BORON

ANNUAL SURVEY COVERING THE YEAR 1979 *

Part II

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CONTENTS

Although the material is grouped into major sections, this guiding principle is not strictly adhered to. Various compounds can be classified differently and related topics occasionally prompted simultaneous presentation of data. Moreover, some aspects are included that are not strictly organometallic in nature but nevertheless should be of interest to the reader.

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* Boron, Part II, Annual Survey covering the year 1978 see J. Organometal. Chem., Vol. 180(1979) p. 65-100.

1 REVIEWS AND SUMMARY ACCOUNTS

A historic perspective on the use of boranes for organic reductions has been compiled (13) and non-catalytic hydrogenation _via_ organylboranes has been surveyed (53). Summary accounts are also available for the application of trialkylhydroborates in organometallic syntheses (14) and on metal sandwich complexes of cyclic planar and pyramidal ligands containing boron (80). A correlation of ^{13}C chemical shifts of the _para_ carbon atoms of a variety of phenylboranes and the corresponding carbon atoms of borylated aromatic heterocycles with ^{11}B chemical shift data suggests a mesomeric interaction of the boryl group with the aromatic system (21).

The 20th volume of the New Supplement Series of the GMELIN Handbook dealing with boron compounds has been published (23); boron hydrides containing five or more boron atoms as well as their derivatives are described. This is the final volume of the series wherein coverage extended far beyond the GMELIN principle and arrangement was made by topics. However, since an alphabetical formula index for the cited 20 volumes (24) appeared simultaneously with the last volume, the series now seems to be extremely useful and major topics as well as specific compounds are readily located.

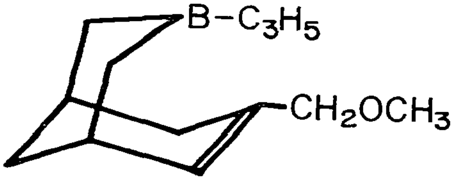
2 ORGANYLHYDROBORANES AND TRIORGANYLBORANES

Redistribution of diisopinocampheylborane with borane yields monoisopinocampheylborane (193). Regiospecific functionalization of cyclic allenes with catecholborane has been studied (163) and the stereochemistry of the protonolysis of organylboranes has been investigated.

The thermolysis of tetraalkyldiboranes(6) has been studied by NMR techniques (31); 1,1,2-trialkyldiboranes(6) are the principal products if the organic moiety is a lower alkyl group and the amount of trialkylborane in the equilibrium mixture was found to increase with the size of the organic group.

Detailed studies on the hydroboration of alkynes (124) and allenes (161) with 9-borabicyclo(3.3.1)nonane have been published (124) and syntheses of B-halo-9-borabicyclo(3.3.1)nonane have been accomplished by cyclic hydroboration of 1,5-cyclooctadiene with dimethylsulfide-monohaloboranes (128) and by exchange reactions (110). Various other exchange and substitution reactions of 9-borabicyclo(3.3.1)nonane have also been described (110). B-Alkyl-9-borabicyclo(3.3.1)nonanes undergo a facile olefin-alkyl group exchange when refluxed with an olefin in tetrahydrofuran (200); the reaction seems to occur in a dehydroboration-hydroboration process. 9-Borabicyclo(3.3.1)nonane can readily and selectively hydroborate double bonds in the presence of triple bonds, thus facilitating a new route to acetylenic organylboranes (198). Steric effects as a factor in the stability of addition compounds of amines with 9-borabicyclo(3.3.1)nonane have been evaluated (88). For the reaction of B-(1-alkenyl)-9-borabicyclo(3.3.1)nonanes with isocyanates, see (213); and for unusual kinetics for the hydroboration of alkenes with 9-borabicyclo(3.3.1)nonane, see (225).

Propargyl methyl ether reacts with triallylborane *via* three successive stages to give the following 3-borabicyclo-(3.3.1)non-6-ene derivative (26).



Treatment of the latter with methanol gives the B-methoxy species, the hydroboration of which has been studied in detail.

Methods for the preparation of (alkyl)diallylboranes and (dialkyl)allylboranes have been described (34, 35). These unsymmetrical triorganylboranes react with carbonyl compounds by addition of the boryl-allyl fragment across the C=O group accompanied by allyl rearrangement (36).

Both the 1-stanna-4-bora-cyclohexa-2,5-diene $(CH_3)_2Sn(CCH_3{=}CH)_2BCH_3$ and a 3-diethylboryl-1-stannacyclopenta-2,4-diene react with (dibromo)methylborane to yield nido-2,3,4,5-tetracarbahexaborane derivatives (15). - The photochemical reaction of $(C_5H_5)_2Co(CO)_2$ with $(CH_3)_2Si(CH{=}CH)_2BC_6H_5$ (= L) yields the new complex $(C_5H_5)CoL$ (113); acetylation of the latter species and subsequent hydrolysis effects ring opening of the ligand with loss of boron.

For reactions of triorganylboranes with 2,5-dihydroxy-1,4-benzoquinone and related compounds in organic syntheses, see (201). Displacement reactions in (alkyl)dicyclohexylboranes and (alkyl)di-exo-norbornylboranes have been studied (147) and the first direct syntheses of carboxylic acids from organylboranes have been described (219). For the selective transformation of organylboranes to GRIGNARD reagents, see (218). The lithium tri-t-butoxyhydroaluminate/triethylborane combination has been found to be an effective agent for the reductive opening of cyclic ethers (89) and triethylborane was used to initiate grafting of methyl methacrylate onto chitin (156). 2-Alkylation reactions of thiophene and 1-methylpyrrole employing trialkylboranes have been described (167). For the selective elimination of a secondary alkyl group from trialkylboranes by the successive treatments with anisole and DMSO, see (44).

An improved synthesis of tertiary alcohols involves the reaction of organylboranes with 2-lithio-1,3-benzodithiols (179) and interaction of organylboranes with 2-lithio-2-alkyl-1,3-benzodithiols has provided for an improved synthesis of ketones (180).

Hydroboration-carbonylation (in the presence of potassium triisopropyloxyhydroborate) was found to be an excellent method for converting alkenes to primary alcohols or aldehydes (154). Various organic syntheses employing triphenylborane have been described (164).

For a study on chiral trialkylboranes as reducing agents, see (174); and for aromatic substitution via organylboranes, see (151, 173). Also, a new stereospecific cross-coupling by the palladium-catalyst reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides has been reported (176) and the reaction was used for the synthesis of arylated (E)-alkenes (152).

The stereochemistry at the migration terminus on the base-induced rearrangement of alpha-haloorganylboranes has been investigated (203); in the absence of solvent the migration was found to be stereopecific.

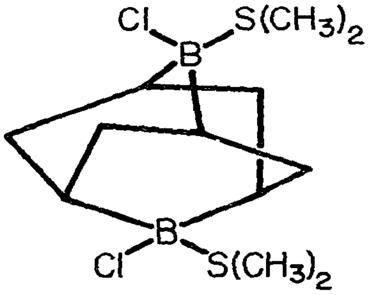
A new method for isotopically labelling of organic compounds involving triorganylboranes has been described (172). For new studies on the chromium trioxide/pyridine oxidation of diorganylboranes (120) and triorganylboranes (112), see the indicated references.

For studies on the ^1H NMR spectra of (alkenyl)disiamylboranes, see (129); and for NMR studies on 1-stanna-4-boracyclohexadienes, see (135). The vibrational spectrum of $B(CH_3)_3$ has been recorded and force constants were calculated (216). Vibrational as well as NMR spectroscopic data have also been reported for (dimethyl)-vinylborane (61).

3 (HALO)ORGANYLBORANES

Various isotopically labelled boron trichloride species have been prepared by reacting boron with silver chloride (77) and an improved synthesis of tetrachlorodiborane(4), B_2Cl_4, by radiofrequency discharges through boron trichloride has been described (92); both of these developments are of interest to (halo)organylborane chemistry. In this context it is also of interest to note that the reaction of tris(trimethylstannyl)-amine with boron trichloride yields the long searched for $N(BCl_2)_3$ (105); by the same basic procedure the compounds $RN(BCl_2)_2$ with R = $SiCl_3$, $SiCl_2(CH_3)$, $SiCl(CH_3)_2$ and $Si(CH_3)_3$ have also been obtained.

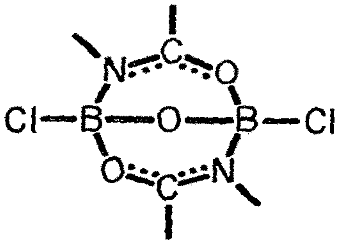
(Dialkyl)haloboranes, R_2BX, are readily obtained by the reaction of $(CH_3)_2S{\cdot}BH_2X$ (X = Cl, Br, I) with alkenes (132). The cyclic dihydroboration of 1,3,5,7-cyclooctatetraene with $(CH_3)_2S{\cdot}BH_2Cl$ gives a polymeric material which, on thermal treatment, affords 2,6-dichloro-2,6-diboraadamantane as $(CH_3)_2S$ adduct (197):



Reaction of 1,3-butadiene with B_2X_4 (X = F, Cl) yields $X_2B\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}BX_2$, but if X = Cl an additional B_2X_4 can be added to the double bond of the former species (104). The five-membered heterocycles ($-BCl-CH_2-CH_2-BCl-X-$) where X = S or NCH_3 are readily formed on interaction of $Cl_2B\text{-}CH_2\text{-}CH_2\text{-}BCl_2$ with $((CH_3)_3Si)_2X$ (115); attempts to displace the boron-bonded chlorine of the heterocycles were accompanied by extensive ring cleavage.

(Cyclopentadienyl)dihaloboranes, $CpBX_2$, as well as related species such as $CpB(OR)_2$ and $CpB(NR_2)_2$ have been prepared by the interaction of haloboranes with (cyclopentadienyl)trimethylsilanes (125); the NMR spectra of the species were studied and some of them were found to exhibit dynamic behavior. (Borylcyclopentadienyl)trimethylsilanes interact with $TiCl_4$ with the formation of (borylcyclopentadienyl)titanium trichlorides (50). Bis(dihaloboryl)cyclopentadienes have been prepared in similar fashion as outlined above (122) and the boron-bonded halogen was found to be readily displaced by, for example, dimethylamino groups. (Pentamethylcyclopentadienyl)boranes have been obtained by the reaction of (pentamethylcyclopentadienyl)trimethylgermane with haloboranes (106); the fluxional structure of the former species has been studied.

1,5-Dichloro-2,6,9-trioxa-4,8-diaza-1,5-dibora-bicyclo-(3.3.1)nonadiene derivatives of the type



react with pseudohalide ions (CN, CNO, N_3) dy displacement of the chlorine (8).

A quantitative ^1H and ^{11}B NMR study of the redistribution equilibria between dimethylamino groups and the Cl, SCH_3, OCH_3 and F substituents of mono- and difunctional boron centers, R_2B and RB, respectively, has been reported (114). A preferential affinity of the amino group towards dialkylated boron centers was observed.

The dehalogenation of (dihalo)organylboranes by metal reducing agents has been examined in detail (111). No evidence for the formation of a borene, BR, was obtained; however, the results can be interpreted by the formation of an intermediate borenoid, BRMX, which can undergo alpha-elimination or rearrangement. For the reaction of (dihalo)organylboranes with cobaltocenes, see (183); and for reactions of aromatic aldehydes with boron halides, see (71).

The microwave spectrum of (difluoro)methylborane has been studied (188). For the vibrational spectrum and force constants of (dichloro)methylborane and the deuterated species, see (215).

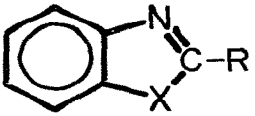
4 CHALCOGEN DERIVATIVES

Vinyloxyboranes obtained on interaction of trialkylboranes with $R\text{-}CO\text{-}CHN_2$ are almost exclusively the E-isomers, but they can be isomerized to the Z-form (166). For the stereoselective formation of vinyloxyboranes, see also (217). Vinyloxyboranes habe been employed for stereoselective organic syntheses (57, 58).

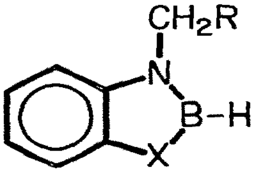
(2-Methyl-1-propenyloxy)boranes of the type $(CH_3)_2C{=}CR\text{-}O\text{-}BR^1R^2$ have been prepared by addition of boranes, BRR^1R^2, to dimethylketene and by transfer of $(CH_3)_2C{=}CR\text{-}O$ groups from the species $ZnBr(O\text{-}CR\text{-}C(CH_3)_2)$ to bromoboranes, R^1R^2BBr (143). The compounds dissociate thermally to dimethylketene and the unsymmetrical borane. Interaction of $(CH_3)_2{=}CBr\text{-}O\text{-}B(CH_3)_2$ with aldehydes yields $O{=}CBr\text{-}C(CH_3)_2\text{-}CHR\text{-}O\text{-}B(CH_3)_2$ (143).

(Isopropylideniminoxy)diphenylborane, $(CH_3)_2C{=}N\text{-}O\text{-}B(C_6H_5)_2$, is readily obtained by the interaction of (dimethylamino)diphenylborane with acetone oxime. The compound forms a 1:1 molar adduct with 2-aminopyridine, which is directly obtained when (2-pyridylamino)diphenylborane is reacted with acetone oxime (10).

Reaction of diborane(6) with benzo-fused heteroaromatic compounds of the type



where X = O, S or Se occurs with rearrangement to yield borole derivatives (82):



An efficient preparation of pinacol iodomethaneboronate and dibutyl iodomethaneboronate has been devised (121). A series of alkoxyboryl bridged encapsulation compounds of iron(II) of the type $FeL_3(BX)_2$ where X = OH, OCH_3, OC_2H_5, <u>etc.</u> have been synthesized by an *in situ* procedure using $FeCl_2$ and dione dioximes (78).

Organylboron heterocycles containing the -O-BR-O- moiety can undergo intermolecular association rendering the boron four-coordinate (20). This coordination provides for crystalline species and prevents intermolecular rearrangement to form larger ring systems. Such rearrangements have been observed for heterocycles of the 1,3,2-dioxaboracycloalkane-type and species containing more than one anular O-BR-O unit have been obtained (19). This rearrangement process occurs without cleavage of the B-to-R bond and can be utilized to transfer BR groups from one ring system to another.

Allenylbis(organyloxy)boranes, $RR^1C{=}C{=}CH{-}B(OR^2)_2$, with $R = R^1 = H$ or $R = H$, $R^1 = CH_3$, react with HBr to form 2-bromoalkenyl derivatives if $B(OR^2)_2$ is a cyclic moiety (33). Additional HBr yields the 2,2-dibromoalkyl species. If $R = R^1 = CH_3$, the 3-bromo-3-methyl-1-butenyl derivative is obtained initially and with the second HBr the corresponding 1,3-dibromo species is formed.

For the use of chlorobis(dimethylamino)borane (*via* cyclic bisoxyboranes) in diastereoselective alcohol syntheses, see (12). Chiral allylbis(organyloxy)boranes have been employed in enantionselective syntheses of komoallyl alcohols (11). (4-Iodobutyl)dihydroxyborane is a selective agent for the trace determination of bifunctional compounds (40); for 1,2-ethanediol, (*n*-butyl)dihydroxyborane has been recommended (48).

Various solid alkali metal (Li, Na) polyalcohol (mannitol, sorbitol, galactol, fructol) borate complexes have been prepared and some of their molecular molecular properties have been determined (6). In the solution of catechol and borax at pH 11, the equilirbrium between catechol and the monomeric borate anion to form the 1:1 and 1:2 molar complexes has been determined by ^{11}B NMR (146). In the solution of L-dopa and borax, the 2:1 molar complex is not observed at pH 11 but is detected below pH 7. The addition of boric acid or (dihydroxy)phenylborane to either 1,2- or 1,3-diols has been shown to produce substantial alterations in the ^{13}C chemical shifts of the parent compounds (131); this observation can be used for structural assignments since *cis* diols react to the exclusion of the *trans* isomer. For the transformation of pyrocatechols with (diaryl)hydroxyboranes to yield paramagnetic borate complexes, see (170).

Tris(2-mercaptoethoxy)borane and cyclic derivatives thereof containing the $O_2B{-}O{-}CH_2{-}CH_2SH$ group have been prepared by various routes (206); infrared and ^1H NMR spectral data of the various species are reported. Tris(alkyloxy)boranes are readily oxidized to aldehydes and ketones with pyridinium chlorochromate (169).

The mass spectral fragmentation of C_6H_5BO derivatives of acyclic tetraols have been studied (65) and the fragmentation of diphenylboron and monophenylboron chelates has also been studied (75). The structures of cyclic tris(boronic) esters of the inositols have been examined by electron ionization mass spectrometry (123).

A refractometric study (76) and thermal conductivities of tris(alkyloxy)boranes (86) have been reported. For the RAMAN spectra of polyborates, see (5); and for studies on the gas-phase electronic absorption spectrum of catecholborane, see (220).

Alkoxytriphenylboranyl radicals have been observed by optical absorption spectroscopy when t-butyloxy radical was reacted with triphenylborane (130); the data provide for conclusive evidence for the stepwise nature of the radical reaction at the boron center:

$$t\text{-}C_4H_9O\cdot + BR_3 \rightarrow t\text{-}C_4H_9O\dot{B}R_3 \rightarrow t\text{-}C_4H_9OBR_2 + R\cdot$$

For the oxidation of tris(alkyloxy)boranes in the liquid state, see (185).

Open cage borane and heteroborane thiols have been synthesized (175) and a chemical and spectroscopic study of the $B(SCH_3)_3/B(NCS)_3$ system has been reported (157).

Tris(ethylthio)borane reacts with oxiranes to yield substituted (ethylthio)propanols (107). Similarly, the cited thioborane is a convenient reagent for the ketalization of carbonyl compounds (99); with amides, amide thioacetals are obtained. Cyclic ethylene thioketals and thioacetals can be prepared from 2-phenyl- and 2-chloro-1,3,2-dithiaborolanes (109). Tris(ethylthio)borane reacts with ammonium hydrosulfides, $(NR_4)SH$, in liquid hydrogen sulfide to yield thioborates (1).

Differently substituted 1,2,4-trithia-3,5-diborolanes have been found to exchange boron substituents with preservation of the boron-to-ligand bond (18). This observation is explained by the formation of a ten-membered cyclic intermediate <u>via</u> intermolecular S-B coordination and subsequent cleavage of the original B-S bonds. If unsaturated 1,2,5-thia-diborolene, $S(BCH_3\text{-}CC_2H_5{=})_2$, is reacted with elemental potassium, sulfur is abstracted as K_2S and a C_4B_4 carborane is formed (139). For C-C bond formation <u>via</u> an (alkylthio)allylboronate, see (96).

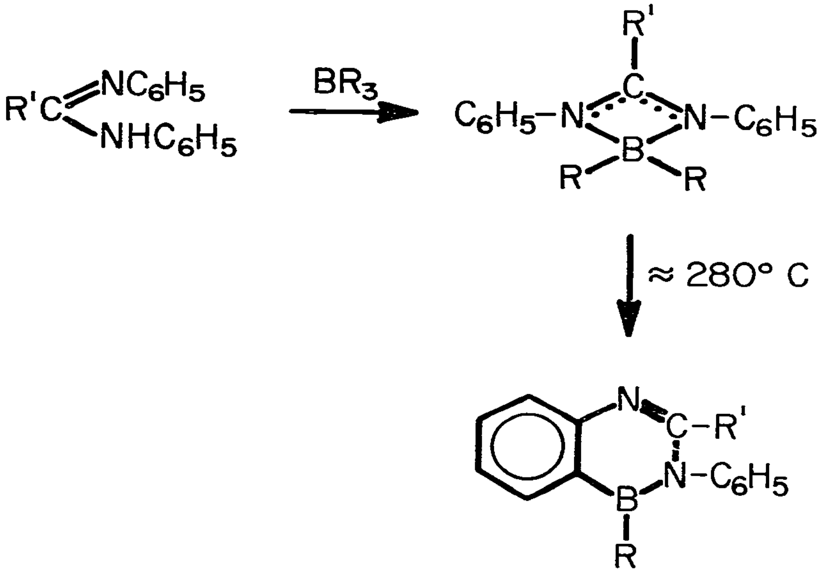
Tris(methylseleno)borane and tris(phenylseleno)borane have been employed for the conversion of aldehydes and ketones into selenoacetals (74); the latter compounds have also been obtained by exchange reactions between acetals and tris(phenylseleno)borane (52).

5 BORON-NITROGEN COMPOUNDS

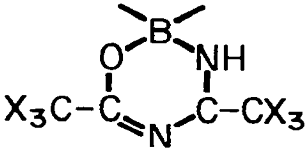
SCHIFF bases react with <u>n</u>-butyllithium by a 1,2-addition (2); subsequent treatment of the resultant N-lithiated amines with monohaloboranes, XBR_2, yields the corresponding aminoboranes. Syntheses of new aminoboranes include those of bis(trimethylsilyl)amino- and (<u>t</u>-butyl)(trimethylsilyl)aminoborane (189) and the reaction of trimethylsilylsulfonamides with (halo)diorganylboranes was found to yield the corresponding sulfonaminoboranes, $RN(C_6H_5)(BR_2)$ (100).

The aminoboronation of ketene with (dimethylamino)diorganylborane yields triorganylborane and N,N-dimethylacetamide (as products of the decomposition of the intermediate $R_2B\text{-}CH_2\text{-}CO\text{-}N(CH_3)_2$) as well as oxazoniaboratacyclohexane derivatives (originating from the alternate intermediate $CH_2{=}CN(CH_3)_2)_2\text{-}OBR_2$) (142); aminoboronation of ketene with $XB(N(CH_3)_2)_2$ (X = halogen) yields $((R_2N)XB\text{-}CH_2\text{-}CO\text{-}NR_2)_2$. The reaction of trimethylsilylcarbonamides, R-CO-NR'-Si$(CH_3)_3$, with haloboranes, R_nBX_{3-n} (n = 0, 1, 2) yields the corresponding N-borylated species which exist either as monomers or monocyclic or bicyclic dimers (3); see also (207).

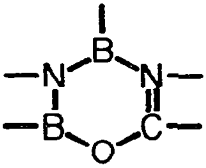
N,N'-Diphenylamidines when reacted with trialkylboranes form N-dialkylboryl-N,N'-diphenylamidines, which are readily transformed into 3,4-dihydro-4-boraquinazolines (30):



Reaction of X_3C-CO-NH-Si$(CH_3)_3$ with haloboranes yields the following ring system (140):

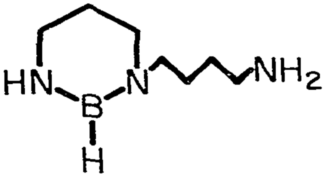


Derivatives of the related systems containing the heterocycle

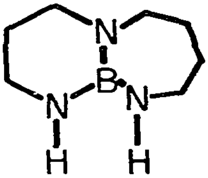


are also reported (140)

The reaction of tris(aminoalkyl)amines with tris(dimethylamino)borane leads to polymeric species and no discrete molecules could be identified (199). 1,3-Dimethyl-2-methylthio-1,3,2-diazaboracyclohexane, $CH_3S-B(-NCH_3-CH_2-)_2CH_2$, interacts with anhydrous ammonia by simple displacement of the CH_3S group by NH_2. In contrast, the reaction of the corresponding 1,3,2-diazaboracyclopentane with ammonia proceeds with simultaneous condensation and a diborylamine is obtained (16). The reaction of spermidine with borane(3) yields the monocyclic ring system



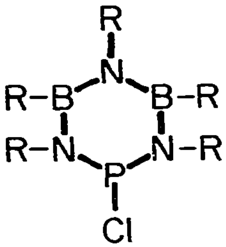
which, on thermal treatment, undergoes intramolecular condensation with the formation of 1,10,11,9-triazabora-bicyclo(4.5.0)nonane (9):



The electronic structure of the related species 1,8,10,9-triazaboradecalin has been studied (4).

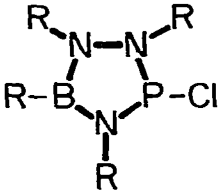
Both N,N,N'-tris- and N,N,N',N'-tetrakis(1,3-dimethyl-1,3,2-diazaborlin-2-yl)hydrazine have been prepared via the N,N'-dilithiated N,N'-bis(1,3-dimethyl-1,3,2-diazaborolin-2-yl)-hydrazine (98). Structural changes during the oxidation of substituted hydrazines including borylated species have been studied by PE and ESR spectroscopic techniques (41). Other ESR and NMR spectroscopic studies deal with isomerization processes of five- and six-membered heterocycles containing the B_2N_3 and B_2N_4 anular skeletons (22). The NMR data were correlated and relative electron densities within the ring systems were evaluated. One-electron oxidation of the isomers $RB(NR-NR)_2BR$ and $R_2N-N(BR-NR-)_2$ was found to yield the identical stable radical cation $RB(NR-NR)_2BR^+$, the ESR spectrum of which was recorded and interpreted.

The BN_2Sn heterocycle has been obtained as a dimeric species which exhibits fluxional behavior at temperatures above 60°C (134). NMR parameters on 2-chloro-pentamethyl-1,3,5,2,4,6-triazaphosphadiborine



R = CH_3

and 3-chloro-tetramethyl-1,2,4,3,5-triazaphosphaborolidine



R = CH_3

and their corresponding phosphinylium cations have been determined (17). The geminal ^{31}P-^{13}C coupling constants are consistent with non-planar ring systems and the non-planarity is greater in the neutral than in the cationic species. For the heat of atomization of unsymmetrically N-substituted tetrazaborolines, see (150).

New investigations on borazine, $(-BH-NH-)_3$, include *ab initio* studies of the low-lying pi-states (60) and the protonation (55) of the species as well as of the electronic spectrum (62). Also, the emission spectrum of B-trifluoroborazine has been studied (56); and for the crystal structure of hexaphenylborazine, see (66). Macrocyclic and linear polyborazine species in which the borazine moieties are linked *via* difunctional phenyl derivatives have been described (137).

Various aminohaloboranes have been employed in organic syntheses such as enantioselective aldol formation (158), aldol condensations (159, 160, 165), specific *ortho* formylation of secondary anilines (214) and *ortho* alpha-chloroacetylation of anilines (7). A directed aldol condensation using (vinyloxy)aminochloroborane has also been described (72).

Indirect ^{10}B-^{11}B spin-spin coupling has been observed in tetrakis(dimethylamino)diborane(4) (204). For the microwave spectrum of aminoborane, see (83).

6 TETRACOORDINATE BORON SPECIES

6.1 SIMPLE LEWIS ACID-BASE ADDUCTS

The adduct $(CH_3)_2ClP-BH_3$ reacts with $NaNH_2$ to yield $(CH_3)_2(H_2N)P-BH_3$, whereas Ag_2O will form the complex species $O(P(CH_3)_2(BH_3))_2$ (223). The former compound can be converted to $HN(P(CH_3)_2(BH_3))_2$ which, in turn, is readily N-lithiated (223). $CH_2(P(CH_3)_2(BH_3))_2$ can be converted to the anion $CH(P(CH_3)_2(BH_3))_2^-$ but can also be halogenated at the boron site to give $CH_2(P(CH_3)_2(BH_2Br))_2$ (224). Reaction of $((R_3P)_2BH_2)^+Br^-$ ($R = CH_3$) with two molar equivalents of LiC_4H_9 and treatment of the resultant $Li((CH_2PR_2)_2BH_2)$ with one half molar equivalent of $(R_3P)_2MCl_2$ ($M = Ni, Pd, Pt$) results in the formation of $H_2B(-PR_2-CH_2-)_2M(-CH_2-PR_2-)_2BH_2$ (117). Reaction of the cited lithium salt with triethylamine-chloroborane yields the heterocycle $H_2B(PR_2-CH_2-)_2BH_2$ and with (bromo)dimethylborane the species $(CH_3)_2B(PR_2-CH_2)_2BH_2$ is obtained (138). The chlorine in the heterocyclic species $N(PCl_2-NCH_3)_2BCl_2$ is readily displaced, usually starting with the boron-bonded halogen (127). Borane(3) complexes of various (cyclopentadienyl)fluorophosphines have been described and were characterized by spectroscopic data (108). The vibrational spectrum of triphenylphosphine-borane has been recorded and assignments to the fundamental vibrations are supported by a normal coordinate treatment (97). The microwave spectrum of *t*-butylisocyanide-borane has been studied (186) and potential constants of carbonyl-borane have been reported (85). The acid-catalyzed hydrolysis of amine-boranes has been reexamined (94).

Pyridine-borane in CF_3COOH has been employed as agent for the reduction of aldehydes to yield ethers (95). The same reagent was used in acidic medium for the reduction of aldehydes and ketones (155) as well as oximes (205) and betahydroxy sulfoximine-boranes have also been employed as reducing agents (192). The interaction of BX_3 (X = F, Cl, Br) with $H_3N\text{-}BH_3$ was studied by NMR spectroscopy (90).

Bromoborane adducts of the type $L\text{-}BH_2Br$ (L = pyridines, quinoline) and boronium(1+) salts, $L_2BH_2^+Br^-$ (L = pyridines) have been prepared by interaction of $(CH_3)_2S\text{-}BH_2Br$ with the respective bases (181).

Ethylenediamine and boron trifluoride interact in ether to give the insoluble 1:1 molar adduct (145). In contrast, the same amine reacts with dialkylboranes to form 1:2 molar complexes from which, on treatment with BF_3, the dialkylborane is readily released. N,N,N',N'-Tetramethylethylenediamine reacts with BF_3 to form a 1:2 molar complex whereas the same amine forms either 1:1 or 1:2 molar complexes with monoalkylboranes (144); either of the latter releases the monoalkylborane on treatment with BF_3, see also (195). For the electronic structure of some BF_3 complexes, see (208).

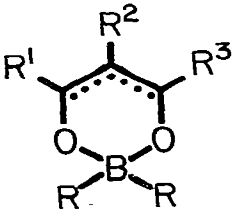
Bis(dialkylamino)tin(II) compounds interact with BF_3 to form 1:3 molar complexes (209); based on NMR data, initial coordination of BF_3 occurs at the tin sites.

Amine- and diamine-cyanoboranes of the type $L\text{-}BH_2CN$ have been prepared from the corresponding amine hydrochlorides and sodium cyanotrihydroborate (177). Alkylation of the amine-cyanoboranes with $(C_2H_5)_3OBF_4$ yields N-ethylnitrilium salts which hydrolize to the amine-carboxyboranes. Some of these species exhibit biological activity.

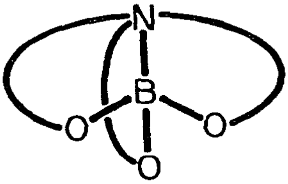
Triarylboranes from 1:1 molar complexes with hydroxylamine and its derivatives in which the nitrogen acts as the donor site (38). Thexylborane forms a stable complex with N,N-di ethylaniline which readily hydroborates alkenes without displacement of thexene (70).

6.2 CHELATES

Based on an analysis of infrared spectral data, boron derivatives of the type

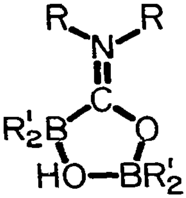


have a non-planar environment about the boron atom (37). Fragmentation of trioxaazaboratricycloalkanes of the type



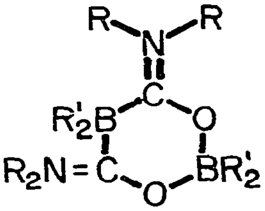
under electron impact occurs characteristically by splitting one of the rings with removal of the radical $C_nH_{2n+1}O$ (39).

(Bromo)diphenylborane reacts with diisopropylcarbamoyllithium to form the following heterocyclic species (168):



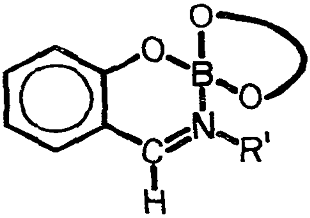
R = $\underline{i}$-C_3H_7
R' = C_6H_5

The same ring structure was obtained in an analogous reaction employing (bromo)di-$\underline{n}$-hexylborane (171). However, in this latter case a small amount of an additional species was obtained; X-ray diffraction data confirm the following structure:

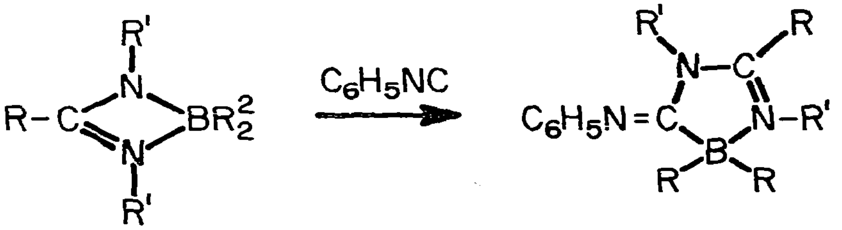


R = *i*-C_3H_7
R' = *n*-C_6H_{13}

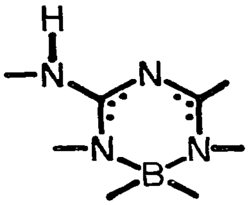
Unsymmetrical cyclic isopropyloxyboranes, (-O-R-O-)BO-*i*-C_3H_7, react with N-substituted benzaldimines and salicylaldimines *via* release of the OC_3H_7 group (51); the resulting species appear to be stabilized by intramolecular coordination, *e.g.*:

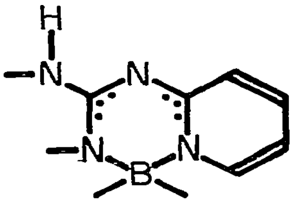


Borylated amidines react with phenylisonitrile to form inner complexes (25):

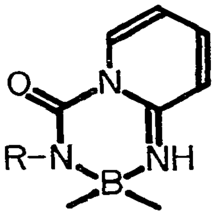


Similar reaction between borylated amidines or (pyridylamino)diorganylboranes and heterocumulenes where found to yield the following structures:

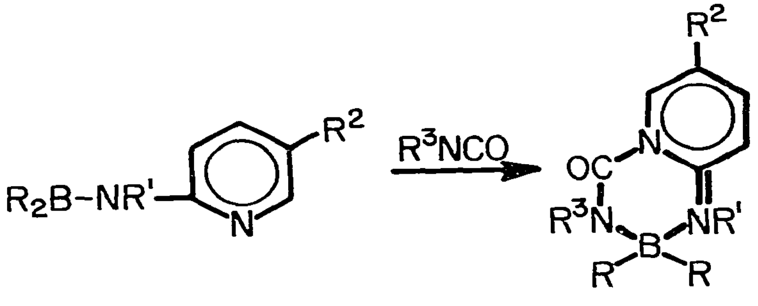




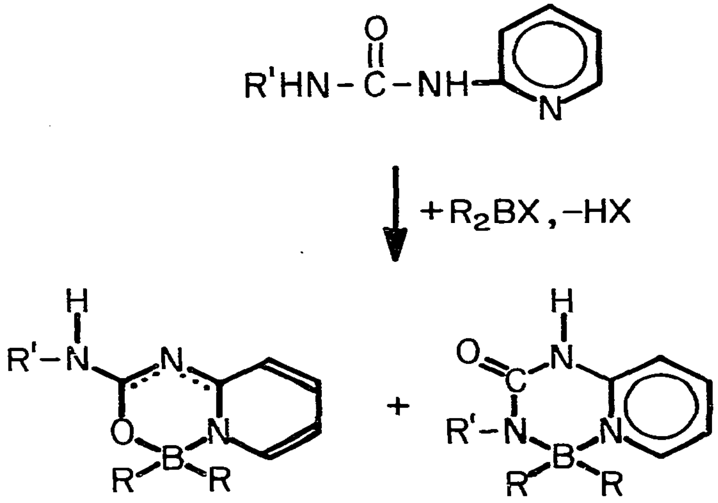
Also, isocyanates and (2-pyridylamino)dialkylboranes interact in a fashion where the latter serve as 1,4-dipolar systems to yield compounds of the type (25):



A more detailed study on the interaction of (2-pyridylamino)-boranes with isocyanates and isothiocyanates confirms this unusual addition and was found to result in the formation of 1-carbamoylpyridon-2-imine derivatives (222):

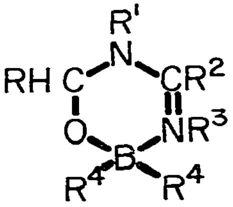


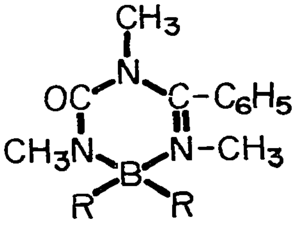
The reaction of N-aryl-N'-(pyrid-2-yl)ureas with trialkylboranes or (butylthio)diphenylborane proceeds smoothly in tetrahydrofuran to yield a mixture of isomeric compounds (226):



The O-boryl derivatives can isomerize to the N-boryl species upon thermal treatment.

For a study on the structure of dialkylborylamidines (obtained from N,N'-disubstituted amidines) and their reactions with aldehydes or isocyanates to form six-membered heterocyclic boron compounds such as the following two, see (28).



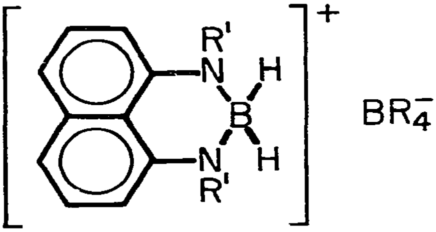


The mass spectral fragmentations of dialkylborylacylamidinates and dialkylborylacylaminopyridinates are similar, in principle, to those of dialkylborylimidoylaminates (29).

Chelates obtained from the interaction of catecholamine with phenyl- and p-tolylhydroxyboranes have been described (87) and complexes prepared by addition of carboxylic acids, alcohols and water to substituted 3,4-dihydro-4-boraquinazolines have benn shown by infrared spectroscopic studies to undergo tautomeric conversions in the amidine system. For the use of dialkylboryl beta-diiminates in organic syntheses, see (27).

6.3 BORONIUM(1+) AND BORATE(1-) SPECIES

1,8-Bis(dimethylamino)naphthalene reacts with diborane(6) or boron trifluoride, respectively, to form boronium(1+) salts of the type (R = H, F) (93):



The reaction of diborane(6) with other chelating bidentate ligands such as 2,2'-bipyridinyl, L, has been found to give $LBH_2^+B_2H_7^-$ salts in a one-step synthesis (91). For boronium(1+) salts of the type $L_2BH_2^+Br^-$, see also (181).

The molecular structures of tetra-t-butoxytriberyllium bistetrahydroborate (182) and dimethylaluminum as well as dimethylgallium tetrahydroborate (67) have been determined. For the photochemistry of $U(BH_4)_4$ and $U(BD_4)_4$, see (210); and for the vibrational spectrum of $Rb(B(CH_3)_4)$, see (216). Trihaloboranes, BX_3 (X = Cl, Br), react with ammonium hydrosulfides,

$(NR_4)SH$, in liquid hydrogen sulfide to yield thioloborates, $(NR_4)(X_3BSH)$ (1).

The dihydrobis(indazol-1-yl)borate ion has been prepared and its ligand properties have been investigated (178). The dihydrobis(pyrazol-1-yl)borate ion has been employed in reduction processes (47).

New poly(pyrazol-1-yl)borate complexes of the following metals have been prepared and/or structure determinations have been carried out: copper (42, 64), silver (59), zirconium (68), technetium (102), rhenium (49), rhodium (73, 101), nickel (63) and thorium (45).

Lithium triethylhydroborate reduces elemental sulfur to yield anhydrous Li_2S or Li_2S_2 and lithium thiolates are obtained on the interaction of the cited borate with disulfides (194). For the reduction of methoxy ethoxy methyl ethers with lithium triethylhydroborate, see (191); and for the use of lithium trialkylhydroborates as reducing agents in carbohydrate chemistry, see (190).

Lithium trialkylhydroborates are readily formed on the interaction of trialkylboranes with $Li(HAl(OCH_3)_3)$ in tetrahydrofuran (119) or by the reaction of $LiAlH_4$ with trialkylboranes in the presence of triethylenediamine (228). Addition of equimolar or catalytic amounts of trialkylboranes to a tetrahydrofuran solution of $Li(HAl(O\text{-}\underline{t}\text{-}C_4H_9)_3)$ results in rapid loss of active hydride with the concurrent formation of butanol (from the reductive cleavage of the tetrahydrofuran) (118); chemical and spectroscopic evidence suggests the intermediate formation of lithium trialkylhydroborates.

Trialkylboranes interact with lithium ethoxyacetylide to yield the corresponding lithium ethoxyethynyltrialkylborates (221). The latter interact with iodine to form 1-ethoxyalkynes, whereas with methyl iodide or an allyl halide ethoxymethylacetylene and ethoxyallylacetylenes, respectively, are obtained. With primary trialkylboranes, the cited borates interact to form lithium 1-alkynyltrialkylborates and ethoxydialkylboranes.

Potassium triisopropyloxyhydroborate readily reacts with trialkylboranes to form potassium trialkylhydroborates (202). In the presence of small amounts of free trialkylborane, alkali metal trialkylhydroborates react rapidly with carbon monoxide (196). Potassium enoxytrialkylborates have been employed for the alpha-alkylation of ketones (47).

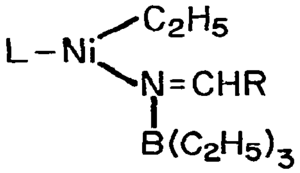
For the reaction of copper(I) methyltrialkylborates with 1-(1-pyrrolidinyl)-6-chloro-1-cyclohexene, see (43). 2-Furyllithium forms borate complexes with trialkylboranes which, on interaction with iodine, give access to 2-alkylfuranes (212).

Solubility products and transfer activity coefficients of potassium tetraphenylborate in water/methanol mixtures ar 25°C have been determined (84). Fur nucleophilic biphenylyl transfer with the tetraphenylborate ion, see (227). For the use of the tetraphenylborate ion as a phase transfer agent for acid catalysis, see (149).

Electron spin resonance studies and the electronic spectrum of the diphenylboron dibenzamide radical anion have been reported (148).

7 METAL DERIVATIVES

Sodium iminoborates $Na((C_2H_5)_3B{-}N{=}CHR)$ react with $NiBr_2$ in the presence of 2,2'-bipyridyl (L) to yield species of the type (126):



The structure is confirmed by X-ray diffraction studies.

Some complexes of the composition $(C_6H_5)_nPM(H_3BCO_2R)$ (n = 2 or 3; M = Cu, R = CH_3 or C_2H_5; M = Ag, R = H or C_2H_5) have been prepared and possible factors influencing the bidentate or monodentate nature of the anion are discussed (133).

A modified synthesis of $(C_5H_5)Fe(CO)_2(CNBH_3)$ and the preparation of $((C_5H_5)Fe(CO)_2(CNBH_2N(CH_3)_3)^+$ have been described (211).

Molecular orbital calculations of bis(borabenzene) complexes of transition metals of the type $M(C_5H_5BR)_2$ (R = H, M = Cr, Mn, Fe, Co; R = CH_3, M = Fe, Co) have been performed (79) and nucleophilic and electrophilic substitutions in borabenzene iron complexes have been studied (153). Some cationic borabenzene complexes of the type $(LM(C_5H_5BC_6H_5))^+$ have been described and were found to be considerably more electrophilic than the corresponding $(LM(C_5H_5))^+$ species (141); some ring contractions of the borabenzene ligand were also described.

8 PHYSIOLOGICAL AND RELATED ASPECTS

The antivirial activity of 1-boraadamantane complexes has been studied (184) and the biological activity of some amine-cyanoboranes and amine-carboxyboranes has been screened (177).

DNA has been removed from RNA by chromatography on acylated N-(N'-(m-dihydroxylborylphenyl)succinyl)aminoethyl cellulose (187) and phenyl(dihydroboryl)polyacrylamide beads have been used for the chromatography of ribonucleosides in tissue extracts (81).

For studies of the effect of boron deficiency on cell divisions in sunflowers, see (69). Also, a report is available on the effect of boron on amino acid and flavonoid levels in tomato plants (54).

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