methane and tetrakis(diphenylarsinomethyl)-methane (235). Triphenylmethylenephosphorane forms adducts of the type $(C_6H_5)_3PCH_2 \cdot BX_3$ with boron tribromide or boron triiodide (232).

Trimethylamine-borane and triethylamine-borane react with tri-n-butylphosphine by base exchange to form tri-n-butylphosphine-borane and the corresponding amine (79). The reactions are second order overall and an SN2-B mechanism was proposed to account for this circumstance. In an extension of this work on nucleophilic substitution at tetrahedral boron, the four isomeric trimethylamine-butylboranes and several o- and p-substituted trimethylamine-arylboranes were examined as the nucleophile (80). Kinetic data gave good evidence for second order SN2-B displacement reactions in all cases except that of trimethylamine-t-butylborane; this compound gave a predominant first order SN1-B displacement. In contrast, p-substituted methylamine-diarylboranes react with 2,2-diphenylethylamine in diglyme solution first in order in respect to amine-borane and the data were suggestive of an SN1-B mechanism involving the rate-determining dissociation of amine-borane (81).

The structure of 2-methoxy-cis-4,6-dimethyl-1,3,2-dioxaphosphorinane-borane, 45, has been determined by



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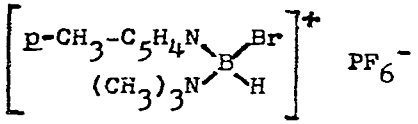
three-dimensional single crystal analysis (99). The heterocycle has a chair conformation with a mean P-O bond length of 1.56 Å.

The first crystal structure of a stable optically active compound haveing a boron atom as the asymmetric center has been studied (101). The salt 46 crystallizes in



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in the monoclinic system and an almost regular sp^3 hybridization of the boron atom results from the favorable arrangement of the surrounding ligands.

Reactions of various polyamines with the mono- and diiodoborane adducts of trimethylamine yields chelated and polynuclear boron(n+) ions such as

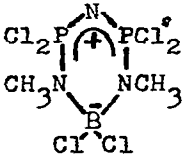
$TED[(CH_3)_3NBH_2]_2^{2+}$, $TED[(CH_3)_3NBHI]_2^{2+}$

$PMDT[(CH_3)_3NBH_2]_3^{3+}$

TED = triethylenediamine

PMDT = pentamethyldiethylenetriamine (220).

Phosphorus pentachloride reacts with ammonia-trifluoroborane, $H_3N{\cdot}BF_3$, to yield the salt $(Cl_3P{=}N{-}PCl_3)(BCl_4)$ (111). This salt undergoes a complex reaction with sulfur dioxide and affords products such as $Cl_3P{=}NBCl_3{-}POCl_2$ and $Cl_3P{=}N{-}PCl_2{-}O{-}BCl_3$. Ammonium isothiocyanate reacts with the hexachlorodiphosphazonium tetrachloroborate or with $(CH_3NPCl_3)_2$ to produce the new anion $[B(NCS)_4]^-$ which is isolated as the $[(NCS)_3P{=}N{-}P(SCN)_3]^+$ derivative (112). Methylamine-trifluoroborane reacts with excess phosphorus pentachloride to form the adduct $CH_3NPCl_3{\cdot}BCl_3$ (148) and an analogous material is formed with aniline-trifluoroborane. With strong Lewis bases such as pyridine, displacement of the weaker base N-methyltrichlorophosphinimine is readily accomplished. Reaction of $(PCl_3{=}N{-}PCl_3)(BCl_4)$ or of $CH_3NPCl_3BCl_3$ with methylammonium chloride yields a compound of the composition $(CH_3)_2N_3P_2BCl_3$ which is said to have the structure 47 (231). Dimethylamine-trifluoroborane reacts with phosphorus pentachloride to yield the salt $((CH_3)_2NPCl_3)(BCl_4)$ (105). The same compound can be



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obtained from the interaction of dimethylaminodichloroborane with phosphorus pentachloride. However, action of the latter agent on trimethylamine-trifluoroborane merely results in halogen exchange and formation of trimethylamine-trichloroborane, $(CH_3)_3N{\cdot}BCl_3$.

Boron trichloride reacts with glycine to yield the novel compound $[B(O\text{-}CO\text{-}CH_2\text{-}NH_3^+)_3](BCl_4)$ (54); however, amino acid ester hydrochlorides react with boron trichloride to form tetrachloroborates having the general composition $(RO\text{-}CO\text{-}R'\text{-}NH_3)(BCl_4)$.

Diborane was found to react in ethers with lithium dimethylphosphide to produce lithium bis(borane)dimethylphosphide(1-) according to the following equation (92):

$$LiP(CH_3)_2 + B_2H_6 \longrightarrow Li[(CH_3)_2P(BH_3)_2]$$

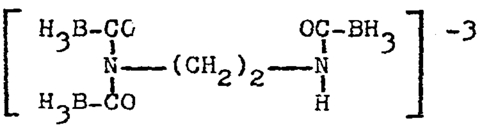
Lithium tetrahydridoborate and aluminum trichloride interact in benzene to produce aluminum tetrahydridoborate (202); however, on evaporation of the solvent a compound of the composition $AlH_2BH_4\cdot C_6H_6$ is isolated.

Sodium tetrahydridoborate reacts with tetraethylammonium bromide in isopropyl alcohol to give the tetraethylammonium tetrahydridoborate (100). This salt has a polymeric transformation at ca.120° and decomposes at 210° to yield triethylamine-borane.

Aminolysis of O-ethylboranocarbonate ion, $(H_3BCOOC_2H_5)^-$, in ethanol solution yields boranocarbamates in consonance with the following equation (102):

$$(H_3BCOOC_2H_5)^- + HNR_2 \longrightarrow (H_3BCONR_2)^- + C_2H_5OH$$

However, with ethylenediamine, reaction occurs in a 3:1 molar ratio and the ethylenediaminetris(boranocarboxylate) ion 48 is formed. The basic hydrolysis of O-ethylborano-



$$\left[\begin{array}{ccc} H_3B\text{-}CO & & OC\text{-}BH_3 \\ N & \text{—}(CH_2)_2\text{—} & N \\ H_3B\text{-}CO & & H \end{array}\right]^{-3}$$

48

carbonate ion in aqueous solution follows first order rate law.

Trifluoromethylsulfur trifluoride, CF_3SF_3, reacts with boron trifluoride to form a 1:1 adduct (103). On the basis of infrared spectral data the adduct has the structure of a tetrafluoroborate, $(CF_3SF_2)(BF_4)$. However, in the gas phase the compound readily dissociates to the original species.

Potassium tetrafluoroborate reacts with the acetylene Grignard by forming tetraethynylborates; potassium, tri- and tetramethylammonium, dimethylammonium, and pyridinium salts were isolated (150). In acidic medium it is possible to isolate the free acid $H(B(CCH)_4)$ which was found to have a pK value of 2.81 (in water), close to that of chloroacetic acid. Concentrated solutions of the acid are unstable and decompose with the formation of a solid polymer along with some unidentified gaseous products.

The low temperature vibrational spectra of lithium (219), sodium, and potassium (218) tetrahydridoborate have been studied. The BH_4^- ion site symmetry was found to be T_d for the potassium salt, D_{2d} for the sodium salt, and C_s for the lithium tetrahydridoborate.

The nuclear magnetic resonance spectrum of HBF_4 in aqueous solution (223) and the vibrational spectrum of single crystal $NaBF_4$ (224) have been discussed.

The reaction of lithium tetraalkylborates with a series of alkylating agents has been investigated (157). The initial step in the reaction of $LiBR_4$ with organohalides, R'X, appears to be the formation of a carbonium tetraalkylborate complex, $(R')^+(BR_4)^-$, which subsequently decomposes by either:

(a) α- or β-elimination of hydride ion from a boron-bonded alkyl group, or

(b) dealkylation of the tetraalkylborate ion.

Trialkylcyanoborates can be converted to trialkylcarbinols in a convenient manner employing trifluoroacetic anhydride (72). The process is similar to the carbonylation-oxidation reaction of carbon monoxide-trialkylboranes (73) but requires no drastic reaction conditions; hence, the cited reagent may offer distinct advantages in preparative organic chemistry when compared to the carbon monoxide-trialkylboranes. In this context it may also be noted that sodium cyanotrihydridoborate in hexamethylphosphoramide is a very selective agent for reductive removal of I, Br, and (indirectly) OH groups (74) and a broader utilization of cyanoborates in preparative chemistry may be in the making. Thus, the same reagent was found to reduce a variety of ketones, oximes, and enamines with remarkable selectivity (88). Macrocyclic cyanoboranes, $(H_2BCN)_n$ with n = 5, 6, 7, have been obtained as byproducts in the reaction of tetrahydrofuran-borane with hydrogen cyanide (75).

Rhodium and iridium complexes containing the cyanotrihydridoborate group as ligand, e.g., $[Rh(NCBH_3)(CO)(PR_3)_2]$ (R = C_6H_5), have been prepared and were found to be stable in air (200).

Lithium tetramethylborate has been studied extensively by spectroscopic means (106) such as proton magnetic resonance, X-ray, and mass spectroscopy. The resultant data have been used to elucidate the structure of the compound which is considered as a four-center and linear three-center methyl bridged electron-deficient species. The $^{11}B-^{1}H$ coupling of sodium tetraethylborate is solvent independent in such solvents as ether, dimethylsulfoxide, tetrahydrofuran, and 1,2-dimethoxyethane (145).

Tetraphenylborate ion is quantitatively oxidized by hexachloroiridate(IV) in aqueous solution in accord with the following equation (159):

$$B(C_6H_5)_4^- + 2\ IrCl_6^- + H_2O \longrightarrow (C_6H_5)_2BOH + C_6H_5C_6H_5 + 2\ IrCl_6^{-3} + H^+$$

The kinetics of the reaction have been interpreted in terms of a mechanism involving tetraphenylboron radicals.

A photochemically induced electron transfer from the tetraphenylborate anion to singlet oxygen was observed with rearrangement of the sodium tetraphenylborate to biphenyl (107) and the photochemical decomposition of diazonium tetrafluoroborate has been used in the synthesis of ring-fluorinated imidazoles (104). Also, (dimethylamino)phenyl-(2-phenylvinyl)oxosulfonium tetrafluoroborate, 49, has been

$$[C_6H_5-CH=CH-SO(C_6H_5)N(CH_3)_2]^+BF_4^-$$

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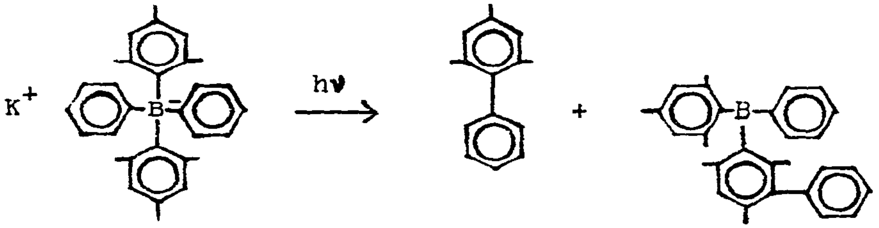
utilized as a novel reagent for ethylene transfer to dibasic nucleophiles (204).

The photolysis of potassium dimesityldiphenylborate results in a rearrangement involving a 1,3-shift of a diarylboron species (108).



A mechanism involving bridged intermediates was suggested for this reaction.

Chromium(I) tetraphenylborate can be prepared by thermal decomposition of bis(arene)chromium tetraphenylborate (208). Chromium(I) tetraphenylborate reacts with mercury(II) chloride whereby the first step involves an exchange reaction (209) as depicted in the following euqation:

$$\mathrm{Cr(BR_4) + HgCl_2 \longrightarrow CrCl + RHgCl + BR_3} \qquad (\mathrm{R} = \mathrm{C_6H_5})$$

In an analogous reaction of bis(arene)chromium tetraphenylborate with $HgCl_2$ (207) it was noted that initial reaction likewise results in displacement of the tetraphenylborate ion by chloride ion without decomposition of the sandwich structure about the chromium.

The vibrational spectra of some p-substituted tetraphenylborates have been recorded on solid dtate species (109). Tentative assignments were suggested for absorptions arising from the low frequency phenyl ring modes, the tetrahedral skeleton, and vibrations that are either internal modes of the p-substituent (such as OCH_3, CH_3, F, Cl, Br, CF_3) or vibrations involving the aromatic ring to substituent bond. No information was obtained which could be correlated with the electron densities about the central boron atom.

The crystal structure of $(NiLBr)(BR_4)$ (L = bis(diethylaminoethyl)(2-diphenylphosphinoethyl)amine, R = C_6H_5) indicates that the chromphore of the molecule is the NiN_2PBr grouping and one nitrogen atom of the ligand is not bonded to the metal atom (110).

Bis(dimethylamino)boranes react with dibenzonitrilepalladium dichloride in different ways (234). Bis(dimethylamino)chloroborane yields complexes of the type $Cl_2Pd(R_2N)_2BX$ (R = CH_3). On the other hand, bis(dimethylamino)bromoborane and bis(dimethylamino)iodoborane react with the coordinated benzonitrile to give give bisboryl-palladium complexes of the type $C_6H_5(CX_2)\text{-}N\{B(NR_2)_2\}_2PdCl_2$. The latter are probably dimeric and the B-N group presumably acts as π-ligand.

Some new organoboron species containing boron-metal sigma bonds have been described (229). For example, several (diphenylboryl)methylstannens, $(R_2B)_{4-n}Sn(CH_3)_n$ (R = C_6H_5), were obtained from the interaction of $(diphos)_2Co(BR_2)_2$ with methylchlorostannanes. However, analogous dibromoboryl derivatives are known only in stabilized (by coordination) form, i.e., $(Br_2B)_{4-n}Sn(CH_3)_n \cdot x diphos$, containing boron-phosphorus bonds.

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