BORON

ANNUAL SURVEY COVERING THE YEAR 1975

PART II

Kurt Niedenzu
Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506 (U.S.A.)

CONTENTS

1. REVIEWS AND SUMMARIES

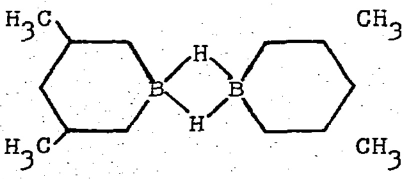
Syntheses and uses of organoboranes in organic research are outlined in a new book (74) and a summary by H. C. BROWN also describes the utilization of boranes in organic chemistry (55). A relatively brief article illustrates the use of organoboron derivatives as selective agents for organic syntheses (259) and dynamical processes in boranes, borane complexes, carboranes and related compounds have also been reviewed (121). A detailed discuss of three-center bonds in electron deficient compounds on the basis of the localized molecular orbital approach (124) certainly is of interest to the boron chemist.

Other reviews are concerned with the chemistry of boron subhalides (123), rearrangement reactions in organoboron chemistry (28 the coordination chemistry of the 1-pyrazolylborates (122), as well as the properties, structure and methods for preparing the covalent tetrahydridoborates of several metals (205). An evaluation of the flame retardant potential of some 25 organoboron compounds having various different structures (157) presents some guidelines for future work.

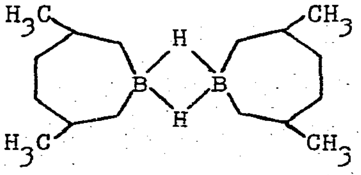
2. TRIORGANOBORANES AND RELATED SPECIES

2.1 Syntheses and Reactions

The hydroboration of 2,4-dimethyl-1,4-pentadiene and 2,4-dimethyl-1,5-hexadiene to yield the dimeric species bis(3,5-dimethyl)-borinane, I, and bis(3,6-dimethyl)borepane, II, respectively, has now been described in detail (147) ; the two heterocycles should



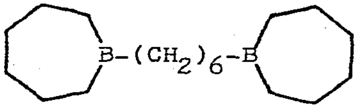
I



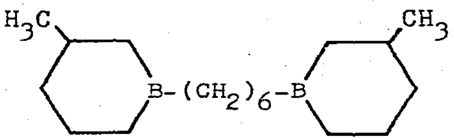
II

be extremely valuable as reagents for free-radical reactions of organoboranes.

Hydroboration of 1,5-hexadiene with borane in a 3:2 molar ratio leads to the borepane III, which can be thermally isomerized to yield IV.



III



IV

When the latter is treated with additional borane, BH_3, 2-methylborinane and borepane are obtained (223).

The reaction of lithium tetrahydridoborate with 3,4-bis(dichloroboryl)-2,2,5,5-tetramethylhexane (98) can be described by the following equation:

$$(CH_3)_3C\text{-}CHBCl_2\text{-}CHBCl_2\text{-}C(CH_3)_3 + 4\ LiBH_4 \longrightarrow$$

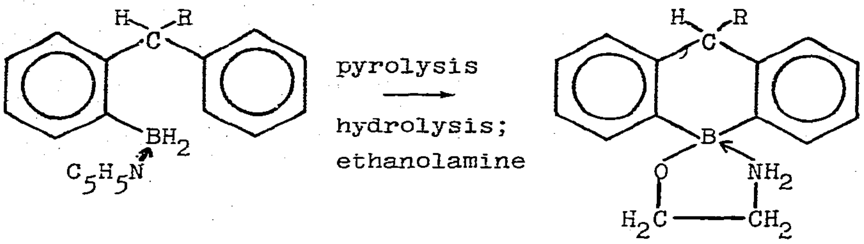
$$4\ LiCl + 2\ B_2H_6 + C_{10}H_{20}B_2H_4$$

The structure of the resultant organoborane is supposedly analogous to that of the cyclic organodiborane(6) species obtained by the hydroboration of butadiene.

A detailed description is given for the preparation of trimethylborane in high yield from the reaction of tri(n-butoxy)borane with $Al_2(CH_3)_3Cl_3$ (221); triethylborane can be obtained in similar fashion from boron trifluoride-etherate and triethylaluminum. A modified procedure for the preparation of 9-borabicyclo(3.3.1)nonane has also been described (246). Triphenylborane is readily obtained from the thermal decomposition of trimethylammonium tetraphenylborate; a detailed procedure for the preparation of the latter reagent is now also available (137).

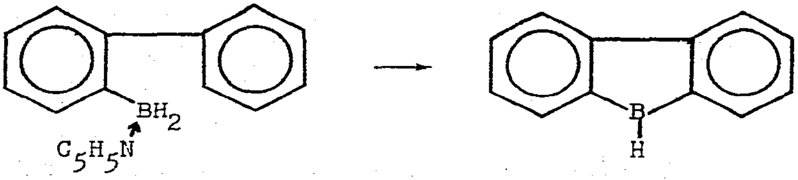
Pyrolysis of trimethylborane in a closed tube at 450° yields material having the composition $(BCH_3)_6(CH_2)_4$ (189). A structure similar to that of adamantane has been proposed for the material. structure, based on nuclear magnetic resonance data, is one in whi the BCH_3 groups are linked in the cage structure <u>via</u> methylene bridges.

Pyrolysis of pyridine-(2-benzylphenyl)borane or of pyridine-(benzhydrylphenyl)borane provides access to the 9,10-dihydro-9-bora anthracene system (14); the **products** were isolated as the ethanola esters, V.

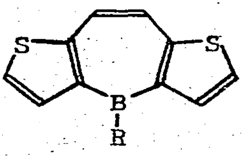


V

Similarly, pyrolysis of pyridine-(2-biphenyl)borane proceeds as shown:



Several derivatives of the borepinothiophene system, VI, have been prepared by conventional syntheses; remarkably, the ultraviole spectra of these organoboranes are very simlar to that of tropone (285).



VI

(2-Alkoxyvinyl)boranes can be obtained by the hydroboration of acetylenic ethers with tetraalkyldiborane(6) or diborane(6) (38):

$$(RBH_2)_2 + R'OC{\equiv}CH \longrightarrow R'OC\text{-}CH{=}CH\text{-}BR_2$$

$$BH_3 + 3\ ROC{\equiv}CH \longrightarrow B(CH{=}CHOR)_3$$

The tris(trans-2-alkoxyvinyl)boranes are stable to at least 130°. On treatment with alcohols, one or two of the boron-carbon bonds cleave to provide (alkoxy)vinylboranes. The latter compounds can also be obtained by a ligand exchange reaction, e.g.:

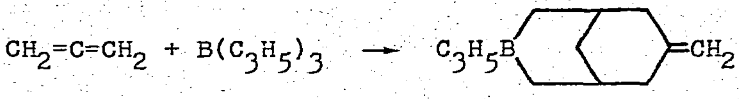
$$B(OR)_3 + B(CH{=}CHOR')_3 \longrightarrow (RO)_2B(CH{=}CHOR') + ROB(CH{=}CHOR')_2$$

Sterically pure 2-cis-silylated vinylboranes have been obtained by the reaction of chlorotrimethylsilane with alkali metal trialkyl-1-alkinylborates (207). This latter reaction is depicted in the following equation:

$$Na(R_3B\text{-}C{\equiv}C\text{-}CH_3) + ClSi(CH_3)_3 \longrightarrow R_2B\text{-}CR{=}CCH_3\text{-}Si(CH_3)_3 + NaCl$$

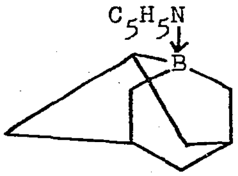
Hydroboration of alkynes with disiamylborane yields vinylboranes which, upon addition to tetrahydrofuran solutions of the hindered base lithium 2,2,6,6-tetramethylpiperidide, produce a red solution (79). The latter supposedly contains a boron-stabilized carbanion. Additional representatives of such boron-stabilized carbanions have been described elsewhere (53) and the triphenylcarbenium ion has been stabilized with BH_3 (224). The reaction of t-butoxy radicals with diborane(6) has been shown (71) to yield t-butyl radicals.

Interesting studies of the chemistry of allylboranes are continuing in the laboratories of B. M. MIKHAILOV. It has now been found (72) that, in contrast to the reaction of triallylborane with 1-chloro-3-methyl-1,2-butadiene, allene or 3-methyl-1,2-butadiene react with triallylborane only at elevated temperatures to yield derivatives of 3-borabicyclo(3.3.1)nonane as shown in the followin equation:



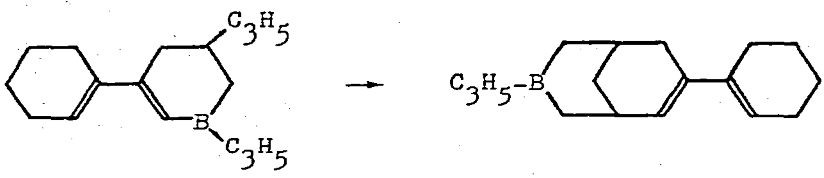
The illustrated product can be hydrogenated to the B-n-propyl derivative (46). If the latter is reacted with tetra-n-propyldiborane(6) hydroboration occurs to produce VII. This latter compour rearranges on addition of pyridine to yield tri-n-propylborane and the pyridine adduct of a 1-boratricyclodecane, VIII.

VII



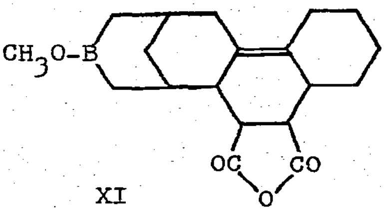
VIII

Triallylborane reacts with 1-ethynylcyclohexene to yield the cyclic organoborane IX, which thermally rearranges to X (39). Methanolysis of this product results in the replacement of the boron-bonded C_3H_5 group by OCH_3, and the resultant material was found to undergo a DIELS-ALDER reaction with maleic anhydride to produce the polycyclic system XI.



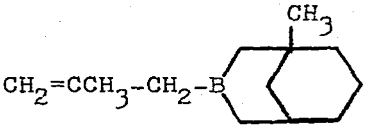
IX

X

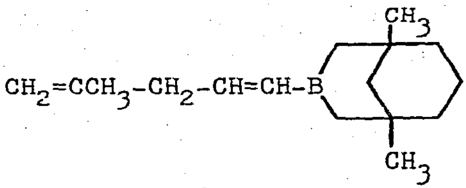


XI

Tris(2-methylallyl)borane is less reactive towards acetylene or 1-hexyne than triallylborane. For example, reaction with acetylene requires the use of an autoclave and temperatures of 140-150° (40). Depending on the ratio of reactants, the novel boranes XII or XIII are obtained.



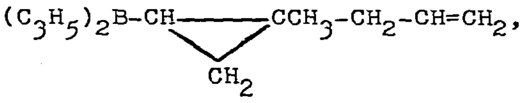
XII



XIII

Triallylborane reacts with 1-methylcyclopropene by

(a) cis addition of the diallylboron and allyl fragments to the double bond of the alkene leading to the formation of (cis-2-allylcyclopropyl)diallylborane,



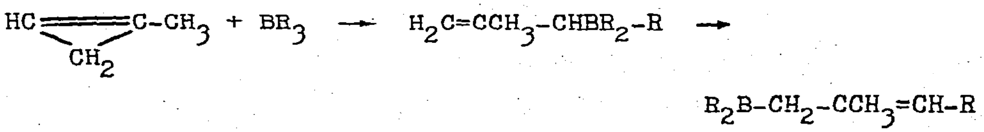
$$(C_3H_5)_2B\text{-}\underbrace{CH\text{———}CCH_3}_{CH_2}\text{-}CH_2\text{-}CH{=}CH_2,$$

and by

(b) cleavage of an annular bond of the alkene, whereby diallyl(2-methyl-2,5-hexadienyl)borane, $(C_3H_5)_2B\text{-}CH_2\text{-}CCH_3{=}CH\text{-}CH_2\text{-}CH{=}CH_2$, is obtained.

It was found (14) that the addition reaction occurs with allyl rearrangement whereas in the ring cleavage reaction the configuration of the allyl group is preserved.

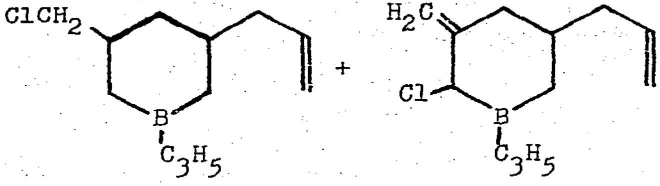
The reaction of 1-methylcyclopropene with trialkylboranes in a molar ratio of 2:1 seems to involve only ring cleavage and subsequent allylic rearrangement (24), as is illustrated below:



$$\underbrace{HC{=}C\text{-}CH_3}_{CH_2} + BR_3 \longrightarrow H_2C{=}CCH_3\text{-}CHBR_2\text{-}R \longrightarrow R_2B\text{-}CH_2\text{-}CCH_3{=}CH\text{-}R$$

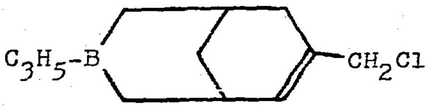
At room temperature, triallylborane reacts with 3-chloropropyn to yield an equilibrium mixture of products (274):

$HC\equiv C-CH_2Cl + B(CH_2-CH=CH_2)_3 \rightarrow$



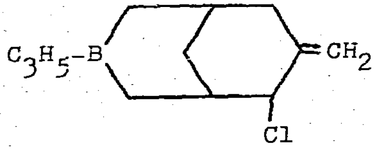
XIV XV

Compound XIV slowly cyclizes subsequently under formation of XVI.



XVI

On slow heating to 130° the cyclization occurs more rapidly and, und those conditions, XV isomerizes to XIV. Rapid heating of the equilibrium mixture to 130° also prompts the cyclization of XIV to XVI but XV is converted to XVII.



XVII

In other work (214) complex formation between triallylborane and 2,2'-bipyridine has been studied.

Hydroboration of 3-phenyl-1,2-butadiene with disiamylborane produces a substituted allylborane, i.e., disiamyl(3-phenyl-2-butenyl)borane, $CH_3-CC_6H_5=CH-CH_2-BR_2$ (88). The species undergoes the typical organoborane reactions with unsaturated compounds and a six-membered transition state involving allylic rearrangement was discussed for these processes.

(Allyl)aminoboranes are isoelectronic analogs of 1,4-dienes which have been found to undergo a photochemical reaction involving the 1,3-shift of an aminoboryl fragment to yield an isomeric species (222). But-1-en-3-yl(dimethylamino)ethylborane, $(CH_3)_2N\text{-}BC_2H_5\text{-}CHCH_3\text{-}CH{=}CH_2$, is a rather stable (allyl)aminoborane (146). Only when the compound is treated for several hours at 150°, thermal isomerization to yield $(CH_3)_2N\text{-}BC_2H_5\text{-}CH_2\text{-}CH{=}CHCH_3$ is accomplished. The rearrangement follows first order kinetics with the equilibrium being completely in favor of the latter compound.

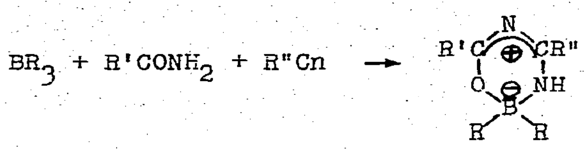
2.2 Applications and Physicochemical Studies

There seems to be no end to new applications of organoboranes in organic syntheses. A novel, general route from trialkylboranes to the corresponding carbon structures involves the base-induced reaction of boranes with α,α-dichloromethyl ethers (235,237); for example:

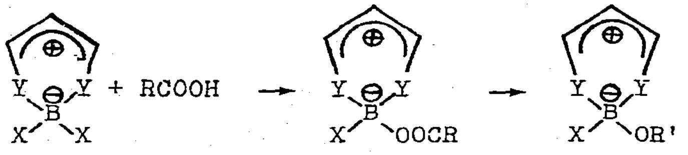
$$RR'R''B + CHCl_2OCH_3 \xrightarrow[-HCl]{\text{base}} RR'R''C\text{-}BCl\text{-}OCH_3$$

Other work (261) shows that pyridine promotes the 1,4-addition of tricycloalkylboranes to crotonaldehyde. Anodic oxidation of trialkylboranes (268) is a new type of alkyl coupling reaction of the organoboranes.

Details for the synthesis of N-acylamidines by the interaction of primary amides with nitriles in the presence of trialkylboranes have been reported (8). In this procedure, dialkylborylacylamidinates are obtained as intermediates; these can be hydrolyzed to give the respective N-acylamidines, $R\text{-}CO\text{-}N{=}CR'\text{-}NH_2$. A very convenient method for the preparation of the dialkylborylacylamidinates involves the direct synthesis as depicted below (276):

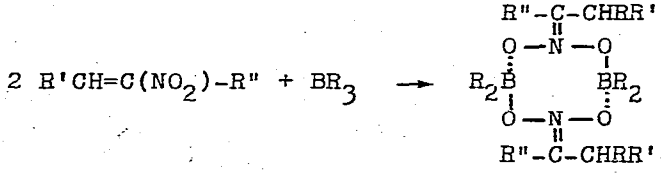


One of the boron-bonded alkyl groups is readily displaced with ace acid to give the corresponding B-acetoxy derivative. The structure of these chelates was confirmed by boron-11 ($\delta_{^{11}B}$ -5 ppm) and prot magnetic resonance studies as well as by infrared spectral data. When (2,4-pentanedionato)dipropylboron or (benzimidoylbenzamidinat dibutylboron is heated with carboxylic acids, one alkyl group on tl boron is replaced by acyloxy ; the chelate ring remains intact (273). The acyloxy group can subsequently be replaced by an organoc group.



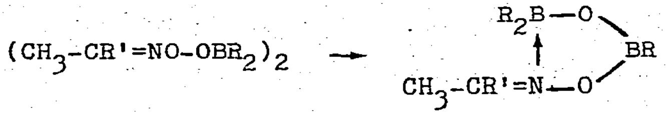
X = C_3H_7
Y = O, NH

Triethylborane reacts with nitro olefins to yield dimeric O-(diethylboryl) derivatives of aci-nitroalkanes (278):



R = C_2H_5

The structure of these coordinated cyclic species was confirmed by elemental analysis and spectroscopic data. Identical products are obtained by reacting diethylhaloboranes with sodium salts of aci-nitroalkanes (290). On standing the products rearrange spontaneously as shown below:



The light-induced reaction of bromine with thexyldialkylboranes (257) and with boracyclanes (279) in the presence of water has been studied. In the latter case, ring contraction of the boracyclanes occurs to produce carbocyclic structures. Also, N-bromosuccinimide has been used as halogenating agent for the α-bromination of triorganoboranes in the presence of water (42).

Other applications of organoboranes include the polymerization of acridine with trialkylboranes (175), of vinyl bromide with an alkylboron catalyst (156), of N-carboxy-α-amino acid anhydrides by organoboranes (171), as well as the preparation of organoboron surfactants (210) and a study of the potentials of organoboranes as flame retardants (157).
The oxidation of small quantities of trimethylborane was found to initiate the oxidation of isobutane under conditions where the latter is normally stable (244). In a study of the trialkylborane/oxygen system for radical polymerization by the spin trapping technique it was shown (190), that not only alkylperoxyboron radicals but also alkoxy radicals are formed and together they initiate the polymerization process.

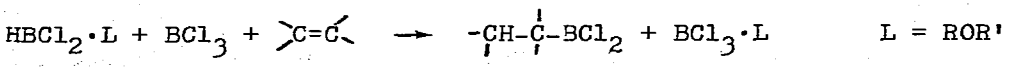
Infrared spectroscopic data as well as X-ray diffraction studies indicate that tris(ferrocenyl)borane exists in two different solid modifications (289), both of which are remarkably air stable. The crystal and molecular structure of bis-9-borabicyclo(3.3)nonane has been determined by X-ray diffraction (172). The molecule exists in the twin-chair form with flattened six-membered rings. An X-ray study of trimesitylborane (149) has confirmed the propeller conformation of the molecule in the crystal lattice; on the basis of nuclear magnetic resonance data, this form is retained in solution at low temperatu However, at higher temperatures, rapid stereoisomerization occurs has been interpreted in terms of a two-ring flip mechanism.

The existence of (ω-dialkylamino)dialkylboranes, $R_2N-(CH_2)_n-B$ as equilibrium mixtures of cyclic B-N coordinated and linear molecu forms is supported by boron-11 and proton nuclear magnetic resonanc data (23).

Boron-carbon coupling constants have been determined by carbon nuclear magnetic resonance spectroscopy (29) for various organoboro species such as triethylborane, triphenylborane, the teraphenylbora anion, BH_3CO and BH_3CN^- as well as for some vinylhaloboranes. The coupling constants were found to be very sensitive to the symmetry of the field surrounding the boron nucleus. Molecular orbital calculations on vinylborane (297) seem to indicate the existence of a considerable amount of boron-carbon π-bonding in vinylboron compo

3. ORGANOHALOBORANES

A new route to alkyldichloroboranes involves the reaction of olefins with dichloroborane-etherate in the presence of an equimola quantity of boron trichloride (78). The reaction can be depicted by the following equation:



$$HBCl_2{\cdot}L + BCl_3 + {>}C{=}C{<} \longrightarrow -\underset{|}{C}H-\overset{|}{\underset{|}{C}}-BCl_2 + BCl_3{\cdot}L \qquad L = ROR'$$

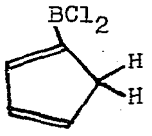
The reaction of chloroborane-etherate with alkynes has been used in similar fashion for the preparation of dialkenylchloroboranes (1

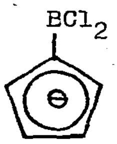
$$2\ RC{\equiv}CR + BH_2Cl \longrightarrow (HRC{=}CR)_2BCl$$

In this context it may also be noted that dichloroborane exhibits a enzyme-like selectivity and a remarkable speed for deoxygenating aliphatic sulfoxides (54); this reaction is shown below.

$$R_2SO + HBCl_2 \longrightarrow R_2S + HOBCl_2$$

Cyclopentadienyldichloroborane has been prepared by adding sodium cyclopentadienide to liquid boron trichloride (173). Apparently, the salt $Na(Cl_3BC_5H_5)$ is formed initially and decomposes near 300° under formation of the desired material. As indicated by proton magnetic resonance data, the structure of the compound is most likely as shown (XVIII); however, XVIII can be deprotonated to give XIX.


XVIII


XIX

Secondary or hindered trialkylboranes , BR_3, react with chlorodifluoromethane, $ClCHF_2$, in the presence of lithium triethylmethoxide, $LiOC(C_2H_5)_3$, to produce highly hindered esters of t-alkylfluoroboronic acids, $R_3C\text{-}BF\text{-}OC(C_2H_5)_3$ (201); the latter are remarkably stable to oxidation or alkaline hydrolysis.

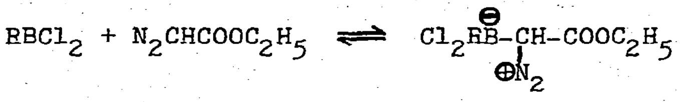
Alkyldichloroboranes react with organic azides in benzene solution with the formation of aminoboranes (77). The latter are readily

$$RBCl_2 + R'N_3 \longrightarrow RR'N\text{-}BCl_2 + N_2$$

hydrolysed; the reaction provides a facile synthesis of secondary amines.

In similar fashion, organodichloroboranes react with 2-iodoalkyl azides to produce β-iodo secondary amines which, on treatment with base, undergo ring closure to give N-organo aziridines (226).

At low temperatures alkyl- or aryldichloroboranes establish an equilibrium with ethyl diazoacetate (174),



$$RBCl_2 + N_2CHCOOC_2H_5 \rightleftharpoons Cl_2\overset{\ominus}{RB}\text{-}\underset{\oplus N_2}{CH}\text{-}COOC_2H_5$$

which is followed by loss of nitrogen from the saltlike structure and concurrent or subsequent migration of the R group or chlorine boron to carbon. The experimental data suggest a decrease in the migratory aptitude in the order aryl > alkyl > chlorine.

Alkyldichloroborane-etherates react readily with 0.5 molar equivalent of oxygen, which can be depicted by the following equat (227):

$$RBCl_2 + O_2 \rightarrow RO_2BCl_2$$
$$RBCl_2 + RO_2BCl_2 \rightarrow 2\ ROBCl_2$$

However, the second reaction step is decreased drastically in the presence of diethyl ether. Consequently, in a solution of the latt the reaction proceeds to take up one molar equivalent of oxygen ar hydrolysis of the reaction product provides alkyl hydroperoxides.

Boron trichloride reacts with cyclic alcohols to give the corresponding alkoxydichloroboranes, $ROBCl_2$; the latter decompose readily to form alkyl halides (242). The reaction of boron trihali with phenylacetylene leads to a mixture of (2-halo-1-phenylvinyl)-dihaloboranes and (2-halo-2-phenylvinyl)dihaloboranes (298). Subse reaction of these boranes with additional phenylacetylene produces bis(vinyl)haloboranes and tris(vinyl)boranes; the preferred stereo selective formation of specific materials in these reactions has t discussed in terms of different reactivity .

The standard enthalpies of formation of o- and p-tolyldichlor borane and, in conjunction with other data, the boron-carbon bond energies of the two compounds have been determined (296). Based on these data it was concluded that the electronic effect of the para methyl group on the B-C bond energy is small, but the ortho methyl substituent imposes a considerable steric effect on the boron-carb bond of aryldichloroboranes.

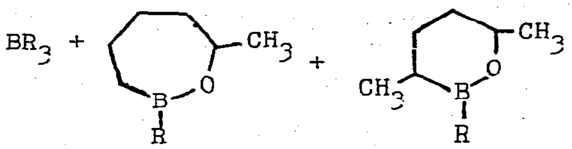
Finally, the halide B_8F_{12} has been synthesized and was found react with carbon monoxide to give the unusual compound $(BF_2)_3BCO$

4. CHALCOGEN DERIVATIVES OF ORGANOBORANES

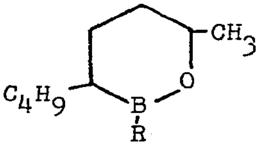
4.1 Organoboron-Oxygen Species

Hydroboration with tetraalkyldiboranes(6) has been used (25) for the preparation of 1,2-oxaborepanes as illustrated below:

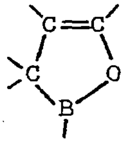
$$(R_2BH)_2 + CH_2{=}CH{-}CH_2{-}CH_2{-}CO{-}CH_3 \longrightarrow$$



The 1,2-oxaborepane ring is readily cleaved with halogenating agents such as phosphorus pentachloride or phosphorus pentabromide. Lithium tri-n-butylvinylborate reacts with methyloxirane to yield the 1,2-oxaborinane, XX, probably via thermolysis of a cyclic borate intermediate (260).The reaction of lithium trialkylalkynylborates with acyl chlorides has been used in a novel preparation of α,β-unsaturated ketones (262). The reaction proceeds via 2-oxa-3-bororenes, XXI.

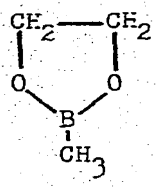


XX

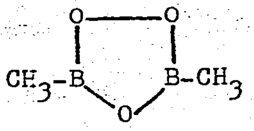


XXI

Pyrolysis of trimethylborane with ethylene glycol at 380° yields 2-methyl-1,3,2-dioxaborolane, XXII (103); the gas phase reaction of 1,1-dimethyldiborane(6) with oxygen at 80° affords 2,5-dimethyl-1,3,4-trioxadiborolane, XXIII, as the ultimate product (30, 140). Mass spectral and infrad data indicate that in this latter process dimethylboryl hydroperoxide, $(CH_3)_2B{-}O{-}OH$, is formed as



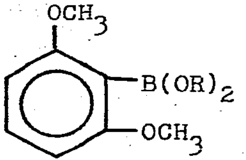
XXII



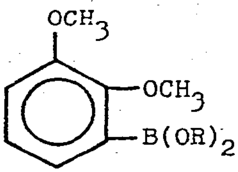
XXIII

an unstable intermediate product, which cocondenses to the borolane or may also rearrange to form dimethoxyborane.

Several new arylhydroxy(alkoxy)boranes of the types XXIV and XXV have been prepared by the interaction of lithium derivatives of alkoxyphenols with tris(methoxy)borane, $B(OCH_3)_3$ (247). A new



XXIV



XXV

R = H, alkyl

procedure for the preparation of alkoxyboranes, $(RO)_{3-n}BR'_n$, involves the interaction of the corresponding alkylthioboranes and tris(alkythio)stibines (64). Ligand exchange occurs in an exothermic reaction and the products are readily separated by distillation.

(Di-*n*-butyl)phenylthioborane reacts with ketene at low temperat under formation of a vinyloxyborane (5):

$$H_2C{=}C{=}O + R_2B\text{-}SC_6H_5 \rightarrow H_2C{=}C(SC_6H_5)\text{-}O\text{-}BR_2 \qquad R = C_4H_9$$

An alternate procedure for the preparation of vinyloxyboranes involv the reaction of trialkylboranes with α-diazocarbonyl compounds (231)

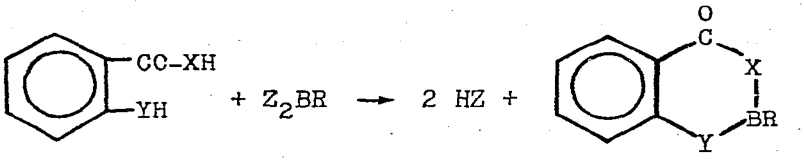
$$BR_3 + N_2CH\text{-}C(O)R' \rightarrow RCH{=}CR'\text{-}O\text{-}BR_2 + N_2$$

Vinyloxyboranes may be quite useful reactants in organic syntheses.

For example, with carbonyl compounds the following reaction has been observed (5):

$$R^1R^2C{=}CR^3{-}O{-}BR_2 + R^4R^5C{=} \longrightarrow R^3CO{-}CR^2R^1{-}CR^4R^5{-}O{-}BR_2$$

Various organoboron heterocycles of type XXVI have been prepared by the interaction of tris(dimethylamino)borane, bis(dimethylamino)phenylborane, or dichlorophenylborane and o-amino(hydroxy)benzenecarboxylic acids(amides) (102).

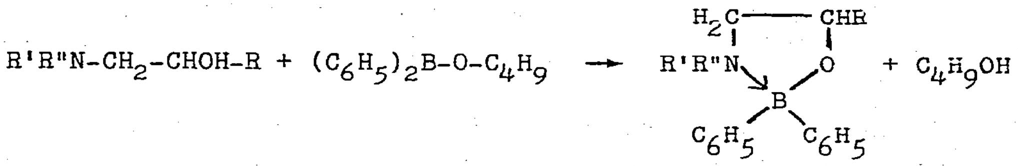


X = NH, O
Y = NH, O
Z = $N(CH_3)_2$, Cl
R = $N(CH_3)_2$, C_6H_5

XXVI

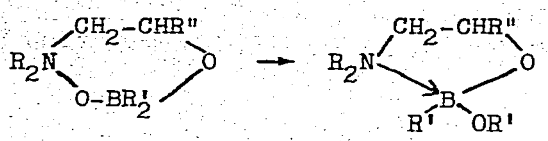
Compounds of type XXVI which contained at least one anular nitrogen atom were found to be hydrolytically quite stable, probably due to intermolecular association.

The interaction of diphenyl(isobutoxy)borane and amino hydroxy derivatives leads to coordinated cyclic species (48), e.g.:



The reaction proceeds even in those cases where R' or R" are fairly bulky groups. The diphenylboryl group is readily removed by transesterification with 1,3-propanediol or via oxidative elimination of phenyl(dihydroxy)borane.

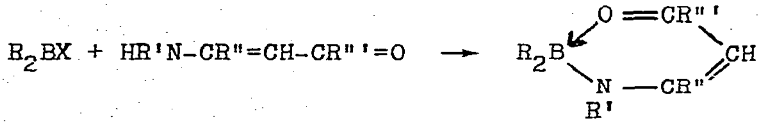
Diphenylboron esters of type XXVI undergo a thermal rearrangement to give XXVII (49).



XXVI XXVII

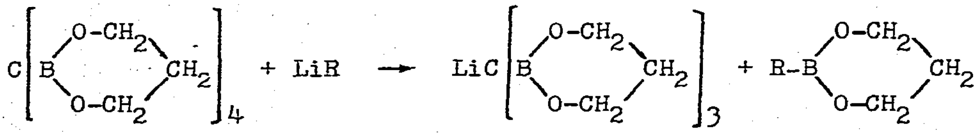
The latter compounds can also be obtained by the direct esterifi of phenyl(dihydroxy)borane with the corresponding aminoalcchols or aminophenols.

Diphenylhydroxyborane or 2-alkoxy-1,3,2-benzodioxaboroles react β-aminoenones to afford chelated compounds (264):

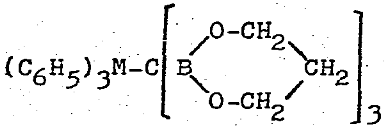


The structure of the latter was confirmed by proton magnetic reso studies. The non-equivalence of the two annular atoms bonded to b does not effect the stability of the chelates to any appreciable extent.

_n_-Butyllithium reacts with tetrakis(trimethylenedioxyboryl)-methane to yield the lithium salt of the tris(trimethylenedioxybo methide ion (229):



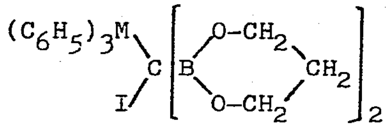
The salt can be isolated; it acts as a strong base, _e.g._, it abst proton from dimethylsulfoxide. However, the salt need not be isol but can be used _in situ_ for other reactions. For example, reactio of the salt with triphenyl derivatives of metals such as germaniu tin, or lead provides compounds of type XXVIII (119).



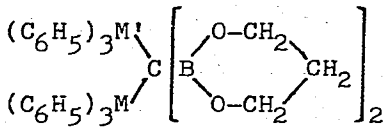
M = Ge, Sn, Pb

XXVIII

Subsequent treatment of XXVIII with n-butyllithium results in cleavage of another boron-carbon bond and the obtained lithium salt can react with elemental iodine to give XXIX, or again with a triphenyl metal derivative to give XXX. This process can be repeated to give acces to a variety of similar novel materials. The cleavage of a boron-carbon bond <u>via</u> treatment with n-butyllithium (or lithium methoxide) can also be effected on tetrakis(bismethoxyboryl)methane (120). Though the lithium salt was not isolated, reactions with triphenyl derivatives of metals such as those cited above are possible.



XXIX



XXX

The reaction of indenyllithium with chloro(dimethoxy)borane, $ClB(OCH_3)_2$, at low temperatures yields 1-indenyl(dimethoxy)borane in small amounts (293). The proton magnetic resonance spectrum of the compound suggests the presence of an allylic structure; this conclusion is also supported by boron-11 nuclear magnetic resonance data; no vinyl isomers were observed. It is interesting to note, however, that the action of water on 1-indenyl(dimethoxy)borane leads to cleavage of the boron-carbon bond, whereas an analogous reaction of water on allyl(dialkoxy)boranes yields the anhydride of the corresponding allylboronic acid.

Triphenylborane reacts with organic peroxides or organoboron peroxides even at room temperature (36). Analysis of the reaction products and the observed kinetic relations indicate that in the first stage of the reaction a radical mechanism predominates:

$$B(C_6H_5)_3 + ROOR' \longrightarrow (C_6H_5)_2BOR + C_6H_5\cdot + R'O\cdot$$

With increasing concentration of oxidation products, these latter may interact with the excess of triphenylborane. Further oxidatior of boron-carbon bonds is effected heterolytically. Alkaneboronic esters, $RB(OR')_2$, react with ($\underline{n}$-$C_4H_9O)_2B$-O-O-$\underline{t}$-C_4H_9 primarily by a molecular reaction though a radical mechanism can be substantiat as a second mode (99). Also, the photolytic decomposition of orgar boron peroxides has been studied (35) and a probable reaction sche for that process has been advanced.

The low temperature nuclear magnetic resonance spectra of alkoxydialkylboranes can be explained in terms of flip mechanisms for stereoisomerization (150). Analysis of the isomerization proce gives evidence of restricted rotation about a boron-oxygen bond.

The kinetics of the Lewis acid-catalyzed dealkoxyboronation c esters of *trans*-2-ethoxycyclohexane-dihydroxyborane in a variety c donor solvents have been studied (288). The dealkoxyboronation reaction seems to proceed *via* a concerted anti elimination transit state in which two donor molecules are associated with the incipie boronium ion. Relative rate studies on the mercuri-deboronation of (dimethoxyboryl)methanes, XCH_2-$B(OCH_3)_2$, with mercuric chloride illustrate the dependency on X for that process (199); the results were satisfactorily interpreted on the basis of a cyclic three-cer and four-center electron pair bonding in the transition state.

Two different crystalline forms of bis(ferrocenyl)hydroxybor have been isolated; they exist as separate entities even in soluti (289). Ferrocenylboronic anhydride exists as a cyclic dimer and trimer.

The light-induced reaction of dialkylhydroxyboranes with bron in the presence of water provides a simple procedure for the prep ationof highly substituted tertiary alcohols (256). *Trans*-1-alker hydroxyboranes react with iodine in alkaline medium (144) to yiel the corresponding trans-1-alkenyl iodides. 4,4,6-Trimethyl-1,3,2-dioxaborinane has been used for the hydroboration of several olefins (13). This reagent is more stable than most other common hydroborating agents and the hydroboration products can be directly isolated and identified.

The reaction of borane with alcohols leads to acid-base adducts, $ROH;BH_3$, as well as to alkoxyhydridoboranes, $(RO)_nBH_{3-n}$ (11). Apparently, adduct formation is the initial step in the interaction of borane and alcohols and the bimolecular rate constant for the reaction of BH_3 with 2-propanol is estimated to be 10^8 liter / mol x sec at 450°K and a total pressure of 4.5 torr.

Finally, a dihydroxyboryl substituted polymer has been used for the column chromatographic separation of neutral sugars (269).

4.2 Compounds Containing the BO_3 Group

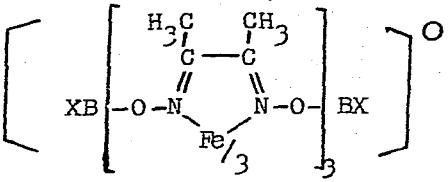
The preparation of tris(sec. alkoxy)boranes and their reactions with acetic anhydride or acetyl chloride has been reported (83). Tris(tri-n-butylgermyloxy)borane and several 2-tributylgermyloxy-1,3,2-dioxaborole, -borolane, and -borinane derivatives have been prepared by the reaction of tri-n-butylgermanium derivatives with appropriate boron compounds (203). The liquid materials are readily distilled and the B-O-Ge antisymmetrical stretching mode was found as a strong absorption near 1310 cm^{-1}.
Tris(tributylstannyloxy)borane, $B(OSnR_3)_3$ ($R = C_4H_9$), has been obtained by the following reaction (22):

$$2\ B(OH)_3 + 3\ (R_3Sn)_2O \longrightarrow 2\ B(OSnR_3)_3 + 3\ H_2O$$

The formation of B-O-Sn bonds has also been accomplished by the interaction of diols , boric acid and bis(tri-n-butyltin) oxide. A strong and broad infrared absorption in the 1275-1290 cm^{-1} region was assigned to the antisymmetric B-O-Sn stretching mode.

Various other boron-substituted derivatives of 1,3,2-dioxaborolane have been reported (178), in which the exocyclic boron substituent is F, Cl, Br, I, NH_2, $NHCH_3$, $N(CH_3)_2$, $P(CH_3)_2$, and CH_3.

Trimethoxyborane reacts readily with salicylhydroxamic acid in acetone solution under formation of a boron chelate (251). Low-spin iron(II) clathro chelates have been prepared in a simple one-step synthesis using iron salts, dimethylglyoxime, and either boron trifluoride or boric acid (96).The resultant cage complexes, XXXI, exhibit high thermal stability.



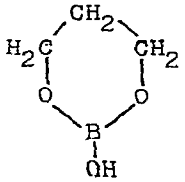
XXXI

X = F, OH, OCH_3, OC_2H_5, O-i-C_3H_7, O-n-C_4H_9

Trialkoxyboranes do not form Lewis acid-base adducts with nitrogen bases (176); rather they form onium salts in which the ani is a tetraalkoxyborate complex. Thermodynamic properties have been elucidated for some of these complexes, e.g., piperidinium tetrameth oxyborate (177).Also, thermodynamic properties have been determined for some substituted aryloxyboranes (271) and a mechanistic study describes the thermal cracking of tris(β-phenylaminoethoxy)borane, $B(O-CH_2-CH_2-NH-C_6H_5)_3$, which leads to reasonable yields of indole (1

The mass spectrum of tris(methoxy)borane indicates the facile l of a CH_3O unit as the most dominant process (181). The heat of formation of gaseous tris(phenoxy)borane has been determined (179) and was used to calculate a mean boron-oxygen dissociation energy of 437 kj/mol.

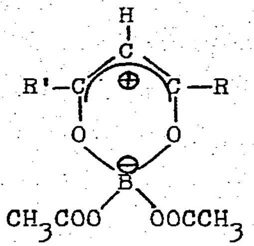
The structure of tetraacetyl diborate has finally been clarified by an X-ray crystallographic study (183). The observation of two abnormally long B-O bonds (1.56 Å) and two rather short ones (1.38 Å) was interpreted in terms of detailed valence neutralization. Other structural studies include an X-ray diffraction analysis of B-triethanolamine (169) and of the trihydrate of tri-n-propanolamine borate, $N(CH_2-CH_2-CH_2-O-)_3B$ (3). The latter molecule was found to have a threefold axis with a transannular B-N coordinate bond of 1.67 Å and the six-membered rings have chair configuration. Proton magnetic resonance studies have been reported on tris(alkoxy)boranes and tris(allyloxy)boranes (187) and tris(methoxy)borane was found to readily lose a CH_3O unit under electron impact (181). A crystal structure determination of meso-2,4-pentanediolhydroxyborane, XXXII, by X-ray diffraction (232) has shown that the $B(OC)_2$ fragment is nearly coplanar. Also, the crystal structure of potassium boromalate monohydrate has been studied (240).



XXXII

Boron-11 nuclear magnetic resonance data indicate that the interconversion of boric acid and the tetrahydroxyborate ion is pH dependent in aqueous solution (230). The interaction of borate anions and 1,2-dioles at pH 12 leads to 1:1 and 1:2 complexes; these are readily identified on the basis of their boron-11 chemical shifts, i.e., 6.1 and 10.1 ppm respectively; shift values for 1:1 complexes of borate ions with 1,3-dioles are 1.5 ppm.

Various spectroscopic data have been recorded for boroacetate complexes of several β-diketones and β-ketoesters (291). The infrared



XXXIII

spectra of these materials, XXXIII, are characterized by absorpti for the chelate group at 1540-1600 cm^{-1}, for the C-C-C arrangemer 1490-1570 cm^{-1}, and boron-oxygen stretching modes at 1365-1385 ar 1040-1075 cm^{-1} respectively.

Chelating agents such as 2-hydroxyacetophenone or salicylaldehyde form difluoroboron chelates (109). Three different basic types of materials were prepared in which the BF_2 group is linked to eithe two oxygen atoms, two nitrogen atoms, or one oxygen and one nitrc atom. On the basis of the experimental data it was concluded that stable chelates can always be obtained if the resultant cyclic sy contain six annular atoms and two formally conjugated bonds.

Bis(aminodiacetatoboranes) of the type $B(OOCR)_2NH_2$ $_2$ with R = $CH_{3-n}X_n$ (X = F, Cl, Br) have been prepared by the reaction of B-t chloroborazine with the appropriate acetic acid derivatives (4). structures of the species were elucidated by infrared and nuclear magnetic resonance spectroscopy and a detailed procedure for the preparation of the parent compound (R = CH_3) has been described e where (138).

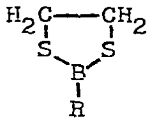
Of interest to the synthetic chemist may be the observation boron tris(trifluoroacetate), $B(OOCCF_3)_3$, can be used equally wel as boron tribromide or boron triiodide for the removal of protect groups in peptide chemistry under mild conditions (125). The ready determination of borate ion as phenylmercuric borate by flameless atomic absorption spectroscopy (211) may be useful for analytical purposes.

4.3 Sulfur and Selenium Derivatives

Diborane(6) was found to react in toluene solution with thiophenol to yield phenylthioborane, $C_6H_5SBH_2$ (32). The latter compound reacts slowly with ethers, but a freshly prepared solution of phenylthioborane in tetrahydrofuran readily dissolves potassium tetrahydridoborate under formation of the salt $K[C_6H_5S(BH_3)_2]$. The latter species was also prepared from equimolar amounts of potassium thiophenolate and diborane in toluene.

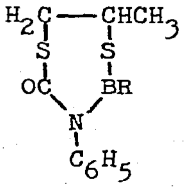
Several thioboranes of the general formula $(C_6H_5)_nB(SR)_{3-n}$ have been prepared by the interaction of lead thiolate and the corresponding haloboranes (154). A boron-sulfur stretching vibration was assigned for these compounds in the 900-960 cm^{-1} frequency range.

Various derivatives of 1,3,2-dithioborolane, XXXIV, have been described (178). These compounds are monomeric in solution and show greater thermal stability than the corresponding 1,3,2-dioxaborolanes.

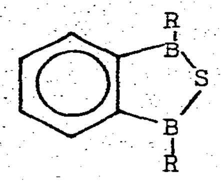

XXXIV

R = F, Cl, Br, I, NH_2, $NHCH_3$
$N(CH_3)_2$, $P(CH_3)_2$, CH_3

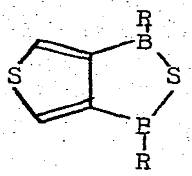
Also, several derivatives of 4-methyl-1,3,2-dithiaborolane have been reported (70). These compounds were found to react with phenyl isocyanate in 1:1 molar ratio to yield ring expansion products of the type XXXV.


XXXV

Other heterocyclic species containing annular boron-sulfur bonds are the two thiodiborole systems XXXVI and XXXVII (166). The sulfur



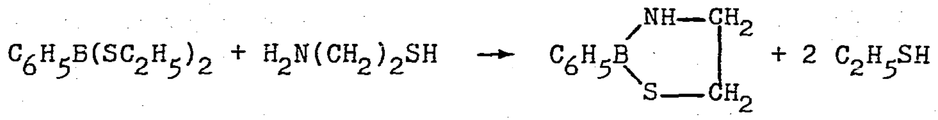
XXXVI



XXXVII

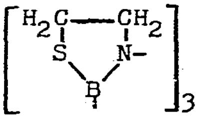
bridge in these materials is readily displaced by proton acti agents such as amines.

Cysteamine (2-aminoethanethiol) derivatives of boron contai skeleton B-S-CH_2-CH_2-NH as a structural unit. Such materials hav been prepared (195) as indicated by the following equation:



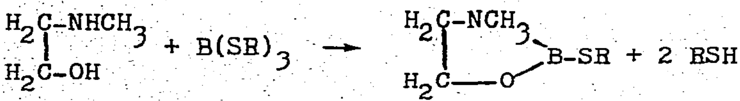
The resultant heterocycle readily dimerizes, a process which can be observed by a frequency shift in the NH stretching mode f 3425 to 3215 cm^{-1}.

Tris(dialkylamino)boranes react with cysteamine in a manne analogous to that depicted in the above equation. However, the resultant heterocycle is unstable and, in the reaction of tris(di amino)boranes with cysteamine, only the condensation product of monocyclic system, i.e., the borazine derivative XXXVIII, can be isolated (195).

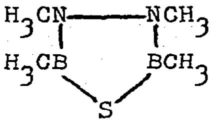


XXXVIII

Tris(alkylthio)boranes react with difunctional organic comp under formation of heterocyclic species (165) as outlined in the following equation:

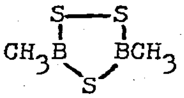


A different heterocyclic system is obtained when bis-(methylthio)methylborane, $CH_3B(SCH_3)_2$, is reacted with N,N'-dimethylhydrazine to yield an intermediate species, $CH_3S\text{-}BCH_3\text{-}NCH_3\text{-}NCH_3\text{-}BCH_3\text{-}SCH_3$ (6). The latter reacts with hydrogen sulfide affording the heterocycle XXXIX.



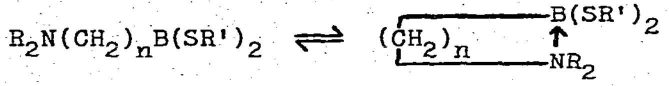
XXXIX

Hydrogen sulfide reacts with boron trihalides, BX_3 (X = Cl, Br, I), under formation of the three possible species X_2BSH, $XB(SH)_2$, and $B(SH)_3$ (255). All of these are rather unstable and cyclize to afford $(\text{-}BX\text{-}S\text{-})_3$ or $(\text{-}BSH\text{-}S\text{-})_3$, respectively. The vibrational spectra of dihalothioboranes, X_2BSH (X = Cl, Br, I), have been studied (17) and the boron atom was found to exhibit the same sp^3 hybridization as in the boron trihalides. The boron-sulfur bonds in $(\text{-}BSH\text{-}S\text{-})_3$ are considerably longer than expected (168) ; experimental values of 1.813 Å (exocyclic B-S distance) and 1.803 Å (anular B-S distance) were determined. The bond distances in thioborane, HBS, are B-H = 1.169 Å and B-S = 1.599 Å (253). Electron diffraction studies on dimethyl-1,2,4-trithio-3,5-diborolane, XL, substantiate a nearly planar arrangement for the anular atoms (92); the observed bond lengths are B-S = 1.80 Å, S-S = 2.08 Å, and B-C = 1.57 Å. Similar values (S-S = 2.07 Å, B-Cl = 1.76 Å) were found for the analogous B-dichloro derivatives (91).



XL

Proton and boron-11 magnetic resonance data demonstrate that bis(alkylthio)(ω-dialkylaminoalkyl)boranes exist as equilibri mixtures of linear and cyclic coordinated forms (23):



$$R_2N(CH_2)_nB(SR')_2 \rightleftharpoons (CH_2)_n \begin{cases} B(SR')_2 \\ \uparrow \\ NR_2 \end{cases}$$

The mass spectral fragmentation patterns of 4-methyl-1,3, borolanes have been discussed in detail (70) and the mass spect of tris(methylthio)borane has also been examined (181). The lat shows a fairly intense peak for the parent ion, which is in co to the spectrum of tris(methoxy)borane, where loss of a OCH_3 g was found to be the most dominant process.

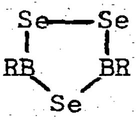
(Di-n-butyl)phenylthioborane reacts with ketene at low te under cleavage of the sulfur-boron bond (5) to yield a vinylbo

$$H_2C{=}C{=}O + R_2B(SC_6H_5) \rightarrow H_2C{=}C(SC_6H_5){-}O{-}BR_2$$

The exothermic reaction of thioboranes with trialkoxystibines by ligand exchange (64); since the resultant alkoxyboranes and (alkylthio)stibines are readily separated by distillation, the can be utilized for the preparation of alkoxyboranes.

The boron-sulfur bond distance in gaseous (methylthio)dim borane, $CH_3SB(CH_3)_2$, has been determined by electron diffracti 1.78 Å (314) as compared to 1.80 Å in tris(methylthio)borane (Both molecules are essentially planar with B-S-C bond angles and 104°, respectively, and sulfur-carbon bond distances of 1.

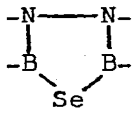
Elemental selenium reacts with a wide variety of boranes, triorganoboranes, diiodoorganoboranes, dialkyldiborane(6), tet diborane(6), to yield triselenodiborolanes, XLI (65).



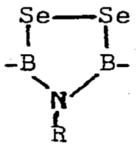
XLI

However, when diorganoboranes, R_2BX (X = H, I), are reactwed with elemental selenium or dicyclopentadienyltitanium pentaselenide, diborylselenanes, $R_2B\text{-}Se\text{-}Se\text{-}BR_2$, can be isolated. The latter decompose on thermal treatment to yield triselenodiborolanes, selenium, and triorganoboranes.

Triselenodiborolanes react with hydrazine or primary amines to form the novel heterocycles XLII and XLIII, respectively (65).



XLII



XLIII

5. BORON-NITROGEN CHEMISTRY

5.1 Aminoboranes

The synthesis of (amino)dichloroboranes by the interaction of alkyldichloroboranes and organic azides (77) has already been mentioned (see Section 3). Pyrolysis of trialkylboranes with primary or secondary amines leads to (amino)dialkylboranes. If triethylborane is used, the addition of diethylborylpivolate catalyzes the reaction and provides for much milder conditions (26). Apparently, the catalyst forms an intermediate adduct with the amine, and this adduct subsequently reacts with an additional amine molecule under transfer of the diethylboryl moiety:

$$(CH_3)_3C\text{-}COO\text{-}B(C_2H_5)_2 + 2\ H_2NR \longrightarrow RHN\text{-}B(C_2H_5)_2 + RNH_3^+\text{-}C(CH_3)_3CO_2^-$$

The salt, in turn, reacts with triethylborane to regenerate the amine/catalyst adduct with the elimination of ethane:

$$RNH_3^+\text{-}C(CH_3)_3CO_2^- + B(C_2H_5)_3 \longrightarrow C_2H_6 + (CH_3)_3C\text{-}COO\text{-}B(C_2H_5)_2 \cdot H_2NR$$

Several (amino)dimesitylboranes have been synthesized by conventional methods and were found to be fairly stable to ai water, and dilute acid or base (200).

Boron trichloride reacts with *t*-butyl-trimethylsilylamin yield the aminoborane $(CH_3)_3Si-NR-BCl_2$ (R = *t*-C_4H_9); at 150° compound eliminates chlorotrimethylsilane under formation of borazocine, $(-NR-BCl-)_4$ (105).

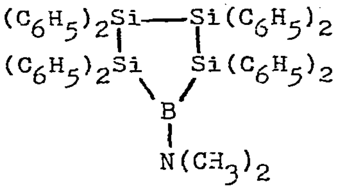
Diborane(6) reacts with (methyl)phenyl isocyanate to yiel N-methyl(phenyl)-N-borylformamide, which exists as a cyclic t $(H_2B-NR-CHO)_3$ (180). It may also be noted that pentameric amin $(H_2B-NH_2)_5$, has been obtained by the decomposition of a soluti $[H_2B(NH_3)_2]BH_4$ in monoglyme in the presence of ammonia (5). Fu more, it has been found that bis(ammine)boronium tetrahydridob will convert to ammonia-borane, $H_3N\cdot BH_3$, in polyether solutio contain diborane(6) (208). No hydrogen gas is evolved during process!

The gas phase cryochemical reaction of boron trichloride ammonia leads to the formation of aminodichloroborane, H_2N-BCl The infrared spectrum of the condensed species (-196°) has bee recorded but no assignment of fundamentals was attempted.

The kinetics of rotational isomerization about the B-N b *p*-substituted aryl(benzylmethylamino)chloroboranes were examin nuclear magnetic resonance studies. The rotational barrier was to decrease as the electron withdrawing power of the para subs (dimethylamino, methoxy, hydrogen, chlorine, nitro) increased

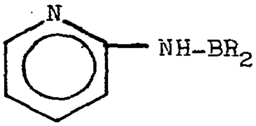
A number of aminoboranes containing a B-N-Si, B-N-Ge, or grouping have been prepared by various organometallic reaction 128). It is noteworthy that N-silylation results in an enhance of shielding at the adjacent boron nucleus as compared to N-st ation (128). Also, several compounds of the type $R_2P(S)-NR'-BR$

been described (129). Thiophosphorylation at the nitrogen of an aminoborane also results in deshielding of the boron atom which was correlated to a weakening of the boron-nitrogen bond. The unusual aminoborane XLIV, containing a boracyclopentasilane ring has been synthesized (126) and was found to exhibit an extremely low boron-nitrogen stretching frequency at 1394 cm^{-1}.



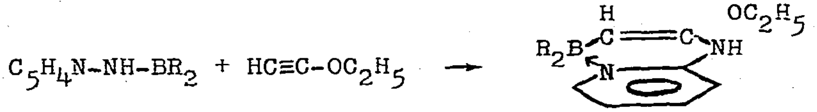
XLIV

Upon refluxing trialkylboranes with 2-aminopyridine in tetrahydrofuran, (2-pyridylamino)dialkylboranes, XLV, have been obtained (73). The (2-pyridylamino)dialkylboranes can add to unsaturated compounds to afford inner complexes:



XLV

R	b.p. (mm Hg)
n-C_3H_7	83-35° (0.6)
n-C_4H_9	113-117° (0.7)
i-C_4H_9	89-90° (0.4)



Supposedly, aldehydes, ketones, isocyanates, and isothiocyanates can undergo analogous reactions with the pyridylaminoboranes.

Various photochemical studies on boron-nitrogen derivatives have been reported. For example, a photochemical rearrangement involving the 1,3-shift of an aminoboryl fragment has been described for allyl(amino)boranes (222):

$$(CH_3)_2N\text{-}BC_6H_5\text{-}CHCH_3\text{-}CH{=}CH_2 \longrightarrow (CH_3)_2N\text{-}BC_6H_5\text{-}CH_2\text{-}CH{=}CHCH_3$$

The B-ethyl derivative of the former species has been found to an analogous isomerization on thermal treatment at 150° for se hours (146).

(Methylphenylamino)alkylphenylboranes undergo a general photoc reaction, i.e., an excited state cleavage of a boron-alkyl bon This process is illustrated by the following example:

$$(CH_3)(C_6H_5)N\text{-}B(C_6H_5)(R) \xrightarrow[CCl_4]{h\nu} \begin{array}{l} (CH_3)(C_6H_5)N\text{-}B(C_6H_5)(Cl) \\ (CH_3)(C_6H_5)N\text{-}B(C_6H_5)(CCl_3) \end{array}$$

This boron-alkyl cleavage has no parallel in the solution phase chemistry of the isoelectronic stilbene analogs!

In carbon tetrachloride solution, tetrakis(dimethylamino)dibora also undergoes a photochemical reaction at 300 nm, affording primarily chlorotris(dimethylamino)diborane(4) (148). Howeve distinct solvent effect was observed for this reaction. Utilizi less chlorinated solvents such as chloroform, some hydrogenatio boron was found to occur; in methylene chloride, tris(dimethyla borane was found to be the major product of the photolysis.

Iminoborane derivatives containing the C=N-B skeletal unit generally linear when carbon substituents are too bulky to perf a bridging role (164). These conclusions are supported by an in and nuclear magnetic resonance study on $[(t\text{-}C_4H_9)_2C{=}N]_2BX$ and o $[(t\text{-}C_4H_9)_2C{=}N]_3B$; the latter apparently adopts a paddle-wheel s More definite proof has been obtained by a X-ray diffraction st on (diphenylmethyleneimino)dimesitylborane (194). The BNC unit this molecule has an allene-like geometry with a boron-nitrogen distance of 1.38 Å, a N-C distance of 1.29 Å and a B-N-C bond angle of 173°; molecular orbital calculations indicate that the B-N bond order is about 1.6, whereas the C-N bond order approximates 1.8. On the other hand, some boron-11 nuclear magnetic resonance and dipole studies (272) do not seem to substantiate the generally assumed similarity of iminoboranes to allenes. These latter investigations were performed on some monomeric iminoboranes derived from the interaction of (dialkylamino)boranes and imine hydrochlorides as depicted in the following reaction scheme:

$$(3-n)\ (C_6H_5)_2C{=}NH_2Cl + R_nB\left[N(C_2H_5)_2\right]_{3-n} \longrightarrow$$

$$\left[(C_6H_5)_2C{=}N\right]_{3-n}BR_n + n\ (C_2H_5)_2NH_2Cl$$

$$R = \underline{n}\text{-}C_3H_7,\ \underline{n}\text{-}C_4H_9,\ C_6H_5$$

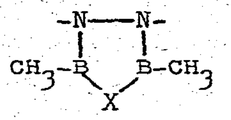
A boronium salt intermediate was postulated for this reaction.

A new type of iminoborane species has been obtained by the reaction of boron trifluoride with S,S-dimethyl-N-(trimethylsilyl)-sulfoximide, $(CH_3)_3Si{-}N{=}SO(CH_3)_2$, which proceeds to form iminoboranes of the type $F_{3-n}B\left[N{=}SO(CH_3)_2\right]_n$ (n = 1, 3) (110).

It may be of interest to note that *ab initio* molecular orbital calculations of the (non-existent) 1,3,2,4-diazadiboretidine, $(-NH-BH-)_2$, have been reported (9). The data appear to indicate that this cyclobutadiene analog would be more stable by about 74.3 kcal/mole. than two iminoborane monomers, HN=BH.

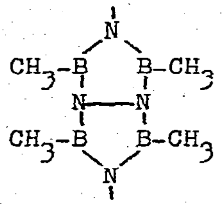
Among the most notable species containing the structural unit B-N-N are the 1-pyrazolylborates. However, since most of their chemistry involves transition metal complexes in which they function as ligands, this group of compounds will be discussed in Section 7. Various other heterocycles containing an anular B-N-N arrangement have been prepared by the reaction of bis(methylthio)methylborane,

$CH_3B(SCH_3)_2$, with hydrazines and subsequent treatment with primary amines, water, or hydrogen sulfide (6). For example, heterocycles o type XLVI have been described and even the bicyclic system XLVII is known.



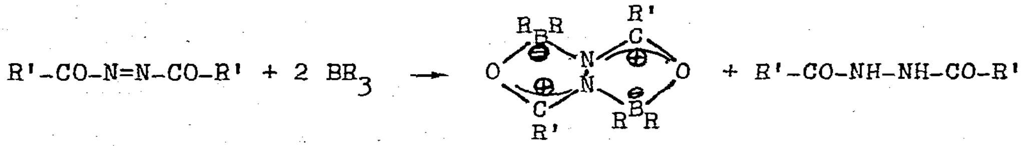
X = O, S, NH, NR

XLVI



XLVII

The skeletal unit B-N-N is also found in several coordinated heterocycles which are best formulated as inner salts. These were obtained (41) when azidodicarbonic acid diethyl esters were reacted with trialkylboranes according to the following scheme:



$R = C_2H_5$, $\underline{n}$-C_4H_9
$R' = OC_2H_5$, C_6H_5

The structure of the heterocyclic system was confirmed by infrared, proton magnetic resonance and mass spectral data.

Boron-11 and nitrogen-14 nuclear magnetic resonance data have been collected for a variety of aminoborane derivatives including heterocyclic species containing anular boron atoms (101). The observe nitrogen-14 chemical shift data were discussed in terms of relative contributions of the free electron pair on nitrogen to the boron-nitr π-bonding. It is noteworthy that the nitrogen-14 nuclear magnetic resonance spectrum of azidodimethylborane, $(CH_3)_2BN_3$, exhibits only two of the three expected resonance lines (87).

Bis(*n*-butylamino)-*n*-butylborane, b.p. 83-85° (3 mm Hg), and ris(*n*-butylamino)borane, b.p. 87-90° (3 mm Hg), were prepared by standard procedures (112); their heats of combustion were experimentally letermined to be -2158 kcal/mole and -2171 kcal/mole, respectively. From these data standard heats of formation were calculated for the wo aminoboranes. Heats of combustion have also been determined for ris(diethylamino)borane (136) and for (dimethylamino)methoxy-butyl-orane, $(CH_3)_2N\text{-}BOCH_3\text{-}C_4H_9$ (135).

Studies on tris(2,2-dimethylhydrazino)borane have shown (93) hat the molecule is planar with respect to the $B(N\text{-}N)_3$ fragment of he molecule and the B-N bond distance was determined to be 1.42 Å. As determined by X-ray diffraction (75), cyclotriborazane, $(H_2N\text{-}BH_2)_3$, he inorganic analog of cyclohexane, exists in the chair form and the oron-nitrogen bond distance is 1.58 Å. An X-ray diffraction study (197) has also shown that $[(C_6H_5)_2P\text{-}BH_2]_3$ exists in two crystalline modifications (α, triclinic; β, monoclinic). The mean B-P distance of 1.85 Å seems to dispute any possibility for B-P π-bonding in that molecule. Also, stuructural parameters of N,N-dimethylaminodiborane(6) have been clarified by microwave spectroscopy (155) and extended ückel calculations have been reported for the yet unknown bis-amino)diborane(4), $H_2N\text{-}BH\text{-}BH\text{-}NH_2$, as well as for (amino)vinylborane, $H_2{=}CH\text{-}BH\text{-}NH_2$ (97).

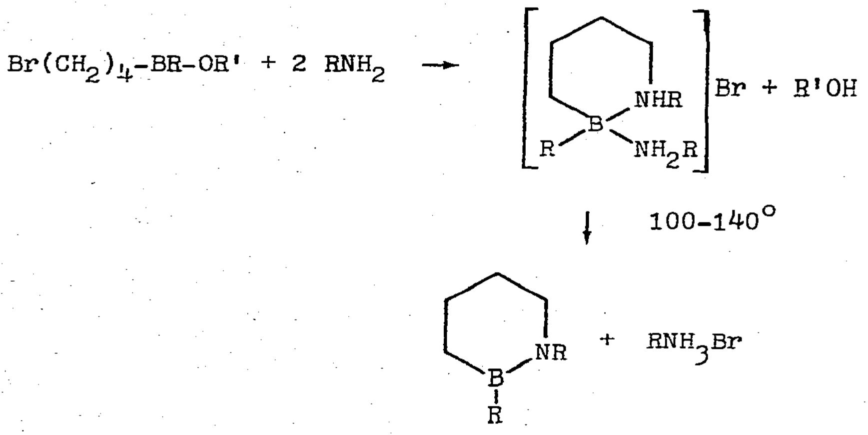
Finally, a practical application of aminoboranes deserves entioning: It has been found (130) that *t*-butylaminoborane forms energy enters for nondevelopable silver centers on silver halide surfaces.

5.2 Boron-Nitrogen-Carbon Heterocycles

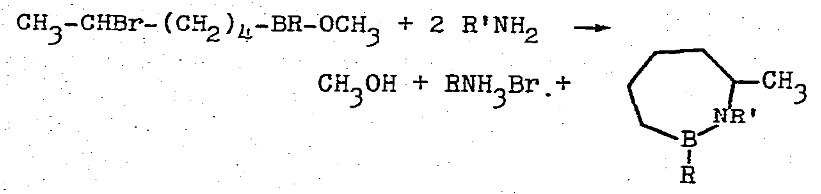
Pyridine dibromide reacts with pyridine adducts of 1-alkylborolanes under cleavage of the borolane ring (265) and this proc has been used for the preparation of (alkyl)(4-bromobutyl)alkoxybc $Br(CH_2)_4$-BR-OR'. The latter react with bisaminoboranes (37) as illustrated in the following equation:

$$2\ Br(CH_2)_4\text{-}BR\text{-}OR' + R''B(NHR)_2 \longrightarrow 2\ Br(CH_2)_4\text{-}BR\text{-}NHR + R''B(OR'$$

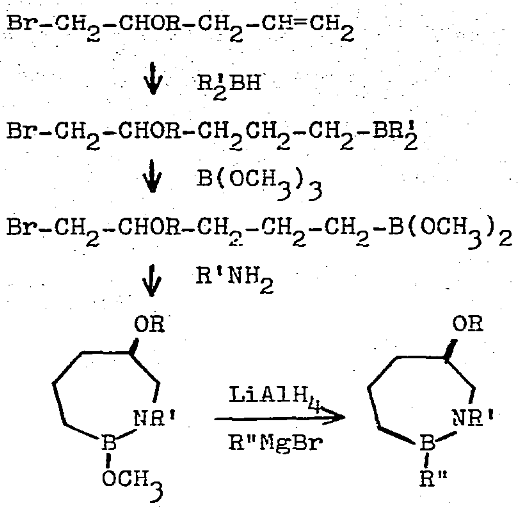
If these same alkoxyboranes are reacted with primary amines, howev boronium salts are initially obtained. At higher temperatures, the latter decompose under formation of cyclic azaborines, as is shown in the following sequence:



Alkyl(bromoalkyl)alkoxyboranes have also been used (100) for the preparation of 1,2-azaborepanes:

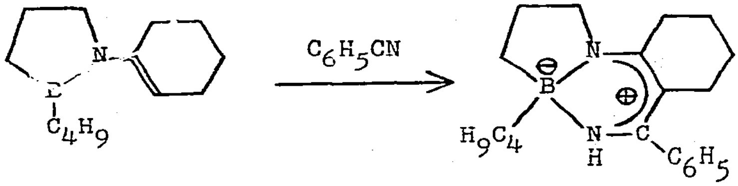


An alternate route to this same heterocyclic system (47) is illustrated in the following sequence:

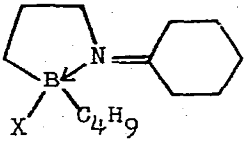


Some general chemical and physical data on 1,2-azaborepanes are presented elsewhere (100).

2-Butyl-1-(1-cyclohexen-1-yl)-1,2-azaborolidine reacts with benzonitrile to a tricyclic chelate (19) as shown in the following equation:



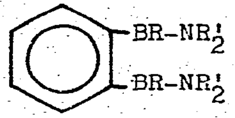
Various other agents such as acetic acid, hydrogen chloride, and alcohols react with the same 1,2-azaborolidine to yield inner complexes having an imino form, XVIII.



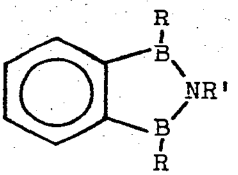
X = Cl, OR, CH_3CO

XLVIII

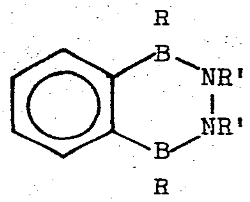
The boron-sulfur bond of the heterocyclic systems XXXVI and XXXVII (see Section 4.3) is readily cleaved under displacement of the sulfur (166). The reaction with secondary amines leads to the formation of ortho-boryl species such as XLIX , whereas with prima amines or N,N'-dialkylhydrazine the novel heterocyclic systems L and LI , respectively, are obtained.



XLIX



L



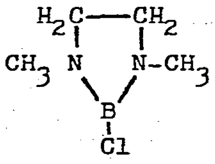
LI

The interaction of bis(dimethylamino)chloroborane and N,N'-dimethyl-α,ω-diamines yields primarily 1,3-dimethyl-2-dimethylamin diazaboracycloalkanes (10).

$$ClB(NR'_2)_2 + HRN-(CH_2)_n-NRH \longrightarrow R'_2NH_2Cl + R'_2N-B(-NR-(CH_2)_n-N$$

No 2-chloro heterocycles are obtained but tris(dimethylamino)boran is formed as a byproduct. These data seem to infer a two-step mechanism for the reaction in which a transamination occurs initial with generation of dimethylamine and is followed by intramolecular condensation under elimination of hydrogen chloride. Competing with this reaction, the free dimethylamine may react with the excess of bis(dimethylamino)chloroborane <u>via</u> aminolysis of the boron-chlorine bond.

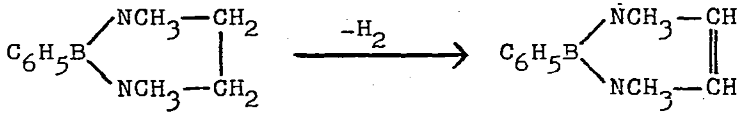
Gas phase electron diffraction studies (127) have shown that t five-membered heterocycle of 1,3-dimethyl-2-chlorodiazaboracyclopen LII, is essentially planar and the boron-nitrogen bond distance is 1.41 Å. Also, the distance B-Cl was found to be 1.77 Å and the obse bond angles were N-B-N = 111° and C-N-B = 109°.



LII

The vibrational spectra, proton and boron-11 nuclear magnetic resonance spectra and the tin-119 Mössbauer spectra of 1,3-dimethyl-2-trimethylstannyldiazaboracyclopentane and the corresponding six-membered heterocycle have been recorded (94). Apparently, the boron-bonded trimethylstannyl group exerts little influence on the electronic environment of the organoboron-nitrogen heterocycle.

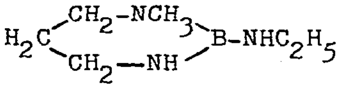
The first 1,3,2-diazaborolin, LIII, has been obtained (86) by dehydrogenation of the corresponding saturated species:



LIII

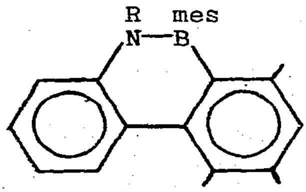
The ring system of LIII is isoelectronic with the cyclopentadienide anion; molecular orbital calculations indicate that the latter and LIII have similar π-electron donor capabilities.

The reaction of tris(ethylamino)borane with N-methyl-1,3-diaminopropane also leads to the 1,3,2-diazaboracycloalkane system (165). However, the resultant compound, LIV, readily loses ethylamine and trimerizes to yield a borazine derivative.



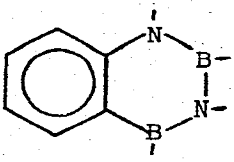
LIV

(Anilino)dimesitylboranes photocyclize in the presence of iodine (200). The reaction is accompanied by a facile 1,2-methyl migration and leads to a B-mesityl-trimethylborazarophenanthrene, LV.

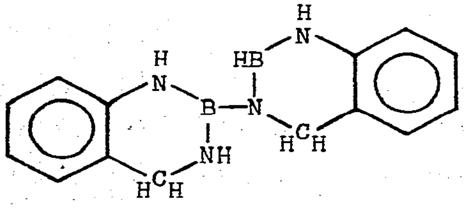


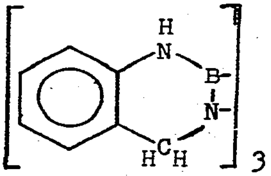
LV

The chemistry of adducts of aromatic amines with boron triiod differs substantially from that of the adducts with the lower boro halides. Most pronounced appears to be the ready formation of 1,3 diaza-2,4-diboranaphthalene derivatives, LVI, in dehydrohalogenati reactions of the amine-triiodoboranes (198). However, the condensa of aromatic amine halides with boron trichloride provides the same heterocycle and. in addition, yields N-asymmetric borazines (249). Spectroscopic data on these species have been reported (282).


LVI

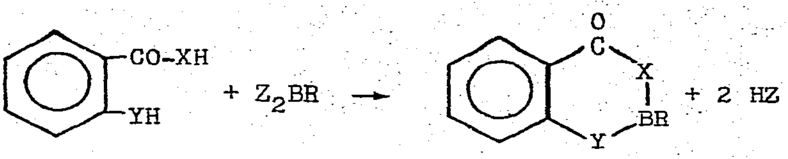
The low temperature (-5 to +35°) reaction of diborane(6) with 2-amino-benzonitrile yields 2-cyanophenylamine-borane, bis(2-cyano-phenylamino)borane, and the heterocycle LVII (111). At elevated temperatures (85°), the borazine LVIII is obtained as the primary product.


LVII


LVIII

Analogous reactions of 2-amino-1-cyano-1-cyclopentene yield only bis(2-cyano-1-cyclopentenylamino)borane and polymeric products.

The condensation of some ortho-substituted benzoic acid derivat with several boranes (102) is illustrated in the following equation:



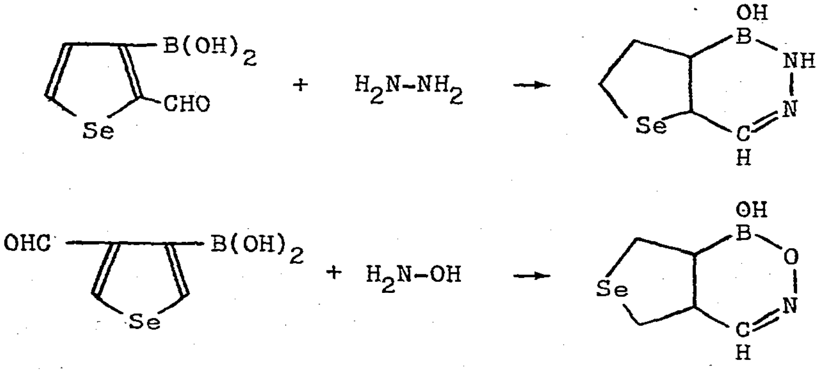
LIX.

$X = NH, O \qquad Z = N(CH_3)_2, Cl$

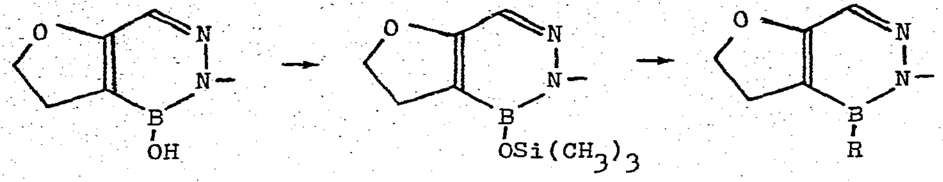
$Y = NH, O \qquad R = N(CH_3)_2, C_6H_5$

Those compounds of type LIX containing at least one NH group bonded to the boron atom were found to be quite stable toward hydrolysis. On the basis of infrared spectroscopic studies, this stability is linked to intermolecular hydrogen bonding.

Several boron-containing selenophene derivatives have been prepared by the replacement of α-hydrogen or of bromine of selenophenes with the dihydroxyboryl group (313). If this is reaction is performed with selenophene aldehydes, subsequent condensation with hydrazine or hydroxylamine provides for an easy entry into bicyclic derivatives as is illustrated in the following equations:



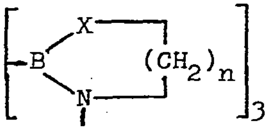
An interesting and novel means of organosubstitution at an annular boron atom involves the use of silyl ether derivatives of hydroxyboranes as intermediates (18); for example, the reaction illustrated:



5.3 Borazine Chemistry

Apart from some syntheses of hexasubstituted polyborazines (3 and mixed polyborazines (307) very little attention has been devot to the development of novel synthetic procedures in borazine chemi However, tris(alkylthio)boranes, $B(SR)_3$, have been reacted with amino alcohols and mercaptans (165) and, provided the amino group a primary one, thorough condensation was found to occur yielding polycyclic borazines as illustrated by the following equation:

$3\ B(SR)_3 + 3\ HX\text{-}(CH_2)_n\text{-}NH_2 \rightarrow 9\ RSH +$



$X = O, S;\ n = 2, 3$

Various unsymmetrically boron-substituted NH-borazines have been prepared in which the boron substituents were H, Cl, CN, and OCN (28, 139). Proton magnetic resonance studies on these compounds indicate an additivity relationship for the effects of the substitu of boron-disubstituted borazines on the chemical shift of the nitrog protons, provided the ortho and para NH protons of the corresponding B-monosubstituted species are magnetically equivalent (139). Proton magnetic resonance spectra of a number of B-substituted N-trimethyl-borazines have also been analyzed in terms of characteristic group contributions to the chemical shift (58). A correlation between the structural and electronic parameters and solvent induced shifts was established. Also, some spectroscopic studies on borazines containin bulky aryl substituents have been reported (282).

Position isomers of some tetrasubstituted borazines have been prepared and were separated by gas chromatography (59). Characterization of the individual compounds was accomplished by using proton magnetic resonance and mass spectroscopic data.
Atropsiomerism in borazines has been observed for the first time (31) when B-tris-o-tolyl-N-triethylborazine was (partially) resolved into cis and trans isomers, which were found to be thermally interconvertible.

The basicity of the dimethylamino group in B-dimethylaminoborazine has been investigated by studying a series of competitive reactions with other bases and using diborane(6) as a reference acid (90). On this basis, the π-electrons of borazine appear partially delocalized and seem to have a significant influence on the chemical properties of a ring substituent. Similar conclusions were reached in a magneto-optical study of the aromatic character of substituted borazines of D_{3h} symmetry (220). The results of a proton magnetic resonance study on hexamethylborazine and B-trichloro-N-trimethylborazine at 110-300°K were compared with the data obtained for the corresponding benzene derivatives (284).

The ion mass spectrum of borazine (309) and the mass spectra of various B-substituted derivatives of borazine and N-trimethylborazine (27,51) have been recorded; data on the latter were analyzed in terms of the relative contribution of the parent ion and certain fragment ion intensities. The results were discussed in terms of relative stabilities of fragment ions arising from substituent effects. In general, boron substituents are more readily cleaved off than the corresponding nitrogen substituents leading to the conclusion that the six-membered ring fragments are stabilized by delocalization of electron density from the nitrogen atoms. Organic substituents bonded to the nitrogen atoms of borazines will cleave at the α-carbon through electron impact. On the other hand, when bonding is effected at the boron a the boron-carbon bonds cleaves under the same conditions.

The composition of the pyrolysis products of hexamethylborazi and its B-deuteriomethyl derivative and the proportions of product of different isotopic composition indicate that thermodegradation accompanied by the homolytic rupture of the bonds between the meth substituents and the borazine ring (277). The boron-carbon bonds were found to cleave a bit easier than nitrogen-carbon bonds.

The first borazine-metal complex was described but four years ago (142). Since that time several additional representatives of th type of compound have been reported and tricarbonylchromium(0) complexes of hexamethylborazine, B-monophenyl-pentamethylborazine, B-monoethyl-pentamethylborazine, and B-trimethyl-N-triethylborazine have now been prepared (141). Spectroscopic data (IR, nmr, UV) on these species were interpreted in terms of metal complexes containi puckered borazine rings with sigma bonding through the anular nitro atoms.

Semi-empirical valence electron molecular orbital calculations on B-trichloroborazine, N-trichloroborazine, and hexachloroborazine (43) substantiate the expected sigma electron drift within the hete cycle toward nitrogen and a pi-electron drift toward boron. Also, CNDO/2 calculations on the parent borazine have been reported (283)

6. ADDUCTS AND SALTS

6.1 Acid-Base Type Adducts

The electrolysis of sodium tetrahydridoborate in ethylamine at ice-bath temperature leads to the formation of ethylamine-borane, $C_2H_5NH_2\cdot BH_3$, in ca. 60% yield (20).

Amine-boranes react with certain alkyl halides such as chlorotriphenylmethane to yield amine-haloboranes and alkanes (80):

$L{\cdot}BH_3 + RX \longrightarrow L{\cdot}BH_2X + RH$

The alkyl halides must be capable to form carbonium ions readily, and the reactivity according to the depicted equation was found to increase with increasing stability of the carbonium ion. On the other hand, amine-boranes may also interact with alkyl halides such as carbon tetrachloride, where it is reasonable to assume a free-radical mechanism to proceed, which is induced by abstraction of halogen from the halocarbon.

Worth mentioning seems to be the use of dimethylamine-borane as the reducing agent in electroless plating systems (310).

Recent spectroscopic studies on amine-boranes deal with the adducts of difluoroborane at low temperature (IR, NMR) (202), trimethylamine-borane (microwave spectrum) (239), and carbonyl-borane (high resolution IR) (7).Furthermore, measurements of molar Kerr constants, dipole moments, etc., in benzene or dioxane have been reported for the trimethylamine adducts with BX_3 where X = H, F, Cl, Br, I (196).

Adducts of mixed boron halides with trimethylamine and 4-picoline have been shown to exist in solution as demonstrated by proton and fluorine-19 magnetic resonance studies (193). Also, based upon magnetic resonance data, boron trihalides appear to form adducts with dialkylurea in which oxygen acts as the donor atom and rotation about the B-O bond is restricted (254).

A kinetic study of the halogen exchange between alkyl halides and boron trihalides, according to the equation

$RY + BX_3 \longrightarrow RX + YBX_2$,

has given evidence for the formation of an intermediate adduct, $RY{\cdot}BX_3$ (192).

The boron-nitrogen bond lengths in ammonia-isothiocyanatoborane,

$H_3N \cdot BH_2(NCS)$, have been determined by X-ray diffraction to be 1.53 for B-N(CS) and 1.58 Å for $B-N(H_3)$, respectively (286).

The core binding energies of boron trifluoride complexes with nitrogen bases such as ammonia, alkylamines, or pyridines were fou to reflect the change in molecular charge distribution which occur when the boron-nitrogen bond is formed (245). Molecular orbital calculations on the boron trifluoride adduct with unsymmetrical dimethylhydrazine support an equilibrium between gauche and trans forms of the complex (68); note that the boron trifluoride is bonde to the dimethyl-substituted nitrogen. Other theoretical treatments (CNDO/2) treat all the possible species from ammonia-borane, $H_3N \cdot B$ to trifluoroamine-trifluoroborane, $F_3N \cdot BF_3$ (238). Analogous calcula on the trimethylamine adducts of boron trichloride and trimethylbor (206) substantiate the concept that donor-acceptor charge transfer increases with increasing electronegativity of the boron substituen

Fluorine-19 chemical shift data have been used to evaluate t relative basicities of boron trifluoride complexes with cycloalkanones (236); also, nuclear magnetic resonance spectra of boron trifl adducts with sulfoxides, amine oxides, phosphine oxides, and arsine oxides (241) and with some steroids and a limonoid (233) have been discussed.

The formation of 1:1 complexes of boron trifluoride with aroma aldehydes was reported last year (258). A proton magnetic resonance study on such adducts with p-substituted benzaldehydes (252) has no been described and upfield shifts of the formyl proton resonance signal are correlated with the delocalization of positivie charges in these complexes. A calorimetric study on the complex formation between aromatic aldehydes and boron trifluoride has also been repo (250). Boron trifluoride forms a 2:1 and two different 1:1 complexes with p-dialkylamino benzaldehydes (243). In the 1:1 adducts, coordi occurs with either the amino group (formation controlled by thermodynamics) or with the carbonyl group (formation controlled by kinetics) as evidenced by ultraviolet and infrared spectra.

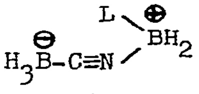
The rates and mechanisms of exchange of some tertiary amine adducts with boron trichloride have been deduced from their temperature dependent proton and boron-11 nuclear magnetic resonance spectra (287). The amine exchange seems to occur via a unimolecular ionization.

The reduction of vanadium tetrachloride with (dimethylamino)-dichloroborane results in the formation of the trichloroborane-stabilized imine $H_3CN{=}CH_2 \cdot BCl_3$ along with dimethylamine-trichloroborane (89). Treatment of $K(CH_3)_2NBH_3$in diglyme with a threefold excess of sodium tetrahydridoborate and one half mole of iodine provides a solution of $Na(CH_3)_2N(BH_3)_2$, which may be converted to μ-dimethylaminodiborane(6) by addition of another half mole of iodine (106).

The enthalpy of formation of the acetonitrile-boron triiodide adduct has been determined (270). The cyclic hydrazinodiphosphine $P(NCH_3{-}NCH_3)_3P$ forms a 1:2 adduct with BH_3 in which the boron is coordinated with the phosphorus. In contrast to the adduct $H_3B \cdot P[N(CH_3)_2]_3$, the borane adduct of the cited hydrazinophosphine is quite sensitive toward hydrolysis (12).

6.2 Ionic Species

The interaction of a solution of diborane(6) and hydrogen cyanide in tetrahydrofuran leads to the internal boronium(-1) salt LX (115).



LX

The reaction may also be effected in other ethers and the tetrahydrofuran in LX is readily displaced by pyridine or trimethylamine.

The structure of these compounds was confirmed by proton and bor nuclear magnetic resonance data and also by infrared spectroscop The neutral isomer of LX in which the ligand is trimethylamine ca obtained by the interaction of trimethylamine-cyanoborane, $(CH_3)_3$ BH_2CN, and tetrahydrofuran-borane; $[(C_5H_5N)_2BH_2]^+[BH_3CN]^-$ has be prepared from sodium cyanotrihydridoborate and bis(pyridine)dihyd boronium chloride.

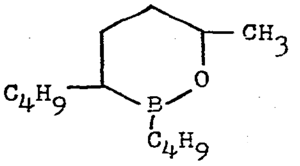
The compound $Na(CH_3)_2As(BH_3)_2$ has been prepared by the react of diborane(6) with $NaAs(CH_3)_2$ (62). On treating the former with methylammonium chloride, the compound $(CH_3)_3N-BH_2-As(CH_3)_2-BH_3$ results. This latter observation suggests that $Na(CH_3)_2As(BH_3)_2$ ar $Li(CH_3)_2P(BH_3)_2$ have similar structures.

Potassium hydride reacts with weak bases such as trialkylbora tetraalkyldiborane(6), or tris(alkoxy)boranes to form the corresponding hindered and complex hydridoborates (228). Similarly lithium hydride interacts with triethylborane in tetrahydrofuran t form lithium hydridotriethylborate (76). This latter salt is a qui powerful nucleophile in displacement reactions with organic halide

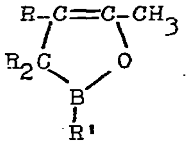
Tetrabutylammonium cyanotrihydridoborate is an unusually sele reducing agent (145). However, the selectivity is strongly depende on the reaction conditions. For example, at room temperature and i hexamethylphosphoramide as solvent, only primary iodides are conve to the corresponding hydrocarbons. In moderately acidic solution (0.1 to 0.12 n) selective reduction of aldehydes was observed, whe in 1.5 n acidic solution ketones are also reduced ; under the same conditions cyano, ester, amido or nitro groups remain intact.

Lithium borates of the type $LiBR_4$ (R = H, CH_3) do not interact with hexamethylditin (116). This lack of reaction is in contrast to the behavior of entities such as $LiAlH_4$ or $LiTl(CH_3)_4$, which readil cleave the tin-tin bond.

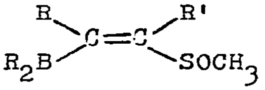
Trialkylalkynylborates are interesting and versatile reagents which continue to receive considerable attention. In recent studies it has been found that lithium tri-*n*-butylvinylborate reacts with methyloxirane to yield an oxaborinane, LXI, probably *via* thermolysis of a cyclic borate intermediate (260). The alkylation and protonation of trialkylalkynylborates has also been studied (204). The reaction of lithium trialkylalkynylborates is known to proceed *via* 2-oxa-3-bororenes, LXII, and has now been used for a novel preparation of α,β-unsaturated ketones (262). Also, the reaction with methanesulfonyl chloride, which proceeds *via* the intermediate LXIII, provides an efficient route to internal acetylenes (263).



LXI



LXII



LXIII

Metathesis of tetraalkylammonium bromides with lithium tetraalkylborates yields tetraalkylammonium tetraalkylborates (234). If at least one of the organic groups (either at the boron or at the nitrogen) is a long alkyl chain, the resultant salts are low melting solids or are liquids at or near room temperature. This reaction provides a new class of solvents which may have an unusual potential (185).

The redox pair cesium ammonium nitrate / ammonium hydridotriethylborate apparently can be used as initiator system for the polymerization of vinyl chloride (67). Binary systems of tetraphenylborates and organic acids can be used for the same purpose (34).

A detailed procedure for the preparation of trimethylammonium tetraphenylborate has been described (137). This salt is quite stab it can be used as ready source of triphenylborane.

The tetraphenylborate ion is a powerful chemical shift reagent for pyridine ions (69). The magnitude and direction of the observed shifts of the nuclear magnetic resonance signals reflects the infl of aromatic ring currents in the anion as well as the geometry of the cation. This use of the tetraphenylborate anion in nuclear magn resonance spectroscopy has been exhaustively explored. For example, in chlorinated hydrocarbon solution, the cited anion promotes a resonance signal shift of protons in the α-position to As or Sb in arsonium and stibonium cations, respectively (95). The use of the tetraphenylborate ion as a shift reagent for quaternary ammonium io (132), anilinium cations (133) and sulfonium compounds (134) has also been described.

Hexaantipyrinelanthanide(III) tetraphenylborates have been studied (217) and the temperature dependency of the nuclear magnetic resonance spectrum of the rhodium salt $Rh[P(OCH_3)_3]_5[B(C_6H_5)_4]$ has been investigated (184). Also, an amperometric method has been developed for the rapid determination of tetraphenylborate ion (216) it can be used for the quantitative determination of potassium ion. The viscosity of sodium tetraphenylborate and its glyme complexes ir ether solvents such as tetrahydrofuran or 2-methyltetrahydrofuran ha been studied (167).

Some unsymmetrical tetraarylborates have been found to show a dynamic nuclear magnetic resonance behavior and only one stereosiome could be isolated from any of the investigated examples (151).

A new synthesis of nitrosyl tetrafluoroborate is based on the reaction of boron nitride with fluorine and oxygen in a quartz react under ultraviolet radiation (294).

It is of interest to note that a comparison of the ionization energies of the electronic valence levels of BeF_4^{-2}, BF_4^{-1} and CF_4 indicates a steady change of the absolute energy levels and of the distances between them with an increase of the degree of chemical bond covalence (299).

Aliphatic amides react with anhydrous HF and BF_3 to give stable amide hydrofluoroborates (15):

$$R\text{-}CO\text{-}NR_2 + HF + BF_3 \longrightarrow R\text{-}COH{=}\overset{\oplus}{N}R_2\ BF_4^{\ominus}$$

The synthesis of 2,4,6-triarylpyrylium fluoroborates from aromatic aldehydes and arylmethylketones has also been described (33).

Platinum complexes of the type $[Pt_2X_2L_4]BF_4$ have been obtained by the reaction of trimethyloxonium tetrafluoroborate with dihalo-bis-ligandplatinum(II) complexes (57); the oxonium salt appears to act as a halide acceptor in these reactions.

The reaction of boron trichloride with MCl (M = K, Rb, Cs, NR_4) in inert solvents leads to the corresponding tetrachloroborates (281); an antisymmetric B-Cl stretch in the 650-710 cm^{-1} region seems to be typical for the tetrachloroborate anion.

7. BORON-METAL DERIVATIVES

In this section those derivatives of boron will be discussed in which a metal to boron bond exists, and also various metal complexes with boron-containing ligands, where there is not necessarily a direct metal-boron interaction. Additional boron-metal species have been mentioned in sections 5 and 6.

The reaction of $KGeH_3$ with trimethylborane yields a 1:1 adduct, which may contain the germyltrimethylborate ion, $[H_3B(CH_3)_3]^{\ominus}$ (44); some studies on the hydrolysis of the adduct have been performed.

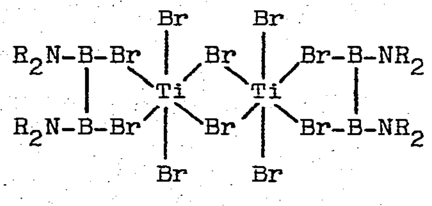
Dicyclopentadienylthallium(III) tetrahydridoborate and dime thallium(III) tetrahydridoborate have been prepared and the infra spectra of these two compounds have been discussed (266). There s to exist some evidence for a metal to boron bonding through hydro Cyclopentadienylindium(I) reacts with BX_3 ($X = F, Cl, Br, CH_3$) to yield monomeric 1:1 adducts, in which the organic ring appears to a diene (monohapto form) structure (143).

Several transition metal complexes containing the coordinate $[BH_4]^\ominus$ or $[H_3BCN]^\ominus$ ion have been described (267). Infrared data s that the BH_4 species is coordinated to the metal via double-hydro bridges, whereas the $[H_3BCN]^\ominus$ ion is bonding through the nitrogen The structure of $(\pi\text{-}C_5H_5)Fe(CO)[(HNCH_3)_2BH_2]$ has been determined X-ray diffraction (63); the six-membered heterocycle Fe-C-N-B-N-C of this compound has a boat geometry.

Treatment of bis(dimethylamino)bromoborane with titanium tet bromide affords a 2:3 complex (60). Based on infrared spectroscop studies, a structure was suggested for this compound in which the coordination sequence is as follows:

$$Br_4Ti\text{-}N(CH_3)_2\text{-}BBr\text{-}N(CH_3)_2\text{-}TiBr_4\text{-}N(CH_3)_2\text{-}BBr\text{-}N(CH_3)_2\text{-}TiBr_4.$$

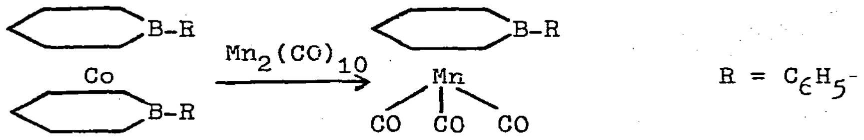
Reaction of titanium tetrabromide with tetrakis(dimethylamino)diborane(4) yields a 1:1 complex (61), for which the following binuc structure was suggested:



$R = CH_3$

Bromodiphenylborane, $BrB(C_6H_5)_2$, reacts with bis tricarbonyl-(phenyl)chromio mercury under formation of tricarbonyl(diphenylbor chromium(0) (152). The orange compound is monomeric and spectroscopic data indicate weaker π-bonding between the boron atom and the phenyl groups as compared to the free ligand.

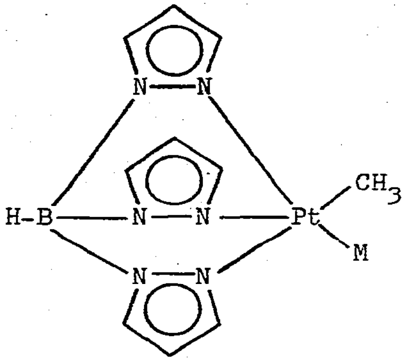
Bis(1-phenylborinato)cobalt reacts with $Mn_2(CO)_{10}$ in boiling toluene in a ligand transfer reaction to yield tricarbonyl(1-phenylborinato)manganese (209):



The reaction of copper(I) chloride with $K[HB(Pz)_3]$ in the presence of carbon monoxide affords $[HB(pz)_3]CuCO$ (pz = 1-pyrazolyl) (294). The carbonyl group can be displaced by other ligands such as $As(C_6H_5)_3$, $P(OCH_3)_3$, et al.; heating of the carbonyl complex leads to $Cu_2[HB(pz)_3]_2$, which subsequently disproportionates to metallic copper and $Cu[HB(pz)_3]_2$.

The crystal and molecular structure of dicarbonyl-hydrotris(pyrazol-1-yl)borato-N(2),N(2)',N(2)"-π-(2-methylallyl)molybdenum has been determined by X-ray diffraction (295). The coordination sphere of the molybdenum atom consists of one nitrogen from each of the three pyrazole rings, two carbon atoms from the sigma-bonded carbonyl groups, and a π-2-methylallyl group. Several additional structures of metal complexes containing pyrazolylborate ligands have been determined. These include the structure of bis[dihydridobis(1-pyrazolyl)borato]-cobalt(II), $[H_2B(pz)_2]_2Co$ (50), and [dihydridobis(3,5-dimethyl-1-pyrazolyl)borato](h^3-cycloheptatrienyl)dicarbonylmolybdenum (56). Crystallographic data on the latter indicate the presence of a three-center B-H-Mo bond, which provides for the molybdenum to attain an effective 18-electron configuration by counting the two electrons of the three-center bond.

The first true mixed sandwich compounds in which a transition met is bonded to a pyrazolylborate and another ligand have reportedly been synthesized, though experimental details are not yet known (The tridentate polypyrazolylborate ligand has also been used to stabilize 5-coordinate platinum(II) (225): Insoluble Pt(CH_3) [HB(p is probably a polymer that is cleaved on treatment with acetylen or other hydrocarbons containing multiple bonds to give complexes of type LXIV.



M = carbon-carbon multiple bond of a hydrocarbon

LXIV

Diiron enneacarbonyl reacts with potassium tris(1-pyrazolyl)-borate in the presence of methyl iodide to yield acetyl(tri-1-pyrazolylborato)(dicarbonyl)-iron in low yield (153). The crystal structure of the material has been studied by X-ray diffraction an the coordination of iron was found to be slightly perturbed from t octahedral arrangement. Allyliron tricarbonyl iodide reacts with polypyrazolylborates by isomerization of the π-allyl ligand to a sigma-propenyl ligand; cleavage of the pyrazolyl ring from the pol pyrazolylborate anion is also observed (16). Likewise, compounds o the type LMo($CO)_2C_7H_7$ with L being a pyrazolylborate ligand have b shown to react with Fe($CO)_5$ to yield Fe($CO)_3$ adducts, e.g.,

$[B(pz)_4](C_7H_7)(CO)_2Mo\cdot Fe(CO)_3$ (117). These adducts seem to be formed by a binding of the $Fe(CO)_3$ group to the butadiene increments of the C_7H_7 rings.

8. BIOLOGICAL AND MEDICINAL ASPECTS

Various reports are of peripheral interest to studies of the biological and medicinal aspects of boron chemistry. These include, for example, the esterification of insulin utilizing triethyloxonium tetrafluoroborate (108) and an investigation of complexing on the boric acid/adonitol system (107) as well as studies on the reaction of boric acid with urea (215). Also, equilibria between boric acid and mannitol in aqueous 3 M $NaClO_4$ solution have been studied in the pH range from 2 to 9 (292). The latter data were obtained by potentiometric (glass electrode) and polarometric measurements and may be explained on the assumption that ternary charged complexes and a binary neutral species, $B(OH)_3\cdot C_6H_{14}O_6$, exist in such solutions.

In other work, organoboranes have been utilized as tools for the syntheses of compounds of medicinal interest, e.g., the preparation of the prostaglandin skeleton (218) or the sterically selective reduction of protein carboxyl groups with disiamylborane or 9-borabicyclo(3.3.1)nonane (219).

The accumulation of B group vitamins under the effect of boron has been studied (21) and an approach to elucidate the physiological function of boron derivatives was described (131). Functional aspects of boron in plants (304) and the occurrence of boron in cultivated soils and irrigation waters (305) have been discussed. Also, the distribution of boron in groundnut leaf cells has been studied (306). It is a bit surprising that the effect of the nitrogen form on boron toxicity, boron absorption and distribution in young cucumber plants has been investigated (186) but not much is known about the interaction of boron derivatives with, for example, such amino acids those found in the human body.

Reactions involving boron compounds and which are of releva to drug research mostly involve the utilization of hydridic spec For example, reduction of saturated steroid mono and diketones w cyanotrihydridoborate has been studied (81) and the same reagent was found to be regioselective in the reductive amination of ste ketones (85). Ureide ring scission of phenobarbital can be accomplished with sodium tetrahydridoborate (84) and BABITCH (82 has reported on the effects of the tetraphenylborate ion on the isolation of neuronal and glial cells from guinea pig brain. The reaction of 16-dehydropregnenolone acetate with tris(2-methylally borane proceeds by the addition of a boron-allyl fragment to the 20-carbonyl group of the steroid molecule (45). Also, the formati of methadol boranes and isomethadol boranes has been described (1

Boron derivatives continue, however, to receive considerable attention in carbohydrate research. For example, the effects of arylhydroxyboranes on the alkaline conversion of D-glucose into D-fructose (159) and the interaction of the same type of boranes monosaccharides (158) have been studied. Also, the use of poly(4-vinylbenzeneboronic acid) resins in the fractionation and interco version of carbohydrates (160) as well as column chromatographic separation of neutral sugars on a dihydroxyboryl-substituted poly (163) have been investigated. A nuclear magnetic resonance study the interaction of sugars and borate (162) and mass spectral dat on phenylboryl derivatives of some hexose pyranosides (161) have been published. Recent work on alkali and ammonium salts of penta-erythrolborates (212), methriclborates (213, 300-302) and este thereof (303) should also be noted in this context.

Also, the differential identification of some sympathomimetic drugs by microcrystalline reaction with sodium tetraphenylborate (66) and a microdetermination of boron in organic compounds have been described (311).

The N-carboxy anhydride of DL-4-boronophenylalanine has been synthesized (312) and was used to prepare soluble copoly (DL-alanyl-DL-4-boronophenylalanyl) bovine γ-globulin. Variations in the ratio of the two anhydrides seem to effect the solubility of the modified globulins; the maximum boron content of the resultant materials was about 36 boron atoms per protein molecule. These results may open another approach to use boron-10 neutron capture in cancer therapy.

References

1. K. G. Hancock and D. A. Dickinson, J. Amer. Chem. Soc., 95 (1973) 280
2. E. Mayer, Inorg. Nucl. Chem. Letters, 9 (1973) 343
3. Z. Taira and K. Osaki, ibid., 9 (1973) 207
4. G. J. Barrett and D. T. Haworth, Inorg. Chim. Acta, 6 (1972) 504
5. T. Mukaiyama, K. Inomata and M. Muraki, J. Amer. Chem. Soc., 95 (1973) 967
6. D. Nolle and H. Nöth, Z. Naturforsch., 27b (1972) 1425
7. L. Lambert, C. Pepin and A. Cabana, J. Mol. Spectry., 44 (1972) 578
8. B. M. Mikhailov, V. A. Dorokhov and L. I. Lavrinovich, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 1545
9. N. C. Baird, Inorg. Chem., 12 (1973) 473
10. P. J. Busse and K. Niedenzu, Syn. Inorg. Metalorg. Chem., 3 (1973) 23
11. T. P. Fehlner, Inorg. Chem., 12 (1973) 98
12. R. Goetze, H. Nöth and D. S. Payne, Chem. Ber., 105 (1972) 2637
13. R. H. Fish, J. Org. Chem., 38 (1973) 158
14. R. Van Veen and F. Bickelhaupt, J. Organometal. Chem., 47 (1973) 33
15. S. S. Hecht and E. S. Rothman, J. Org. Chem., 38 (1973) 395
16. R. B. King and A. Bond, J. Organometal. Chem., 46 (1972) C53

17. J. Bouix, M. Fouassier and M. T. Forel, J. Mol. Structure, 15 (1973) 103

18. B. Roques and D. Florentin, J. Organometal. Chem., 46 (1972) C38

19. V. A. Dorokhov, O. G. Boldyreva, V. S. Bogdanov and B. M. Mikhailov, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 1550

20. L. A. Melcher, I. A. Boenig and K. Niedenzu, Inorg. Chem., 12 (1973 487

21. A. P. Kibalenko, Dopov. Akad. Nauk, Ukr. RSR, Ser. B, 34 (1972) 1113

22. S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, J. Organometal. Chem., 47 (1973) 39

23. V. S. Bogdanov, V. G. Kiselev, A. D. Naumov, L. S. Vasilev, V. P. Dmitrikov V. A. Dorokhor and B. M. Mikhailov, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 1539

24. B. M. Mikhailov, Y. N. Bubnov, O. A. Nesmeyanova, V. G. Kiselev, T. Y. Rudashevskaya and B. A. Kazansky, Tetrahedron Lett., (1972) 4627

25. L. S. Vasilev, M. M. Vartanyan, V. S. Bogdanov, V. G. Kiselev and B. M. Mikhailov, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 1533

26. E. F. Rothgery and R. Köster, Abstr. of Papers, 165th ACS Natl. Mtng., Dallas Texas, INOR (1973) 19

27. J. L. Adcock, G. A. Anderson and L. A. Melcher, ibid., INOR (1973) 18

28. O. T. Beachley, ibid., INOR (1973) 17

29. J. D. Odom, P. D. Ellis, D. W. Lowman and L. W. Hall, ibid., INOR (1973) 9

30. L. Barton and J. M. Crump, ibid., INOR (1973) 11

31. P. M. Johnson and E. K. Mellon, ibid., INOR (1973) 16

32. J. J. Mielcasek and P. C. Keller, ibid., INOR (1973) 12

33. Z. Czurdes, P. Sallay and G. Deak, Acta Chim. (Budapest), 74 (1972) 357

34. T. Sato, E, Kashino, N. Fukumura and T. Otsu, Makromol. Chem., 162 (1972) 9

35. G. B. Sadikov, V. P. Maslennikov and G. I. Makin, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 1563

36. V. A. Shushunov, V. P. Maslennikov, G. I. Makin and A. V. Gorbunov, ibid., 42 (1973) 1568

37. L. S. Vasilev, V. P. Dmitrikov, V. S. Bagdanov and B. M. Mikhailov. ibid., 42 (1972) 1313

38. Y. N. Bubnov, V. S. Bogdanov, I. P. Yakovlev and B. M. Mikhailov, ibid., 42 (1972) 1308

39. B. M. Mikhailov and K. L. Cherkasora, ibid., 42 (1973) 1732

40. Y. N. Bubnov, M. S. Grigoryan and B. M. Mikhailov, ibid., 42 (1973) 1726

41. A. Haag and H. Baudisch, Tetrahedron Letters, (1973) 401

42. H. C. Brown and Y. Yamamoto, Synthesis, (1972) 699

43. V. M. Scherr and D. T. Haworth, J. Inorg. Nucl. Chem., 35 (1973) 660

44. E. R. de Staricco, C. Riddle and W. L. Jolly, ibid., 35 (1973) 297

45. A. A. Akhrem, I. S. Levina, Y. A. Titor, Y. N. Bubnov and B. M. Mikhailov, Bull. Acad. Sci. USSR, Chem. Sci. Div. (Engl. Transl.), 21 (1973) 1580

46. B. M. Mikhailov and V. N. Smirnov, ibid., 21 (1973) 1622

47. L. S. Vasilev, M. M. Vartanyan and B. M. Mikhailov, ibid., 21 (1973) 1632

48. A. M. Yurkevich and O. N. Shevtsova, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 1987

49. W. Kliegel, Liebigs Ann. Chem., 763 (1972) 61

50. L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko and P. J. Jesson, Inorg. Chem., 12 (1973) 508

51. L. A. Melcher, J. L. Adcock, G. A. Anderson and J. J. Lagowski, ibid., 12 (1973) 601

52. C. T. Kwon and H. A. McGee, ibid., 12 (1973) 696

53. G. Zweifel, R. P. Fisher and A. Horng, Synthesis, (1973) 37

54. H. C. Brown and N. Ravindran, ibid., (1973) 42

55. H. C. Brown in "Advances in Organometallic Chemistry", F. G. A. Stone and R. West, editors, Vol. 11 (1973)

56. F. A. Cotton, M. Jeremic and A. Shaver, Inorg. Chim. Acta, 6 (1972) 543

57. P. M. Treichel, K. P. Wagner and W. J. Knebel, ibid., 6 (1972) 674

58. J. L. Adcock, L. A. Melcher and J. J. Lagowski, Inorg. Chem., 12 (1973) 788

59. P. Powell, ibid., 12 (1973) 913

60. M. R. Suliman and E. P. Schram, ibid., 12 (1973) 920

61. M. R. Suliman and E. P. Schram, ibid., 12 (1973) 923

62. L. D. Schwartz and P. C. Keller, ibid., 12 (1973) 947

63. W. M. Butler and J. H. Enemark, J. Organometal. Chem., 49 (1973) 233

64. R. H. Cragg, M. Nazery and A. F. Weston, Inorg. Nucl. Chem. Letters, 9 (1973) 497

65. W. Siebert and F. Riegel, Chem. Ber., 106 (1973) 1012

66. O. N. Yalcindag, J. Pharm. Belg., 27 (1972) 775

67. L. Ulbricht and W. Seidel, Plaste Kaut., 20 (1973) 6

68. M. Graffeuil, J. -F. Labarre, C. Leibovici and E. Taillandier, J. Mol. Structure, 15 (1973) 367

69. G. P. Schliemenz, ibid., 16 (1973) 99

70. R. H. Cragg, J. P. N. Husband and A. F. Weston, J. Chem. Soc. Dalton Trans., (1973) 568

71. K. V. Ingold, J. Chem. Soc. Perkin Trans. II, (1973) 420

72. B. M. Mikhailov, V. N. Smirnov and E. P. Prokofer, Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.), 206, 712 (1973)

73. V. A. Dorokhov and B. M. Mikhailov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 21 (1973) 1847

74. G. Cragg, "Organoboranes in Organic Synthesis", Marcel Dekker, New York, 1973.

75. P. W. R. Corfield and S. G. Shore, J. Amer. Chem. Soc., 95 (1973) 1480

76. H. C. Brown and S. Krishnamurthy, ibid., 95 (1973) 1669

77. H. C. Brown, M. M. Midland and A. B. Levy, ibid., 95 (1973) 2394

78. H. C. Brown and N. Ravindran, ibid., 95 (1973) 2396

79. R. Kow and M. W. Rathke, ibid., 95 (1973) 2715

80. G. E. Ryschkewitsch and V. R. Miller, ibid., 95 (1973) 2836

81. M. H. Boutique and R. Jacquesy, C. R. Acad. Sci. Ser. C, 276 (1973) 437

82. J. A. Babitch, J. Neurochem., 20 (1973) 853

83. G. E. Kacheishoili, N. I. Pirtskhalava and N. A. Nikolaishvili, Soobshch. Akad. Nauk Gruz. SSR, 69 (1973) 73

84. L. Chafetz, T. M. Chen and R. C. Greenough, J. Pharm. Sci., 62 (1973) 512A

85. M. H. Boutique and R. Jacquesy, Bull. Soc. Chim. France, (1973) 750

86. J. S. Merriam and K. Niedenzu, J. Organometal. Chem., 51 (1973) C1

87. J. Müller, ibid., 51 (1973) 119

88. I. Mehrotra and D. Devaprabhakara, ibid., 51 (1973) 93

89. R. Kiesel and E. P. Schram, Inorg. Chem., 12 (1973) 1090

90. O. T. Beachley and T. R. Durkin, ibid., 12 (1973) 1128

91. A. Almenningen, H. M. Seip and P. Vassbotn, Acta Chem. Scand., 27 (1973) 21

92. H. M. Seip and R. Seip, ibid., 27 (1973) 15

93. H. Nöth, R. Ullmann and H. Vahrenkamp, Chem. Ber., 106 (1973) 1165

94. E. B. Bradley, R. H. Herber, P. J. Busse and K. Niedenzu, J. Organometal.

95. P. G. Schiemenz, ibid., 52 (1973) 349

96. S. C. Jackels and N. J. Rose, Inorg. Chem., 12 (1973) 1232

97. A. K. Uriarte and K. G. Hancock, ibid., 12 (1973) 1428

98. M. Zeldin and T. Wartik, ibid., 12 (1973) 1433

99. G. I. Makin and V. P. Maslennikov, J. Gen. Chem. USSR (Engl. Transl.), 42 (1973) 2657

100. L. S. Vasilev, M. M. Vartanyan and B. M. Mikhailov, ibid., 42 (1973) 2664

101. H. Nöth and B. Wrackmeyer, Chem. Ber., 106 (1973) 1145

102. W. L. Cook and K. Niedenzu, Syn. Inorg. Metalorg. Chem., 3 (1973) 229

103. D. W. Wester, F. Longcor and L. Barton, ibid., 3 (1973) 115

104. R. L. Wells and R. H. Neilson, ibid., 3 (1973) 137

105. R. H. Neilson and R. L. Wells, ibid., 3 (1973) 283

106. P. C. Keller, ibid., 3 (1973) 307

107. V. Grundsteins, E. Svares and A. Ievins, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1973) 267

108. D. Levy, Biochim. Biophys. Acta, 310 (1973) 406

109. F. Umland, E. Hohaus and K. Brodte, Chem. Ber., 106 (1973) 2427

110. F. Knoll, M. L. Anagnostopoulos and R. Appel, ibid., 106 (1973) 2089

111. A. Meller and G. Beer, Monatsh. Chem., 104 (1973) 1055

112. G. L. Galchenko, E. P. Brykina, N. N. Shchegoleva, L. S. Vasilev and B. M. Mikhailov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 22 (1973) 209

113. Y. N. Bubnov, O. A. Nesmeyanova, T. Y. Rudachevskaya, B. M. Mikhailov and B. A. Kazanskii, J. Gen. Chem. USSR (Engl. Transl), 43 (1973) 125

114. Y. N. Bubnov, O. A. Nesmeyanova, T. Y. Rudachevskaya, B. M. Mikhailov and B. A. Kazanskii, ibid., 43 (1973) 132

115. E. A. Lavrenteva, G. V. Lagodzinskaya, M. L. Khidekel, O. P. Shitov, S. L. Ioffe, V. V. Negrebetskii and V. A. Tartakovskii, ibid., 43 (1973) 294

116. A. T. Weibel and J. P. Oliver, J. Organometal. Chem., 57 (1973) 313

117. J. L. Calderon, A. Shaver and F. A. Cotton, ibid., 57 (1973) 121

118. D. J. O'Sullivan and F. J. Lalor, ibid., 57 (1973) C58

119. D. S. Matteson and R. J. Wilcsek, ibid., 57 (1973) 231

120. D. S. Matteson and G. L. Larson, ibid. 57 (1973) 225

121. H. Heall and C. H. Bushweller, Chem. Revs., 73 (1973) 465

122. S. Trofimenko, ibid., 72 (1972) 497

123. P. L. Timms, Accounts Chem. Research, 6 (1973) 118

124. W. N. Lipscomb, ibid., 6 (1973) 257

125. J. Pless and W. Bauer, Angew. Chem. Internat. Ed., 12 (1973) 147

126. E. Hengge and D. Wolfer, ibid., 12 (1973) 315

127. H. M. Seip, R. Seip and K. Niedenzu, J. Mol. Structure, 17 (1973) 361

128. I. Geisler and H. Nöth, Chem. Ber., 106 (1973) 1943

129. H. Nöth, D. Reiner and W. Storch, ibid., 106 (1973) 1508

130. D. J. Locker, Photogr. Sci. Eng., 17 (1973) 442

131. E. Takahashi, Kagaku to Seibutsu, 11 (1973) 301

132. G. P. Schiemenz, Tetrahedron, 29 (1973) 741

133. G. P. Schiemenz, Org. Magn. Resonance, 5 (1973) 257

134. G. P. Schiemenz and H. P. Hansen, Angew. Chem., 85 (1973) 404A

135. G. L. Galchenko, E. P. Brykina, R. M. Varushchenko and L. S. Vasilev, Zh. Fiz. Khim., 47 (1973) 1609B

136. G. L. Galchenko, E. P. Brykina, L. I. Chirkova and L. S. Vasilev, ibid., 47 (1973) 1606B

137. K. E. Reynhard, R. E. Sherman, H. D. Smith and L. F. Hohnstedt, Inorg. Synth., 14 (1973) 52

138. D. T. Haworth, ibid., 14 (1973) 55

139. O. T. Beachley, Inorg. Chem., 12 (1973) 2503

140. L. Barton and J. M. Crump, ibid., 12 (1973) 2506

141. J. L. Adcock and J. J. Lagowski, ibid., 12 (1973) 2533

142. H. Werner, R. Prinz and E. Deckelmann, Chem. Ber., 102 (1969) 95

143. J. G. Contreras and D. G. Tuck, Inorg. Chem., 12 (1973) 2596

144. H. C. Brown, T. Hamaoka and N. Ravindran, J. Amer. Chem. Soc., 95,(1973) 5786

145. R. O. Hutchins and D. Kandasamy, ibid. 95 (1973) 6131

146. K. G. Hancock and J. D. Kramer, ibid. 95 (1973) 6463

147. E. Negishi and H. C. Brown, ibid. 95 (1973) 6757

148. K. G. Hancock, A. K. Uriarte and D. A. Dickinson, ibid. 95 (1973) 6980

149. J. F. Blount, P. Finocchiaro, D. Gust and K. Mislow, ibid. 95 (1973) 7019

150. P. Finocchiaro, D. Gust and K. Mislow, ibid. 95 (1973) 7029

151. M. G. Hutchins, C. A. Maryanoff and K. Mislow, ibid. 95 (1973) 7158

152. J. Deberiz, K. Dirscherl and H. Nöth, Chem. Ber., 106 (1973) 2783

153. F. A. Cotton, B. A. Frenz and A. Shaver, Inorg. Chim. Acta, 7 (1973) 161

154. R. H. Cragg, J. P. N. Husband and A. F. Weston, J. Inorg. Nucl. Chem., 35 (1973) 3685

155. E. A. Cohen and R. A. Beaudet, Inorg. Chem., 12 (1973) 1570

156. A. Akimoto, J. Appl. Polym. Sci., 17 (1973) 2257

157. R. Liepins, S. Gilbert, F. Tibbetts and J. Kearney, ibid., 17 (1973) 2523

158. S. A. Barker, A. K. Chopra, B. W. Hatt and P. J. Somers, Carbohyd. Res., 26 (1973) 33

159. S. A. Barker, B. W. Hatt and P. J. Somers, ibid., 26 (1973) 41

160. S. A. Barker, B. W. Hatt and P. J. Somers, ibid., 26 (1973) 55

161. D. S. Robinson, J. Eagles and R. Self, ibid., 26 (1973) 204

162. G. R. Kennedy and M. J. How, ibid., 28 (1973) 13

163. K. Reske and H. Schott, Angew. Chem., 85 (1973) 412

164. K. Wade, E. A. Froman and J. Spencer, Abstr. of Papers, XXIVth IUPAC Congress, Hamburg, Germany, (1973) 370

165. R. H. Cragg and A. F. Weston, ibid., (1973) 368

166. W. Siebert, B. Asgarouladi, R. Full and K. J. Schaper, ibid., (1973) 364

167. J. Smid and A. M. Grotens, J. Phys. Chem., 77 (1973) 2377

168. W. Schwarz, H. D. Hausen, H. Hess, J. Mandt, W. Schmelzer and B. Krebs, Acta Cryst. B, 29 (1973) 2029

169. H. Follner, Monatsh. Chem., 104 (1973) 477

170. H. C. Brown and N. Ravindran, J. Org. Chem., 38 (1973) 1617

171. H. Fukashima, T. Makino, S. Inoue, T. Tsuruta, J. Polym. Sc. A-1, 11 (1973) 695

172. D. J. Brauer and C. Krueger, Acta Cryst. B, 29 (1973) 1684

173. B. Lockman and T. Onak, J. Org. Chem., 38 (1973) 2552

174. J. Hooz, J. N. Bridson, J. G. Calzada, H. C. Brown, M. M. Midland and A. B. Levy, ibid., 38 (1973) 2574

175. R. F. Smirnov, B. I. Tikhomirov and A. I. Yakubchik, Vestn. Leningrad Uni Fiz. Khim., (1973) (2), 130

176. J. W. Wilson, J. Chem. Soc. Dalton Trans., (1973) 1628

177. J. W. Wilson, ibid., (1973) 1631

178. S. G. Shore, J. L. Crist, B. Lockman, J. R. Long and A. D. Coon, ibid., (1972) 1123

179. J. T. F. Fenwich and J. W. Wilson, ibid., (1972) 1324

180. R. Molinelli, S. R. Smith and J. Tanaka, ibid., (1972) 1363

181. R. H. Cragg, J. F. J. Todd and A. F. Weston, ibid., (1972) 1373

182. R. W. Kirk, D. L. Smith, W. Airey and P. L. Timms, ibid., (1972) 1392

183. A. Dal Negro, L. Ungaretti and A. Perotti, ibid., (1972) 1639

184. P. Meakin and J. P. Jesson, J. Amer. Chem. Soc., 95 (1973) 7272

185. W. T. Ford and R. J. Hauri, ibid., 95 (1973) 7381

186. D. Alt and W. Schwarz, Plant Soil, 39 (1973) 277

187. L. Maijs, L. S. Breslers, E. I. Karbanova and I. Strauss, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1973) 182

188. R. Haller and R. Ruehnler, Arch. Pharm., 306 (1973) 524

189. M. P. Brown, A. K. Holliday and G. M. Way, Chem. Commun., (1973) 532

190. T. Sato, K. Hibino, N. Fukumura and T. Otsu, Chem. & Ind., (1973) 745

191. M. Petinaux and J. P. Aune, Bull. Soc. Chem. Fr., (1973) 2490

192. M. Goldstein, L. I. B. Haines and J. A. G. Hemmings, J. Chem. Soc. Dalton Trans., (1972) 2260

193. B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen and J. M. Miller, ibid., (1972) 2603

194. G. J. Bullen, ibid., (1973) 858

195. R. H. Cragg and A. F. Weston, ibid., (1973) 1054

196. R. S. Armstrong, G. J. Peacock, K. R. Skapp and R. J. W. LeFevre, ibid., (1973) 1132

197. G. J. Bullen and P. R. Mallinson, ibid., (1973) 1295

198. J. R. Blackborow and J. C. Lockhart, ibid. (1973) 1303

199. D. S. Matteson and P. G. Allies, J. Organomental. Chem., 54 (1973) 35

200. M. E. Glogowski, P. J. Grisdale, J. L. R. Williams and T. H. Regan, ibid., 54 (1973) 51

201. H. C. Brown and B. A. Carlson, ibid., 54 (1973) 61

202. J.-P. Tuchagues, J.-P. Laurent, H. Mongeot, Jr. Dazort and J. Gueilleron, ibid., 54 (1973) 69

203. S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, ibid., 54 (1973) 139

204. A. Pelter, C. R. Harrison and D. Kirkpatrick, Chem. Commun., (1973) 544

205. K. N. Semenenko, O. V. Kravchenko and V. B. Polyakova, Russ. Chem. Revs. (Engl. Transl.), (1973) 1

206. O. Gropen and A. Haaland, Acta Chem. Scand., 27 (1973) 521

207. P. Binger and R. Köster, Synthesis, (1973) 309

208. E. Mayer, Inorg. Chem., 12 (1973) 1954

209. G. E. Herberich and H. J. Becker, Angew. Chem. Int. Ed., 12 (1973) 764

210. H. Hamanaka, Yukagaku, 22 (1973) 426

211. A. Hofer and R. Heidinger, Fresenius Z. Anal. Chem., 264 (1973) 412

212. R. G. Belousova, E. Svares and A. Ievius, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., (1973) 271

213. A. Vegnere, A. Ievins and E. Svarcs, ibid., (1973) 278

214. K. H. Thiele, S. Schroder and O. Trapolsi, Z. Chem., 13 (1973) 141

215. I. G. Chernysh, V. M. Sleptsov and M. F. Tsurul, Porosh. Met., 13 (1973) 47

216. S. Ikeda and J. Hirata, Nippon Kagaku Kaishi, (1973) 953

217. R. W. Bashioum, R. L. Dieck and Th. Moeller, Inorg. Nucl. Chem. Lett., 9 (1973) 773

218. O. Attanasi, G. Baccolini, L. Cagliotti and G. Rosini, Gazz. Chim. Ital., 103 (1973) 31

219. M. Z. Atassi, A. F. Rosenthal and L. Vargas, Biochem. Biophys. Acta, 303 (1973) 379

220. M. Pasdeloup and J. P. Laurent, J. Chim. Phys. Physicochem. Biol., 70 (1973) 199

221. R. Köster, P. Binger and W. V. Dahlhoff, Syn. Inorg. Metalorg. Chem., 3 (1973) 359

222. K. G. Hancock and J. D. Kramer, J. Amer. Chem. Soc., 95 (1973) 3425

223. P. L. Burke, E. Negishi and H. C. Brown, ibid., 95 (1973) 3654

224. G. A. Olah and J. J. Svoboda, ibid., 95 (1973) 3794

225. H. C. Clark and L. E. Manzer, ibid, 95 (1973) 3812

226. A. B. Levy and H. C. Brown, ibid., 95 (1973) 4067

227. M. M. Midland and H. C. Brown, ibid.,95 (1973) 4069

228. C. A. Brown, ibid., 95 (1973) 4100

229. D. S. Matteson, L. A. Hagelee and R. J. Wilcsek, ibid., 95 (1973) 5096

230. W. G. Henderson, M. J. How, G. R. Kennedy and E. F. Mooney, Carbohydrate Res., 28 (1973) 1

231. K. Inomata, M. Muraki and T. Mukaiyama, Bull. Chem. Soc. Japan, 46 (1973) 1807

232. S. Kuribayashi, ibid., 46 (1973) 1045

233. R. E. Schuster and R. D. Bennett, J. Org. Chem., 38 (1973) 2904

234. W. T. Ford, R. J. Hauri and D. J. Hart, ibid., 38 (1973) 3916

235. H. C. Brown, J.-J. Katz and B. A. Carlson, ibid., 38 (1973) 3968

236. A. Fratiello, G. Vidulich and Y. Chow, ibid., 38 (1973) 2309

237. H. C. Brown and B. A. Carlson, ibid., 38 (1973) 2422

238. M. Bach, F. Crasnier and J. F. Labarre, J. Mol. Structure, 16 (1973) 89

239. J. R. Durig, Y. S. Li and J. D. Odom, ibid., 16 (1973) 443

240. R. A. Mariezcurrena and S. E. Rasmussen, Acta Cryst. B, 29 (1973) 1035

241. R. Bravo, M. Durand and J.-P. Laurent, Org. Magn. Resonance, 5 (1973) 357

242. H. R. Hudson and P. A. Karam, J. Chem. Soc. Perkin Trans. II, (1973) 1141

243. M. Robinowitz and A. Grinvald, ibid., (1973) 514

244. C. F. Cullis and S.C.W. Hook, ibid., (1973) 803

245. M. Barber, J. A. Connor, M. F. Guest, I. H. Hiller and M. Schwarz, J. Chem. Soc. Faraday Trans. II, (1973) 551

246. C. Pinazzi, J. Vassort and D. Reyx, Bull. Soc. Chim. Fr., (1973) 1656

247. D. Q. Quan and F. Sournies, ibid., (1973) 767

248. D. Lemarchand, J. Braun and P. Cadiot, ibid., (1973) 777

249. B. Frange, ibid., (1973) 1216

250. J. F. Gal, L. Elegant and M. Azzaro, ibid., (1973) 1150

251. A. N. Maitra, J. Indian Chem. Soc., 50 (1973) 157

252. V. S. Rao and P. M. Nair, Indian J. Chem., 11 (1973) 82

253. E. F. Pearson and R. V. McCormick, J. Chem. Phys., 58 (1973) 1619

254. J. S. Hartmann and G. J. Schobilgen, Canad. J. Chem., 51 (1973) 99

255. J. Bouix and R. Hillel, ibid., 51 (1973) 292

256. H. C. Brown and C. F. Lane, Synthesis, (1973) 303

257. H. C. Brown, Yi Yamamoto and C. F. Lane, ibid., (1973) 304

258. M. Rabinovitz and A. Grinvald, J. Amer. Chem. Soc., 94 (1972) 2724

259. A. Pelter, Chem. & Ind., (1973) 306

260. K. Utimoto, K. Uchida and H. Nozaki, Tetrohedron Lett., (1973) 4527

261. K. Utimoto, T. Tanaka, T. Furubayashi and H. Nozaki, ibid., (1973) 787

262. M. Naruse, T. Tomita, K. Utimoto and H. Nozaki, ibid., (1973) 795

263. M. Naruse, K. Utimoto and H. Nozaki, ibid., (1973) 1847

264. I. Bally, E. Ciornei, A. Vasilescu and A. T. Balaban, Tetrahedron, 29 (1973) 3185

265. L. S. Vasilev, V. P. Dmitrikev and B. M. Mikhailov, J. Gen. Chem. USSR, 42 (1972) 1015

266. N. Kumar, R. K. Multani and B. L. Kalsotra, J. Organometal. Chem., 59 (1973) 105

267. D. G. Holah, A. N. Hughes, B. C. Hui and K. Wright, Inorg. Nucl. Chem. Letters, 9 (1973) 835

268. T. Taguchi, M. Itoh and A. Suzuki, Chem. Lett., (1973) 719

269. K. Reske and H. Schott, Angew. Chem., 85 (1973) 412

270. J. R. Blackborow and J. C. Lockhart, J. Chem. Thermodyn., 5 (1973) 603

271. J. W. Wilson and J. T. F. Fenwick, ibid., 5 (1973) 341

272. B. M. Mikhailov, G. S. Ter-Sarkisyan, N. A. Nikolaeva and V. G. Kiselev, J. Gen. Chem. USSR (Engl. Transl.), 43 (1973) 857

273. B. M. Mikhaiov, V. A. Dorokhov and V. I. Serekenko, ibid., 43 (1973) 862

274. B. M. Mikhailov and B. I. Bryantsev, ibid., 43 (1973) 1095

275. B. M. Mikhairov, B. I. Bryantsev and T. K. Kozminskaya, ibid., 43 (1973) 1100

276. V. A. Dorokhov, L. I. Lavrinovitch, M. N. Bochkareva, V. S. Bogdanov and B. M. Mikhailov, ibid., 43 (1973) 1106

277. N. A. Vasilenko, A. S. Teleshova and A. N. Pravednikov, ibid., 43 (1973) 1114

278. O. P. Shitov, S. L. Loffe, L. M. Leonteva and V. A. Tartakovskii, ibid., 43 (1973) 1118

279. Y. Yamanoto and H. C. Brown, Chemical Commun., (1973) 801

280. P. I. Paetzold and H. Grundke, Synthesis, (1973) 635

281. K. V. Titova, I. P. Vavilova and V. Y. Rosolovskii, Russ. J. Inorg. Chem. (Engl. Transl.), 18 (1973) 597

282. B. Frange, Bull. Soc. Chim. Fr., (1973) 2165

283. J. Gayoso, B. Maouche and A. Boncekhina, C. R. Acad. Sci. (c), 276 (1973) 257

284. J. Gallier, M. A. Chassonneau and J. Meinnel, ibid., 276 (1973) 1231

285. A. T. Jeffries and S. Gronovitz, Chem. Scripta, 4 (1973) 183

286. D. S. Kendall and W. N. Lipscomb, Inorg. Chem., 12 (1973) 2920

287. J. R. Blackborow, J. Chem. Soc. Dalton Trans., (1973) 2139

288. D. J. Pasto and P. E. Timony, J. Organometal. Chem., 60 (1973) 19

289. G. P. Sollott and J. L. Snead, Abstr. of Papers, 166th ACS Natl. Mtng. Chicago, Illinois, INOR (1973) 29

290. O. P. Shitov, S. L. Loffe, L. M. Leonteva and V. A. Tartakovskii, J. G Chem. USSR (Engl. Transl.), 43 (1973) 1257

291. J. Simpson and G. B. Porter, J. Chem. Soc. Perkin Transact. II, (1973)

292. L. Petterson and I. Andersson, Acta Chem. Scand., 27 (1973) 1019

293. B. M. Mikhailov, T. K. Baryshnikova, V. S. Bogdanov and V. V. Negrebet Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.), 207 (1972) 895

294. M. I. Bruce and A. P. P. Ostazewski, J. Chem. Soc. Dalton Transact., (2433

295. E. M. Holt, S. L. Holt and K. J. Watson, ibid., (1973) 2444

296. A. Finch, P. J. Gardner, N. Hill and K. S. Hussian, ibid., (1973) 2543

297. J. E. Williams Jr. and A. Streitweiser Jr., Tetrahedron Lett., (1973)

298. J. R. Blackborow, J. Chem. Soc. Perkin Transact. II, (1973) 1989

299. V. I. Nefedov, Y. V. Kokunov, Y. A. Buslaev and M. A. Porai-Koshits, Ru J. Inorg. Chem. (Engl. Transl.), 18 (1973) 637

300. A. Vegnere, A. Ievins and E. Svarcs, Latv. PSR Zinat. Akad. Vestis, Kim Ser., (1973) 513

301. A. Vegnere, E. Svarcs, I. Rigerte and A. Ievins, ibid., (1973) 521

302. A. Vegnere, E. Svarcs and A. Ievins, ibid., (1973) 543

303. A. Vegnere, E. Svarcs and A. Ievins, ibid., (1973) 549

304. W. M. Dugger, Advan. Chem. Ser., 123 (1973) 112

305. F. T. Bingham, ibid., 123 (1973) 130

306. N. H. Gopal, Indian J. Exp. Biol., 11 (1973) 262

307. V. A. Zamyatina, V. V. Korshak and N. M. Gnutova, Vysokomol. Soedin., Ser. B., 15 (1973) 846

308. V. A. Zamyatina, V. V. Korshak and R. M. Oganesyan, ibid., 15 (1973) 84

309. R. G. Wilson, J. Appl. Phys., 44 (1973) 5056

310. M. Lelental, J. Electrochem. Soc., 120 (1973) 1650

311. A. M. Farina, Farmaco, Ed. Sci., 28 (1973) 937

312. A. M. Mallinger, E. L. Jozwiak and J. C. Carter, Cancer Research, 32 (1972) 1947

313. D. Senard, C. Paulnier, J. Morel and P. Pastour, Int. J. Sulfur Chem. A, 2 (1972) 257

314. K. Brendhaugen, E. W. Nilsson and H. M. Siep, Acta Chem. Scand., 27 (1973) 2965

315. R. Johansen, E. W. Nilsson, M. Seip and W. Siebert, ibid., 27 (1973) 3015