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The Preparation of 2,4,4',6,6'- Pentamethyldiborazinyl-1-2' by the Reaction of B- Trichloroborazine with Grignard Reagent

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THE PREPARATION OF
2,4,4',6,6'-PENTAMETHYLDIBORAZINYL-1-2'
BY THE REACTION OF B-TRICHLOROBORAZINE
WITH GRIGNARD REAGENT

by

David C. ^{Charles}Sertl, N.C. 1973
" "

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements for Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

May, 1973



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The goal of this research was to prepare crystals of 2,4,4',6,6'-pentamethyldiboraziny1-1,2' in order to obtain vapor pressure data and a gas-phase, infrared spectrum. The synthesis followed, first, the preparation of B-trichloroborazine (via the "Hot Tube" method) and its purification by vacuum sublimation. The second reactant used was a Grignard reagent (methylmagnesium iodide) which was prepared by standard techniques. The reaction of the B-trichloroborazine and the Grignard reagent was carried out in diethyl ether. The main product (30-35%) of the reaction is B-trimethylborazine with the remainder of the reactants forming the diphenyl and possibly the naphthalene analogs of B-trimethylborazine and other higher polymers. The method of product isolation involved vacuum sublimation of the remaining solid.

The main problem encountered was that not all of the ether could be vacuum distilled off (at temperatures up to 50°C). As distillation continued, the reaction mixture became very thick and viscous. Two attempts to isolate the diboraziny1 from this thick reaction mixture failed. (They involved; (1) extraction with benzene followed by vacuum sublimation (at 150°C) of the extract, and (2) redissolution in ether followed by vacuum sublimation (at 150°C) of the resulting supernatant ether layer.)

LB

The failure to isolate the diborazinyll (as well as most of the B-trimethylborazine) leads to the conclusion that most of the product borazines are complexed to the magnesium salts in some manner. (Vacuum sublimation at 150°C, which will break this complex, was never carried out on that part of the reaction mixture containing the magnesium salts.)

To Chuck

The author is especially grateful to Dr. Charles W.J. Scaife for his guidance and experimental assistance during this project. His ability to provide good counsel and support and yet still allow for initiation and originality on the part of the advisee was both admired and appreciated.

The author would also like to thank Dr. H.M. Butzel and the Biology Department for the use of one of their centrifuges during this experiment.

David C. Suttle

" For the wisdom of this world is
foolishness with God."

I Corinthians 3:19

" The fear of the Lord is the begin-
ning of wisdom:....."

Psalms 111:10

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INTRODUCTION

1.1 Nomenclature

There are a few ring systems containing boron that are particularly stable. Such rings are usually boron atoms alternated with atoms of Group V or VI. Borazine, $\text{H}_3\text{N}_3\text{B}_3\text{H}_3$, is an example of such a ring system, other names of which are borazene, borazole and triborane triamine. Although the bonding of borazine is quite different from the corresponding carbon compound (benzene), it has been called "inorganic benzene" and nearly all of the precedents for the nomenclature of borazines come from carbon compounds.

Conventions for the naming and numbering of four, five and six-membered systems containing boron have been put forth by Capell and Patterson¹ in The Ring Index, the American Chemical Society² and by I.U.P.A.C. (The Hantzsch-Wreelman System, I.U.P.A.C., Section B, Rule B-1).

1.2 History of Borazine

Despite the common occurrence of boron compounds (~0.001%) in the earth's crust and the early recognition of boron as an element by Gay-Lussac and Thenard in 1808, studies of the chemical properties of boron were, for a long time, confined to a small area. This was due mainly to the instability of many boron compounds toward hydrolysis and oxidation, which naturally led to problems in the handling of materials. Anhydrous and anaerobic conditions

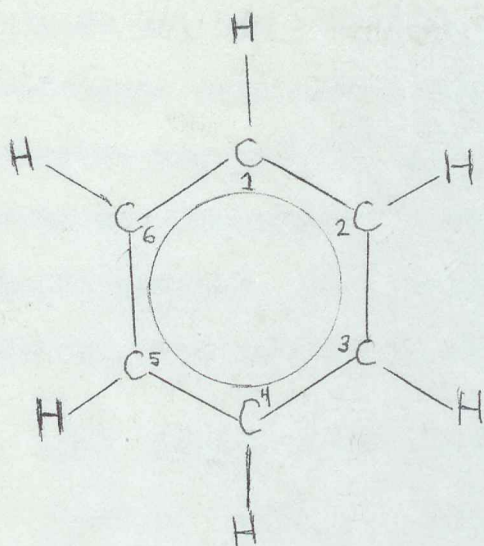
had to be maintained during all stages of experimental work with these compounds. When Alfred Stock developed his vacuum techniques, the door to further study in boron chemistry was open.

It was the experimental techniques of Stock and his coworkers in their investigation of boron hydrides that provided the basic knowledge for a detailed study of boron-nitrogen compounds. In 1926, Stock and Pohland³ investigated the reaction of diborane with ammonia at 200°C and obtained a product whose molecular formula was $N_3B_3H_6$:

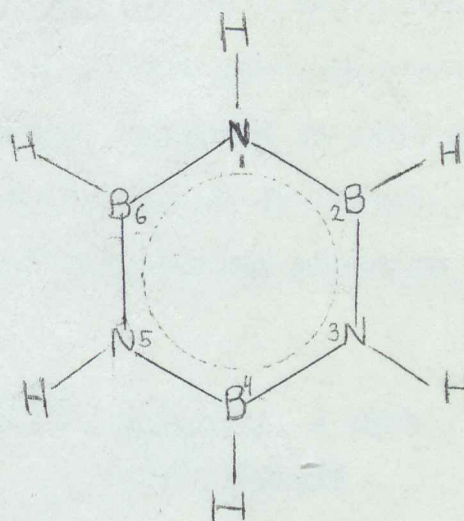


This structure is shown in Figure I. This experiment might be considered to have been the birth of modern boron-nitrogen chemistry. Stock and his coworkers developed some excellent vacuum procedures for the handling and manipulation of boron compounds; however, until the early 1950's the equipment and procedures involved in working with these compounds were still of considerable complexity and therefore, little research effort was devoted to the study of borazine or the synthesis of more of its derivatives.

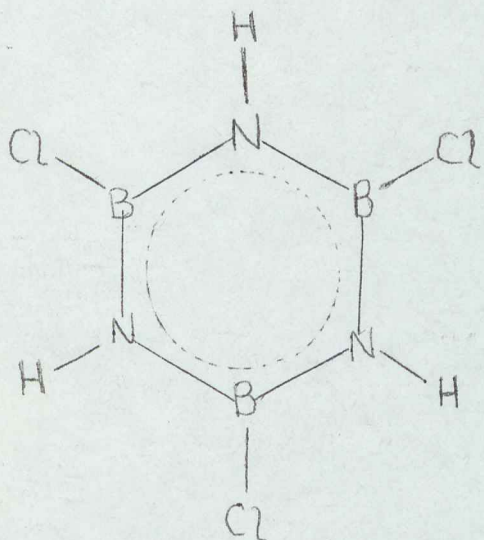
With the discovery of new preparative methods (most notable the Brown-Laubengayer Synthesis of B-trichloro-borazine) during the late 1950's came a new interest and



Benzene



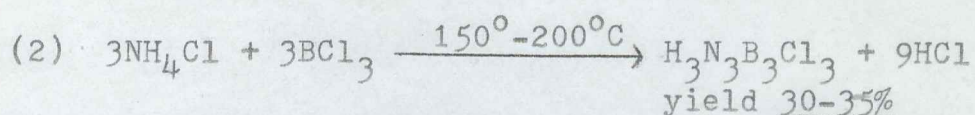
Borazine



B-trichloroborazine

Figure I Structure of Benzene, Borazine
and B-trichloroborazine

research effort in the field of borazines. These new methods provide a partial replacement of the high-vacuum techniques developed by Stock. One of the most important of these new methods was a procedure, reported in 1955 by Brown and Laubengayer⁴, for the synthesis of 2,4,6-trichloroborazine. The reaction involved heating ammonium chloride and trichloroborane :

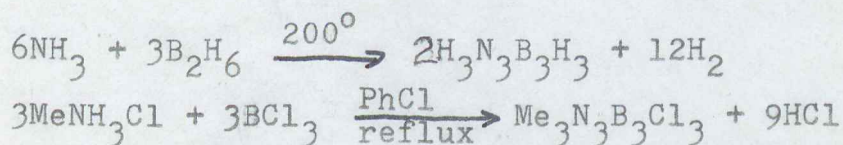


and was carried out either by refluxing a mixture of ammonium chloride in chlorobenzene in the presence of trichloroborane or by passing trichloroborane over heated ammonium chloride (Hot Tube Method). The relative simplicity of the apparatus and procedure of this synthesis allows larger amounts of the product to be made at one time than with procedures involving a vacuum line. The proven excellence of B-trichloroborazine as a starting material for further reactions^{5,10,15} shows how important a step the Hot Tube preparation was in the development of borazine chemistry.

With the increased availability, in quantity, of B-trichloroborazine, many reactions involving this compound were investigated. In 1960, Hohnstedt and Haworth⁵ reported the reaction of B-trichloroborazine with Grignard reagents to yield alkyl and aryl substitution at the boron

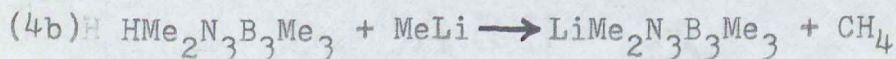
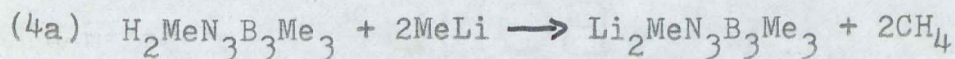
sites; using MeMg-I and PhMg-I to produce the B-trimethyl and the B-triphenyl borazines, as depicted in Figure II.

Until recently, reactions with borazines involved substitutions on the boron site only. In order for atoms or groups to be attached to the nitrogen of a borazine, that group must have been bonded to the nitrogen in the reactant that formed the borazine.



In other words, no reactions seemed to occur at the nitrogen site of borazine or its derivatives.

In 1962, Wagner and Bradford⁶ reported the use of methyllithium to produce an intermediate from which later was formed N-symmetrically and N-unsymmetrically substituted borazines. The boron sites were blocked with methyl groups, as were any nitrogen sites that were not to be attacked by the MeLi. The MeLi substituted Li for any free hydrogens (on the nitrogen atoms), producing methane and the lithio-borazine.



The N-lithioborazines were not isolated but were characterized by treating with methyl iodide to prepare the known N-methyl derivatives, which were identified by

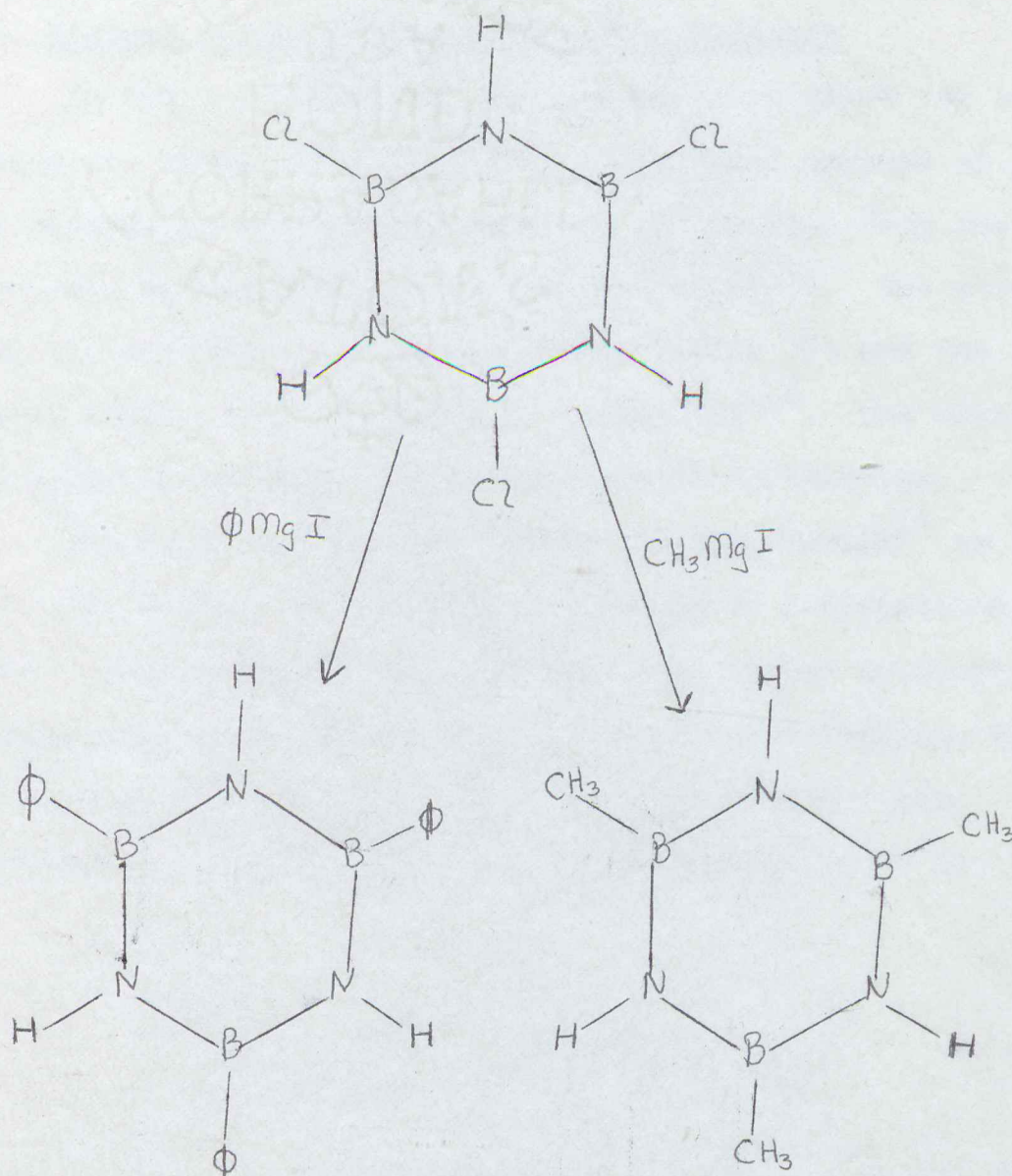


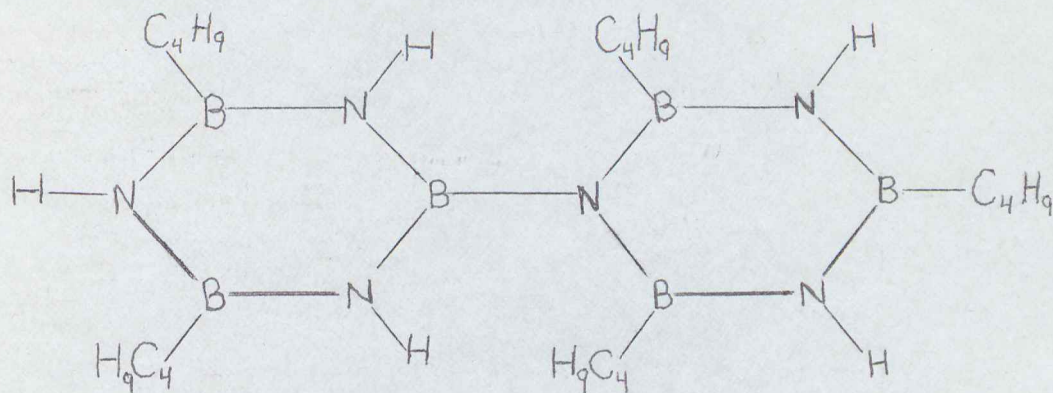
Figure II Grignard Reactions of B-trichloroborazine

infrared and vapor phase chromatography.

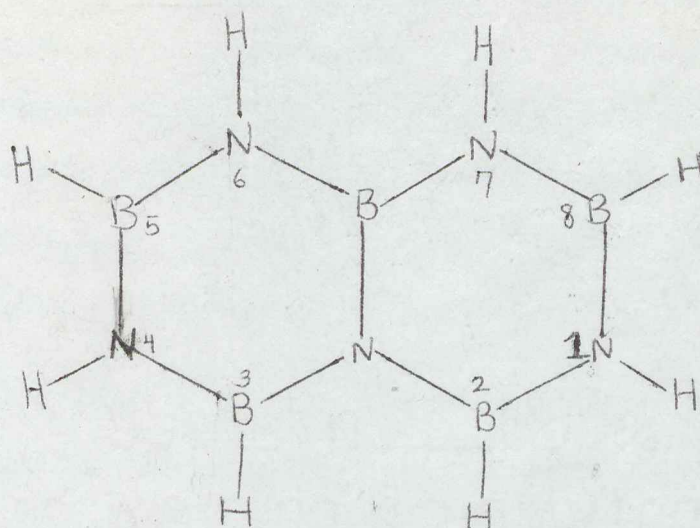
1.3 History of the Diphenyl Analog of Borazine

In 1961, Laubengayer⁷ and coworkers reported the production of, among other products, significant amounts of both the naphthalene and diphenyl analogs of borazine from the pyrolytic dehydrogenation of borazine at 400°C. The structures and numbering of the naphthalene analog (I) and the diphenyl analog (II) are shown in Figure III^{8,9}. The reaction was found to be first order with respect to borazine.

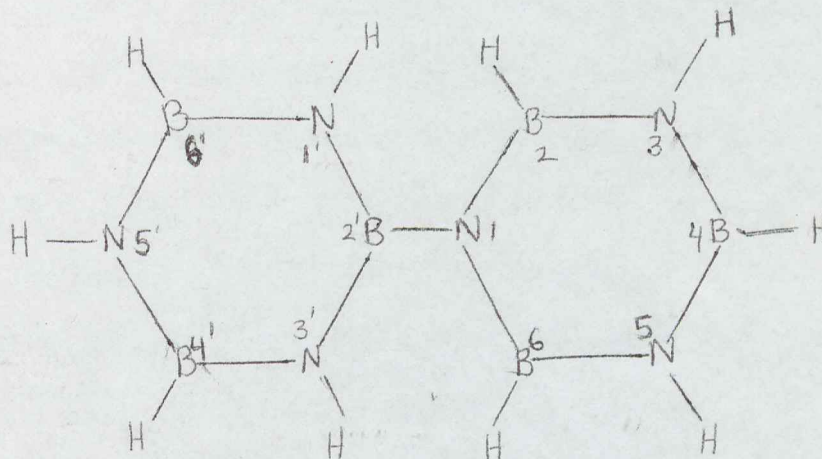
The structure II was reported by J.J. Harris¹⁰ in 1960 as a side product of the Grignard attack on B-trihaloborazines. Butylmagnesium halides were used as the Grignard reagents and were reacted with 2,4,6-trichloroborazine and 2,4,6-tribromoborazine. One of the side products was identified as being the penta-n-butyl derivative of II.



2,4,4',6,6'-penta-n-butyl-1,2'-diborazinylene



Napthalene Analog (I)

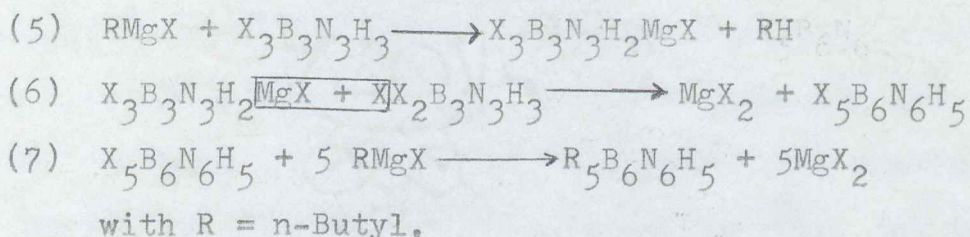


Diphenyl Analog (II)

Figure III

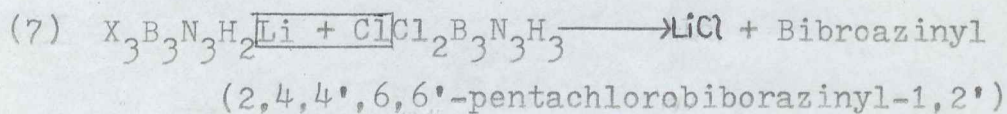
The Diphenyl and Napthalene
Analogues of Borazine

Harris offers the following possible mechanism for the reaction:



Harris also mentions that biborazinyl could have been formed by the pyrolysis of the B-tri-n-butyl-borazine during distillation, but decides that the amount produced at such low temperature (150-200°C) would be negligible (he had read of Laubengayer's pyrolysis results).

Wagner and Bradford¹¹ reported the preparation of B-N linked borazine rings using N-lithioborazines as an intermediate. They successfully condensed methyl-substituted diborazinyl by the elimination of LiCl in a manner similar to (6) but with LiMe substituting Li in place of H on a nitrogen previous to the LiCl elimination.

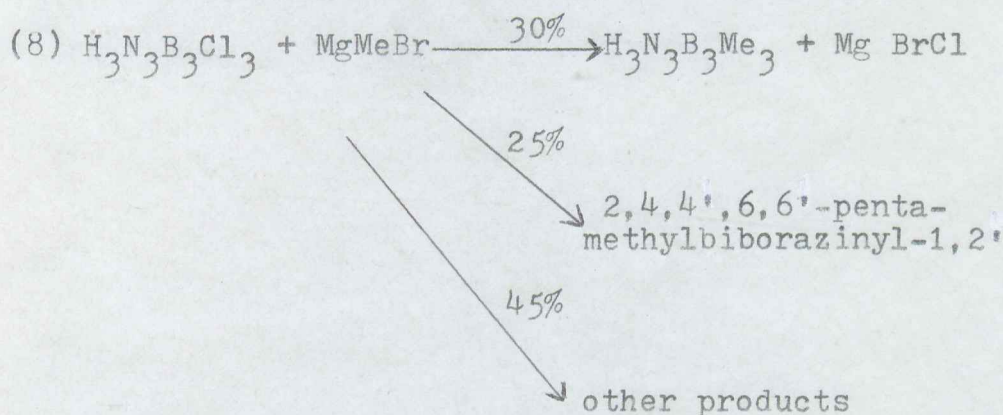


Their attempt to increase the yield of the biborazinyl by using a better solvent (n-hexane) failed due to the lack of formation of the N-Lithio intermediate.

The identification of the naphthalene analog (I) of borazine as a side product of the reaction of B-trichloroborazine with MeMg-Br was made by Boone and Willcockson¹²

in 1965. They found some possible evidence (elemental analysis) for the identification of the structure as II; however, overwhelming evidence (elemental analysis, cryoscopic M.W. Determination, and ^{11}B N.M.R. studies) was obtained in favor of structure I, the naphthalene analog.

Meller and Cowdker^{13,14} reported, in 1965, the same reaction as did Boone and Willcockson, but with a 25% side product that they identified, on the basis of mass spectrum studies, as 2,4,4',6,6'-pentamethylbiboraziny-1,2'.



However, the additional presence of the derivative analogous to naphthalene was not ruled out by the Austrians.

Probably the latest, additional evidence in favor of the biphenyl structure was reported by Johnson¹⁵ in 1969. The diboraziny-1 was prepared by the reaction of B-trichloroborazine with MeMgI in diethyl ether. Data from mass spectra, carbon and hydrogen analyses, IR spectra and ^1H and ^{11}B N.M.R. spectra performed on the sample all lend strong evidence that the structure of the side product of the Grignard reaction with B-trichloroborazine indeed did

have the diphenyl structure.

1.4 Goal of the Research

The goal of this research is to prepare crystals of the biborazinyll compound via the Grignard reaction of B-tri-chloroborazine and to obtain its gas phase infrared spectrum and possibly some vapor pressure data. The infrared data would give information about bonding between atoms (especially B-N) in each biborazinyll molecule. The vapor pressure data will give us information about the forces between individual molecules of biborazinyll.

THEORY

II. THEORY

Borazine ($B_3N_3H_6$) and its organic counterpart benzene (C_6H_6) are isoelectronic and both have a ring structure (Figure IX).

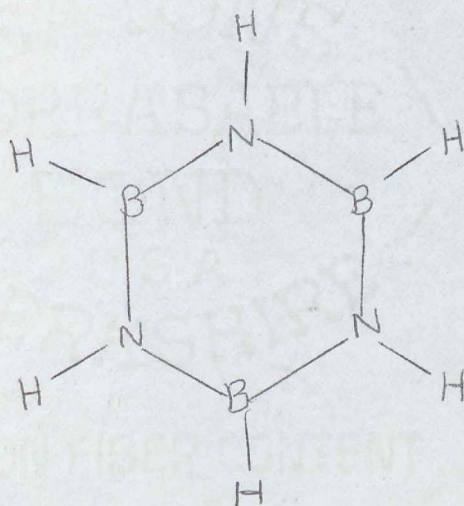
A comparison of physical properties confirms the expectation of similarities in the structure of these two molecules.

Table II

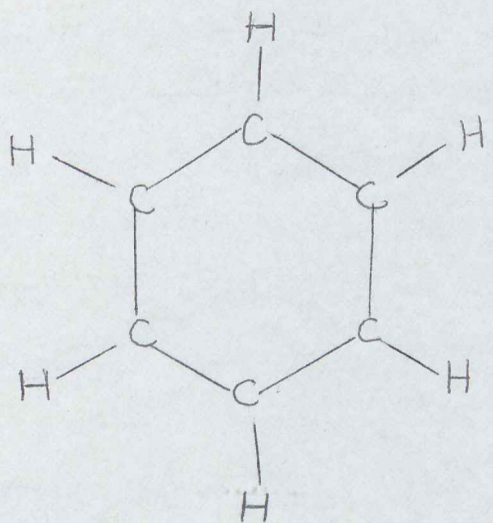
<u>Physical Properties of Borazine and Benzene</u> ¹⁹		
<u>Property</u>	<u>Benzene</u>	<u>Borazine</u>
Molar Mass.....	78.1	80.5
Boiling Point ($^{\circ}C$).....	80	55
Melting Point ($^{\circ}C$).....	6	-57
Critical Temperature ($^{\circ}C$).....	288	252
Liquid Density at mp (g/cm^3).....	0.81	0.81
Crystal Density at mp (g/cm^3).....	1.01	1.00
Surface Tension at mp (dyne/cm)...	31.0	31.1
Trouton Constant (cal/Kmole).....	21.1	21.4

Perhaps the reason for some of the differences in physical properties is that benzene is homocyclic whereas borazine is heterocyclic. Therefore, all members of the borazine ring are not equivalent (as they are in benzene) and the electron density is not equal at all atomic sites in the ring.

A look at the borazine molecule via Valence Bond Theory may depict the situation more clearly. The electronic



Borazine



Benzene

Figure IX Structure of Borazine and Benzene

configurations of boron and nitrogen are $1s^2 2s^2 2p^1$ and $1s^2 2s^2 2p^3$ respectively. We can hybridize the 2s and two of the 2p orbitals of each of the atoms to form three sp^2 hybrid orbitals about each of the atoms (Figure X).

A boron atom thus hybridized would have its 2s and 2p electrons equally distributed in the three sp^2 hybrid orbitals. Nitrogen would have its 2s electrons and one of its three 2p electrons in its sp^2 hybrid orbitals with its two remaining 2p electrons in the unhybridized (p_z) orbital (Figure XI).

In borazine, the three electrons in the sp^2 hybrid orbitals of each ring atom are involved in sigma bonds with two ring members and with hydrogen. The two electrons in the unhybridized p_z orbital of the nitrogens do not remain exclusively in their p_z orbitals but delocalize to some extent into the empty p_z orbitals of the borons. We, therefore, have a π -electron shift from nitrogen to boron, creating some double bond character and aromaticity (Figure XII). This shift in electron density results in a formal positive charge on nitrogen and a formal negative charge on boron as shown (Figure XII).

Nitrogen is, however, more electronegative than boron and hydrogen (3.1, 2.0, and 2.1 respectively on the Pauling Scale). This results in a net sigma electron shift in the ring toward nitrogen (Figure XIII).

Scherr and Haworth²¹ calculated the electronic charge

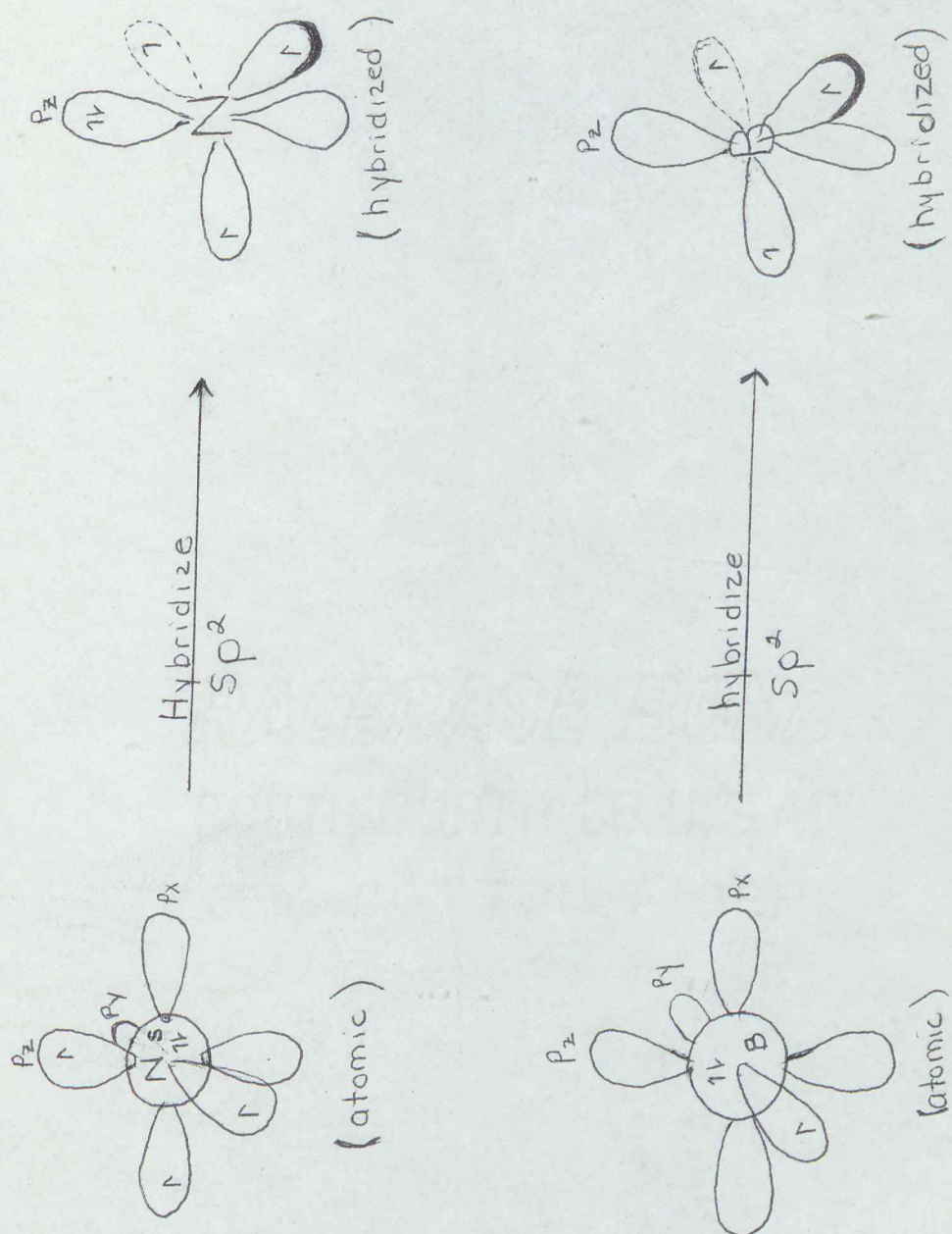
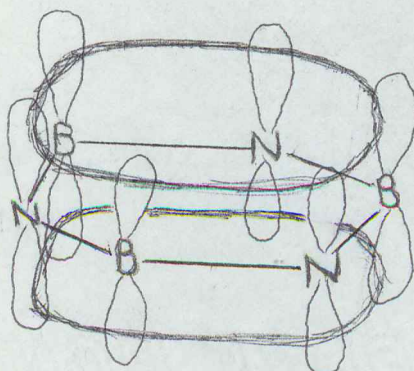


Figure X Hybridization of Boron and Nitrogen in Borazine



π -electrons in Borazine



σ - Orbitals in Borazine

Figure XI Valence Bond Diagrams of Borazine

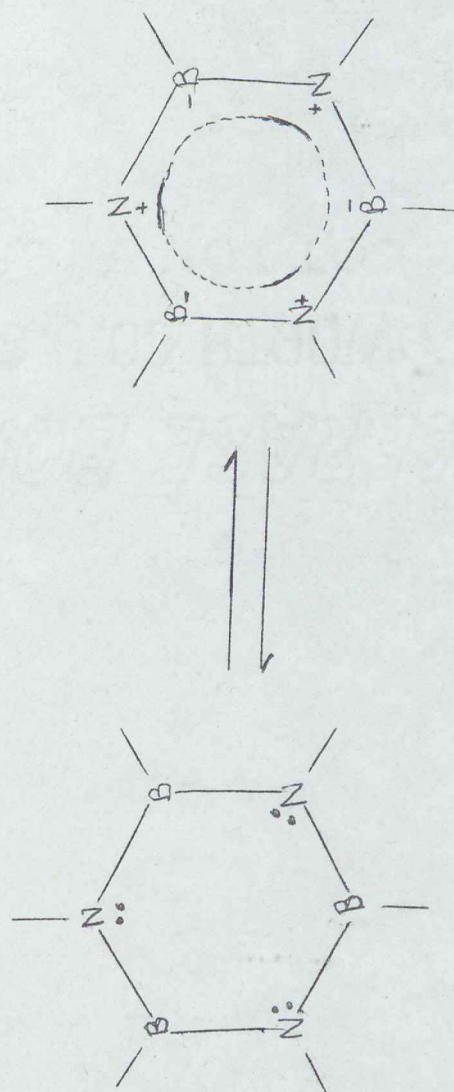


Figure XII Delocalization of p_z -electrons from Nitrogen

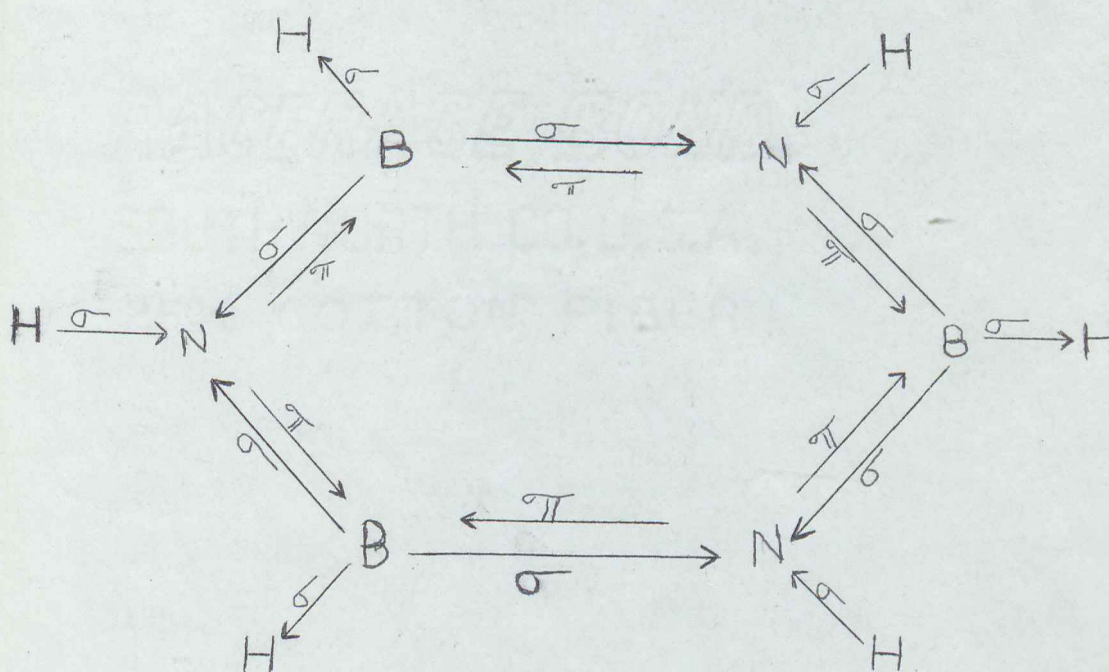


Figure XIII Sigma and Pi Electron Shifts in Borazine

distribution in borazine and obtained the data in Table III. These and other^{17,18} calculations indicate that the sigma electron shift toward nitrogen outweighs the pi electron shift toward boron. Benzene, on the other hand, has equal sigma and pi electron populations at each carbon in the ring. It is this difference that might account for the differences in some of the physical properties compared in Table II (e.g. boiling point, melting point).

Table III
Mulliken population analysis of borazine²²

<u>Analysis</u>	<u>N</u>	<u>B</u>	<u>H(N)</u>	<u>H(B)</u>
π -population	1.3838	0.6162		
π -charge	0.6162	-0.6162		
σ -population	3.7614	2.2723	0.9116	1.0548
σ -charge	-0.7614	0.7277	0.0884	-0.0548
Net charge	-0.1452	0.1115	0.0884	-0.0548
Total ring pop.	24.1011			
π -ring pop.	6.0000			

Penney²² has correlated bond distance with bond character (Figure XIV) by defining a "bond order" such that a single bond has a bond order of 1.00, a double bond an order of 2.00 and a triple bond an order of 3.00. For example, ethane has a C-C bond order of 1.00, ethylene an order of 2.00 and acetylene an order of 3.00.

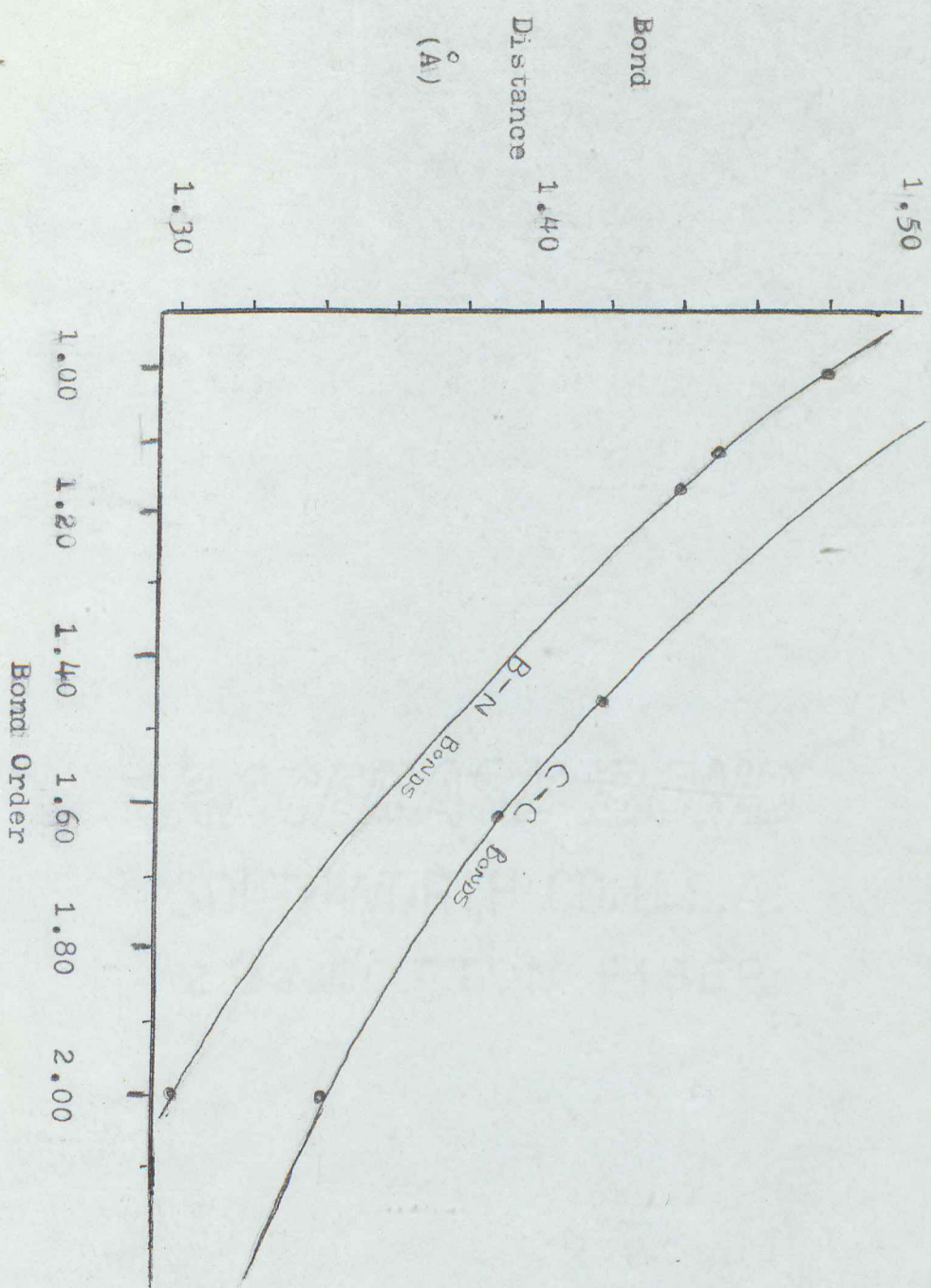


Figure XIV Bond Distance and Bond Order

Table IV

Bond Distance vs. Bond Order : Carbon Compound.

<u>Compound</u>	<u>Bond Distance(\AA)</u>	<u>Bond Order</u>
Ethane	1.54	1.00
Graphite	1.42	1.45
Benzene	1.39	1.62
Ethylene	1.34	2.00

Similarly, bond orders for various boron-nitrogen bonds can be calculated from their bond distances.

Table V

Bond Distance vs. Bond Order : B-N Compound.

<u>Compound</u>	<u>Bond Distance(\AA)</u>	<u>Bond Order</u>
B-N single	1.48	1.00
Boron Nitride	1.45	1.12
Borazine	1.44	1.16
B=N double	1.30	2.00

The B-N bonds are shorter than the respective C-C bonds, despite the fact that the sum of the covalent radii of boron and nitrogen ($0.82 + 0.75$) is larger than the sum of two carbon radii (2×0.77). The charge separation between boron and nitrogen in B-N bonds (due mainly to the difference in electronegativities) is probably responsible for the shorter B-N bond distances.

The difference in electron density around the nitrogens and the borons in borazine produces a chemical property not found in benzene. This property (alternating electron density at different atoms in the ring) causes borazine to add Lewis acids to the ring nitrogens and Lewis bases to ring borons. The partially unbonded electron pair on nitrogen makes borazine easy to hydrolyze by dilute acids (protonation of the nitrogen). In general, hydrogen-halides, alcohols and similar polar reagents add to the ring with the negative group bonding to the boron.

The B-N bond order reported by Penney is so small (1.16) that the bond is only slightly double in nature with correspondingly slight π -electron delocalization in the ring. Such a structure (Figure XV), only slightly aromatic in nature, would account for the addition properties peculiar to borazine and still maintain some similarity to benzene.

SCF (Self-Consistent Field) and CI (Configuration Interaction) Molecular Orbital calculations carried out by Buenker and Peyerimoff¹⁷ on borazine and benzene indicate that, in both systems, the highest occupied sigma molecular orbital is less stable than the most bonding (stable) π -molecular orbital (i.e., that the most easily ionizable electron is a sigma bonding electron). They also conclude that the energy spacings between π -orbitals in borazine are significantly smaller than the corresponding

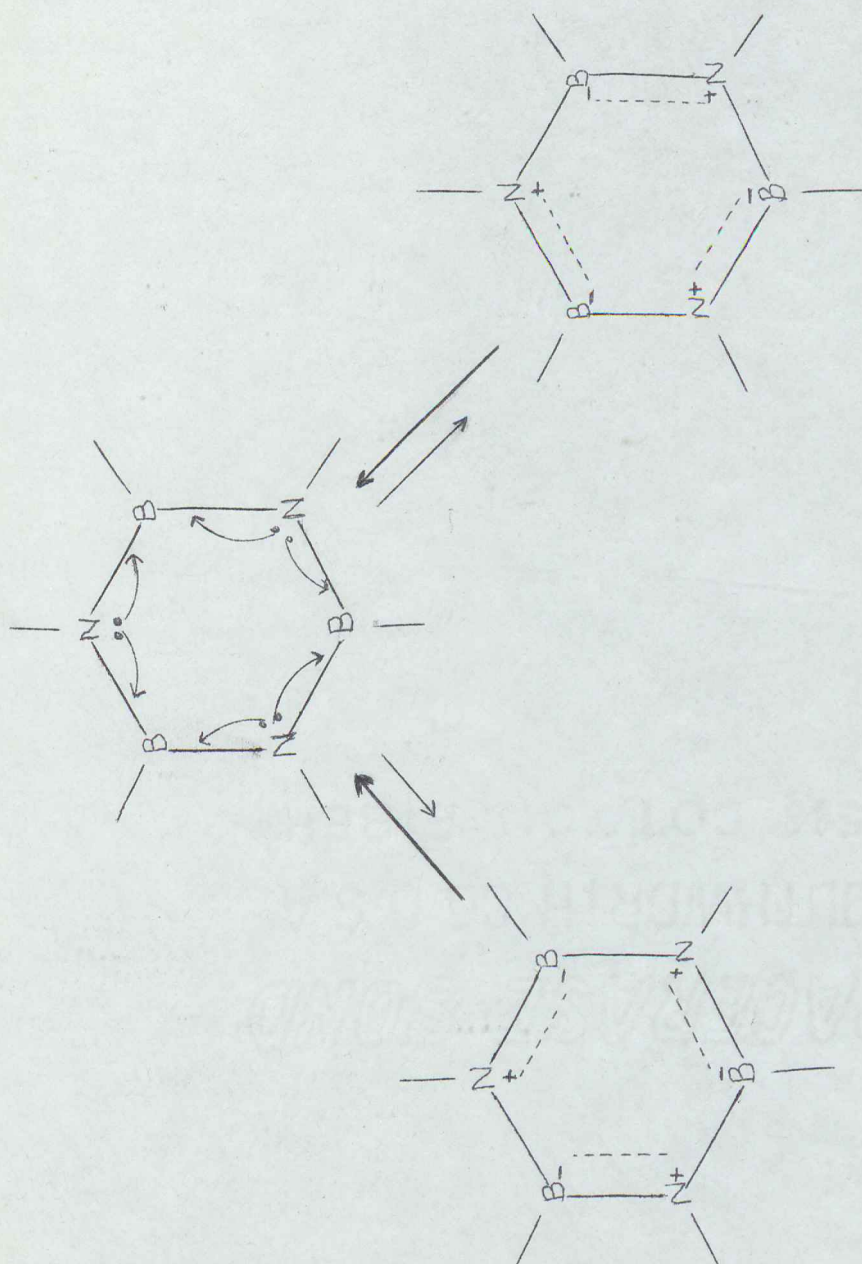


Figure XV Structure of Borazine (Bond Order = 1.16)

spacings in benzene. This is because the occupied (bonding) π -molecular orbitals of borazine are constructed largely from the nitrogen atomic orbitals while the virtual (nonbonding) orbitals possess mostly boron character. Since there are no two equivalent atoms adjacent to one another in the borazine ring, there is less interaction between their respective atomic orbital sets. Therefore, the energy levels in borazine are less widely spaced than they are in benzene, where adjacent carbon atoms each have one unbonded electron and will complete their octet if their p_z orbitals hybridize to form π -orbitals and they share each other's p_z electron.

Buenker and Peyerimoff further say that the three most stable sigma molecular orbitals of the B-N bonding type in borazine show an increasing proportion of nitrogen character with decreasing orbital energy (increasing orbital stability). In addition, the hydrogen on boron appears to enjoy more electron density of the sigma bond with its ring atom than does the hydrogen on nitrogen. (This is consistent with the electronegativity order $N > B < H$). The overall effect is that each boron atom is experiencing a net loss of electron density in its sigma bonds to all of its substituents while each nitrogen atom is experiencing a net increase in electron density in all of its sigma bonds to adjacent atoms.

Buenker and Peyerimoff thus conclude that the $B \rightarrow N$

sigma electron shift outweighs the $N \rightarrow B$ π -electron shift and that there exists, therefore, a net partial negative charge (δ^-) on the nitrogens and a net partial positive charge (δ^+) on the boron atoms.

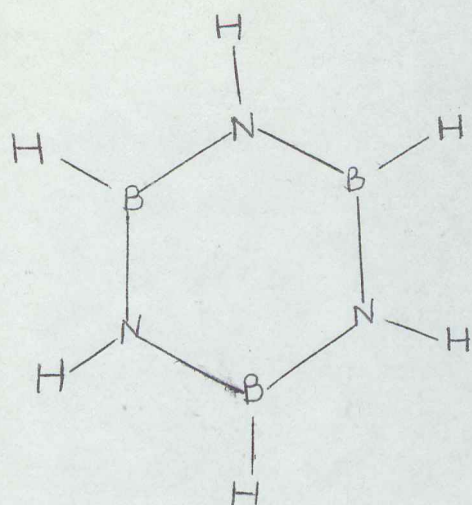
The effects of substituents on the aromatic character of borazine were studied by Rector, Scheaffer and Platt²⁰. They compared the far ultraviolet spectra of chloro and methyl derivatives of borazine with their benzene analogs. Their conclusions were that: (1) substitution on the ring nitrogens of groups having a positive inductive effect (e.g., methyl group) will stabilize the donor-acceptor (π) bonds of the nitrogens in the ring and thus slightly increase the aromaticity; (2) substitution on ring boron atoms of groups having a positive inductive effect will tend to decrease the donor-acceptor (π) bond character between that boron and its adjacent nitrogens; (3) the order of increasing aromaticity in symmetrically substituted borazines is B-trimethyl $<$ borazine $<$ N-trimethyl, and (4) the order of increasing reactivity toward water and hydrogen halide (i.e., order of decreasing aromaticity) in some chloro and methyl symmetrically substituted borazines is N-trimethyl $<$ borazine $<$ B-trimethyl $<$ B-trichloroborazine.

The effects of various symmetric chloro-substitutions on borazine on the electron distribution in borazine was analyzed by Scherr and Haworth¹⁸. They calculated the σ - and π -electron populations of all of the atoms in each of

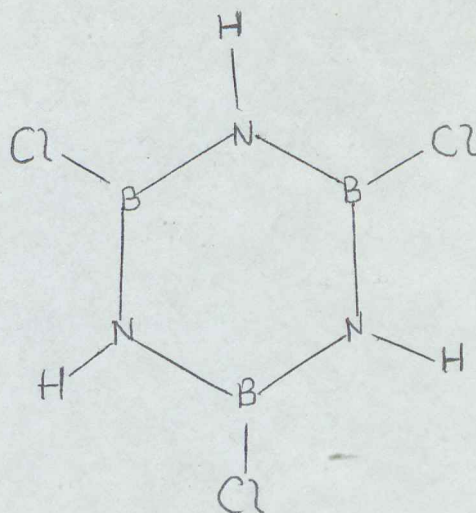
four borazine derivatives (Figure XVI). The results of these calculations are shown in Table VI. Some specific observations which the authors made were that:

- (1)- the sigma electron drift in the ring is toward the nitrogens.
- (2)- the pi electron drift in the ring is toward the borons.
- (3)- the sigma and pi electron populations on nitrogen and hydrogen of B-trichloroborazine and of boron and hydrogen of N-trichloroborazine are nearly identical to their counterparts in borazine.
- (4)- the sigma and pi electron populations of boron and chlorine in B-trichloroborazine and of nitrogen and chlorine in N-trichloroborazine are also similar to their counterparts in B-trichloro-N-trichloro-borazine.

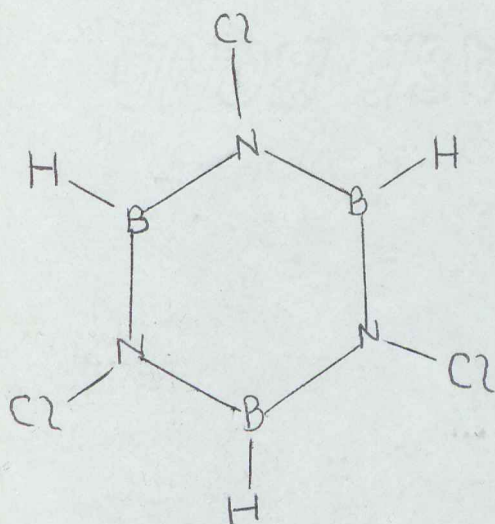
Specific conclusions to be drawn from these observations are: (1) that substitution of a chlorine on one of the heteroatoms of the borazine ring does not significantly change either the pi-electron or the sigma-electron populations of the other heteroatom of the ring: (2) that chlorine substitution on the unsubstituted heteroatom of a trichloroborazine does not significantly affect either the sigma or pi electron populations on the chloro-substituted heteroatom of that trichloroborazine.



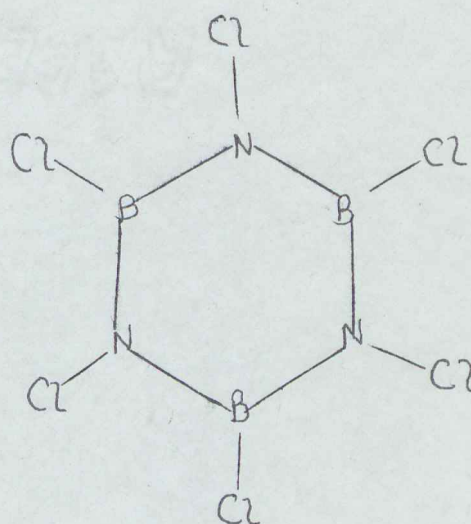
Borazine



B-trichloroborazine

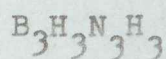


N-trichloroborazine

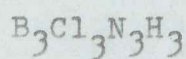


Hexachloroborazine

Figure XVI Borazine Derivatives Stud-
ied by Scherr and Haworth¹⁸

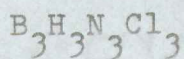


Analysis	N	B	H(B)	H(N)
π -Population	1.3838	0.6162		
π -Charge	0.6161	-0.6162		
σ -Population	3.7614	2.2723	0.9116	1.0548
σ -Charge	-0.7614	0.7277	0.0884	-0.0548
Net Charge	-0.1452	0.1115	0.0884	-0.0548
Total Ring Population		24.1011		
π -Ring Population		6.0000		

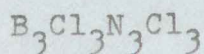


Analysis	N	B	Cl	H
π -Population	1.4451	0.7524	1.7948	
π -Charge	0.5549	-0.7524	0.2052	
σ -Population	3.7384	2.0707	5.2770	0.9219
σ -Charge	-0.7384	0.9293	-0.2770	0.0781
Net Charge	-0.1835	0.1769	-0.0718	0.0781
Total Ring Population		24.0198		
π -Ring Population		6.6925		

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Table VI Mulliken Population Analysis
of Borazine and Chloroborazines



Analysis	N	B	Cl	H
π -Population	1.3943	0.6174	1.9847	
π -Charge	0.6057	-0.6174	0.0153	
σ -Population	3.6904	2.2542	5.0100	1.0495
σ -Charge	-0.6904	0.7458	-0.0100	-0.0495
Net Charge	-0.0847	0.1284	0.0053	-0.0495
Total Ring Population		23.8689		
π -Ring Population		6.0351		



Analysis	N	B	Cl(N)	Cl(B)
π -Population	1.4695	0.7462	1.9891	1.7879
π -Charge	0.5305	-0.7462	0.0109	0.2121
σ -Population	3.6506	2.0578	5.0239	5.2755
σ -Charge	-0.6506	0.9422	0.0239	-0.2755
Net Charge	-0.1201	0.1960	-0.0130	-0.0634
Total Ring Population		23.7723		
π -Ring Population		6.6471		

18

Mulliken Population Analysis
of Borazine and Chloroborazines

Table VI

Some of the general conclusions drawn by Scherr and Haworth are:

- (1)-that the total ring population decreases with halogen substitution on borazine (even more so with fluorine than with chlorine).
- (2)-that boron-halogen substitution has a greater influence on the ring pi electron population than does N-halogen substitution.
- (3)-that B-trihalogen and hexahalogen borazines have about the same pi ring population that borazine does.

Order of Pi Ring Population:*

hexahalogen = B-trihalogen > N-trihalogen = borazine

- (4)-that B-trihalogen substitution increases the energy separation between bonding and antibonding orbitals in the borazine ring, thus stabilizing the borazine system more than the N-trihalogen substitution does.

Structure of B-trichloroborazine

In their detailed study of the structure of B-trichloroborazine, Coursen and Hoard¹⁶ draw many of the same

*"Pi Ring Population" as used in Table VI, is not the same as the population of the pi orbitals of the ring itself. It also includes the pi electron density about the borons due to pi bonding with the chlorines, which does not contribute to the aromaticity of the ring (as does the pi electron population of the pi orbitals lying in the ring).

conclusions that Scherr and Haworth do. They put forth the two limiting structures of B-trichloroborazine shown in Figure XVII.

Coursen and Hoard point out the following results of their study: (1) that, although the structure of B-trichloroborazine is compatible with contributions from both of the limiting structures A and B, their study indicates that double bond resonance in the boron-nitrogen ring is at least as great in the chlorine substituted derivative as in the parent borazine; and (2) that the negative inductive effect of the chlorine as a substituent on boron would seem to be more important than the tendency of this atom to form multiple bonds (i.e., that structure A contributes more to the structure than does structure B).

Coursen and Hoard further conclude that:

- (1)- the molecule of B-trichloroborazine is planar (within experimental error) with no ring atoms departing from the plane of the ring by more than 0.01\AA .
- (2)- the ring has D_{3h} symmetry.
- (3)- B-trichloroborazine is about equal in aromaticity with parent borazine.
- (4)- the B-N bond distance in B-trichloroborazine is slightly (0.01\AA) shorter than in parent borazine.
- (5)- the B-Cl bond distance in B-trichloroborazine is (within experimental error) the same as in BCl_3 (which has some double bond character).

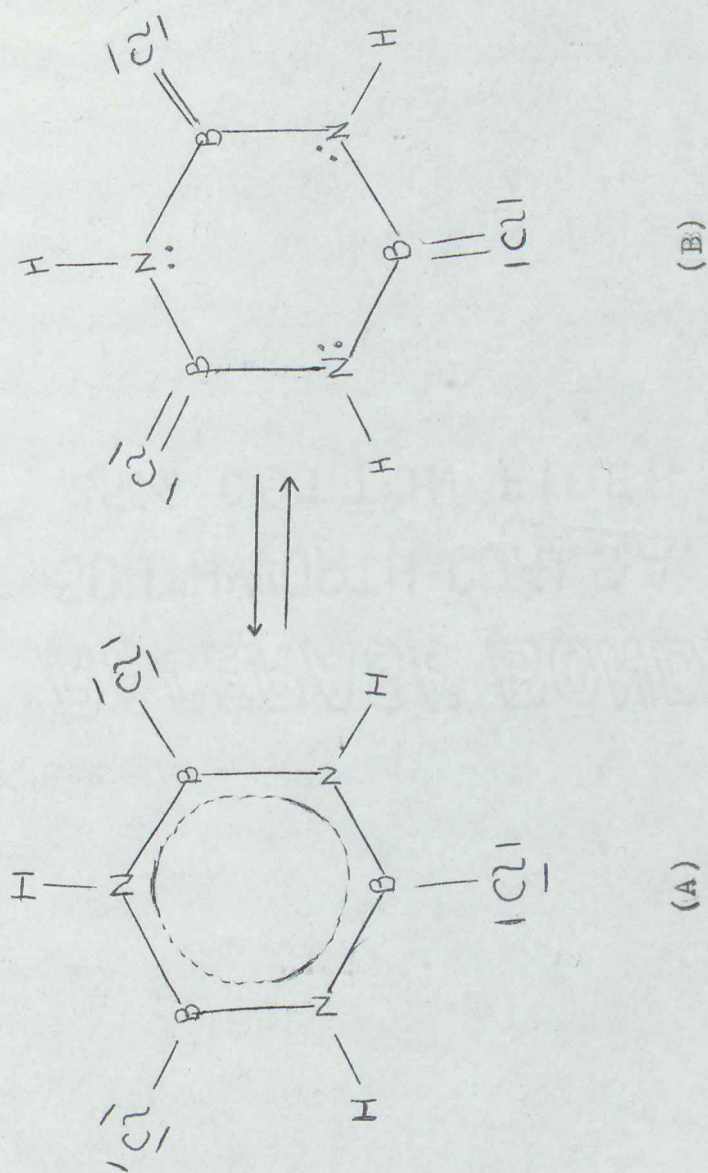


Figure XVII The Two Limiting Resonance Structures of B-trichloroborazine¹⁶

The greater electronegativity of chlorine would cause a slight sigma shift of electrons from the boron toward the chlorine. This would increase the charge separation between the nitrogens and borons in the ring and therefore increase the coulombic attraction between the boron and the nitrogen. As a result, one would predict that the B-N bond distance is shorter in B-trichloroborazine than in parent borazine (as Coursen and Hoard observed).

All of the above discussions of the structure of B-trichloroborazine can really be only qualitative in nature. The picture of the structure of B-trichloroborazine that this author has is one in which there are sigma electron shifts from boron to nitrogen and chlorine; this making the borons slightly positive and the nitrogens and chlorines slightly negative in nature. The two nonbonding electrons of each nitrogen are delocalized (though not entirely) into the pi orbitals of the ring, thus giving the borazine its slight aromaticity. (This describes structure A of Figure XVII.) There is a slight amount of back-donation of two electrons from one of the nonbonding p orbitals of the chlorine into the pi orbitals between the boron and the chlorine (as occurs in BCl_3), producing a double bond that would make the boron slightly negative and possibly decrease the aromaticity in the ring. (This describes structure B of Figure XVII).

Structure A of Figure XVII is, therefore, the major (~80%) contributor to the structure of B-trichloroborazine with structure B composing the final 20%.

Structure and some Properties of 2,4,4',6,6'-pentamethyl-1,2'-diborazinyl

Johnson¹⁵ prepared and characterized 2,4,4',6,6'-pentamethyl-1,2'-diborazinyl (hence to be referred to simply as pentamethyldiborazinyl). His method of production was the reaction of Grignard reagent (MeMgI) with B-trichloroborazine. The main product of the reaction was B-trimethylborazine (35%). His maximum yield of pentamethyldiborazinyl was 0.39%. This was purified by vacuum sublimation at 50°C and had a melting point of 59.0-59.9°C. More recently²⁴, this same sample of diborazinyl was resublimed over a two-hour period using ice in the cold finger. This purified product had a melting point of 59.9-60.2 (corrected). The NMR spectra had resonance frequencies at 4.50 and 0.25 ppm.

The solid phase, nujol mull infrared spectrum showed a broad, strong peak at 1460cm^{-1} . The broadness of the peak is due partly to the boron isotope effect and also to the large number of atoms involved (and thus vibrations possible) in the molecule. The stretch frequency of the B-N bond connecting the two borazine rings should be lower than the other B-N frequencies. This is because the planes of the two borazine rings are probably close to perpendicular to each other. The unhybridized p orbitals of the boron

and the nitrogen would be, therefore, perpendicular to each other and no π -delocalization would be possible, thus making the bridge B-N bond weaker than the other B-N bonds in diborazinyll.

Harris¹⁰ synthesized the n-butyl derivative of the diborazinyll using n-butyl-MgBr as the Grignard reagent. He proposed a mechanism involving an N-MgBr intermediate (Figure XVIII).

Laubengayer, Moews and Porter⁷ produced the parent diborazinyll by vacuum pyrolysis of borazine. They proposed both a free radical mechanism (since the reaction is first order with respect to borazine) and dehydrogenation (as this occurs in the case of benzene) as possible mechanisms of the diborazinyll formation.

Wagner and Bradford¹¹ synthesized a decamethyldiborazinyll by reaction of 1,2,3,4,6-pentamethylborazine with methyllithium. They proposed a mechanism similar to Harris' involving an N-Li intermediate (Figure XIX).

There are many products in the MeMgBr/B-trichloroborazine reaction¹². A maximum of 35% of the yield is B-trimethylborazine with the remainder being composed of the diphenyl analog (diborazinyll), possibly the naphthalene analog plus other higher polycyclic derivatives.

Looking at the mechanism of the reaction forming the diborazinyll, we note that B-trichloroborazine exists mainly

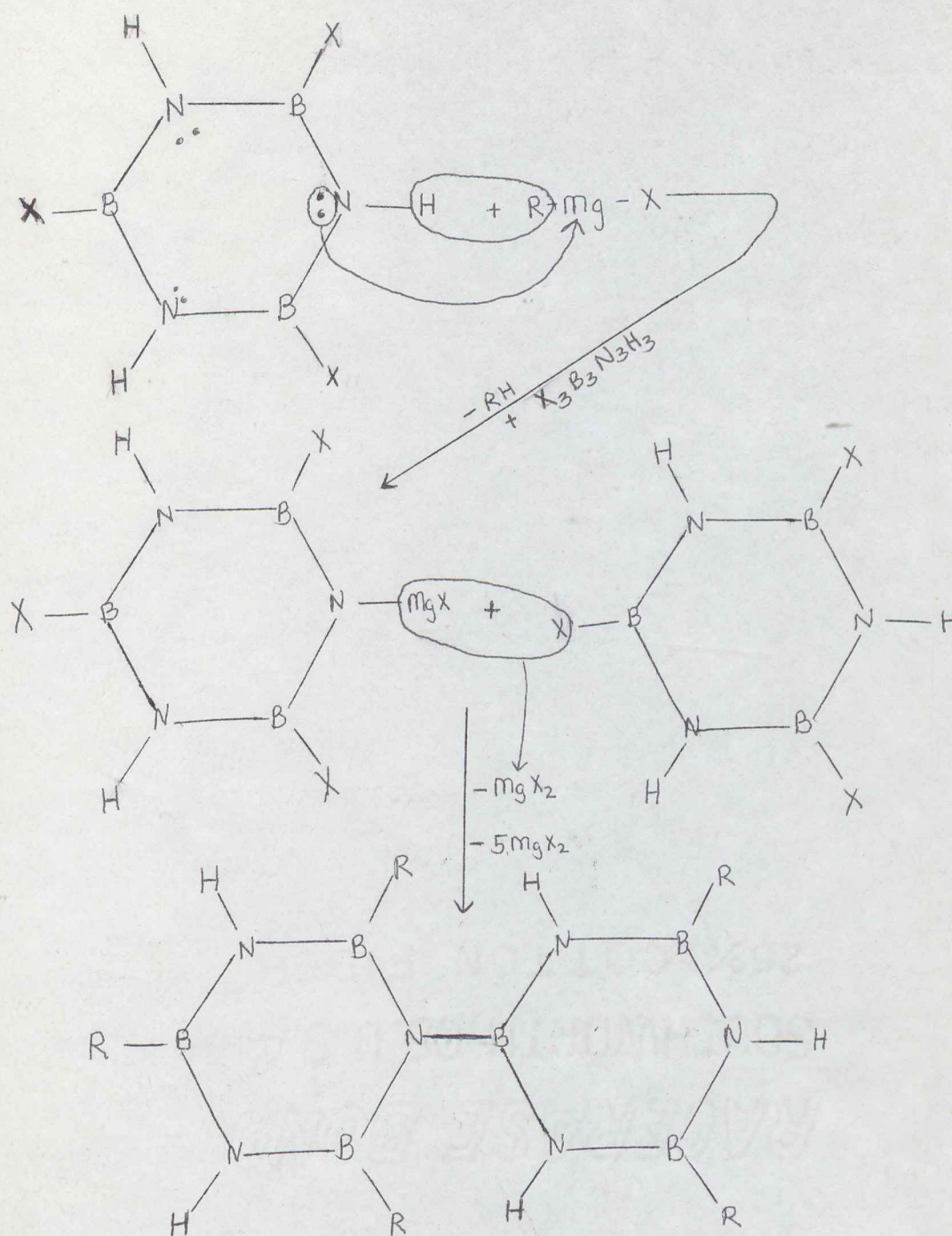


Figure XVIII Harris' Proposed Mechanism for Diborazinyl Production

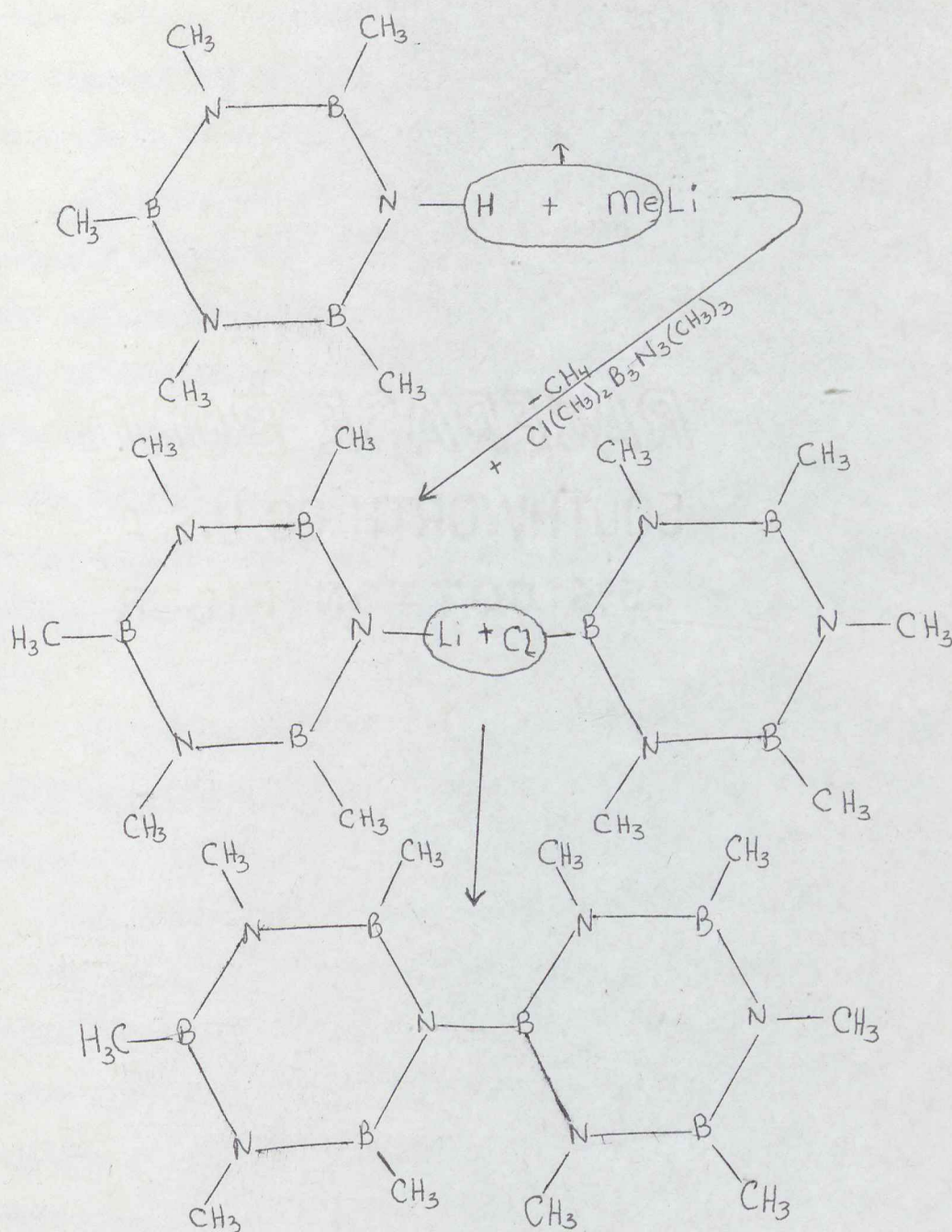


Figure XIX Proposed Mechanism of Reaction of B-trichloroborazine and Methyl lithium

in two resonance structures (Figure XVII). Now, assuming that a Grignard reagent attacks by having some atom on the target molecule donate a pair of electrons to the empty p orbitals of the magnesium, let's look at possible target atoms on both structures A and B of B-trichloroborazine.

In structure A, the nitrogens might be targets for Grignard attack because their p_z electrons are only somewhat delocalized into the ring pi orbitals. However, a much better target would be the chlorines, with their three pair of unbonded p electrons. The chlorines become bonded to the magnesium in the attack and the methyl groups bond to the boron atoms as the chlorines leave. It is this attack (Figure XX) that is thought to produce the B-trimethylborazine.

In structure B, the chlorines have only two pairs of fully unbonded p electrons and Grignard attack is still likely at these sites, though not as likely as in structure A. More importantly, each nitrogen has more (though not all) of its two p_z electrons to itself and, therefore, is more likely to donate these electrons to the magnesium, with the proton splitting off. It is this attack on the nitrogen position of structure B that is thought to account for the N-MgX bond hypothesized as an intermediate in the production of the B-N bicyclic bond (Figure XXI).

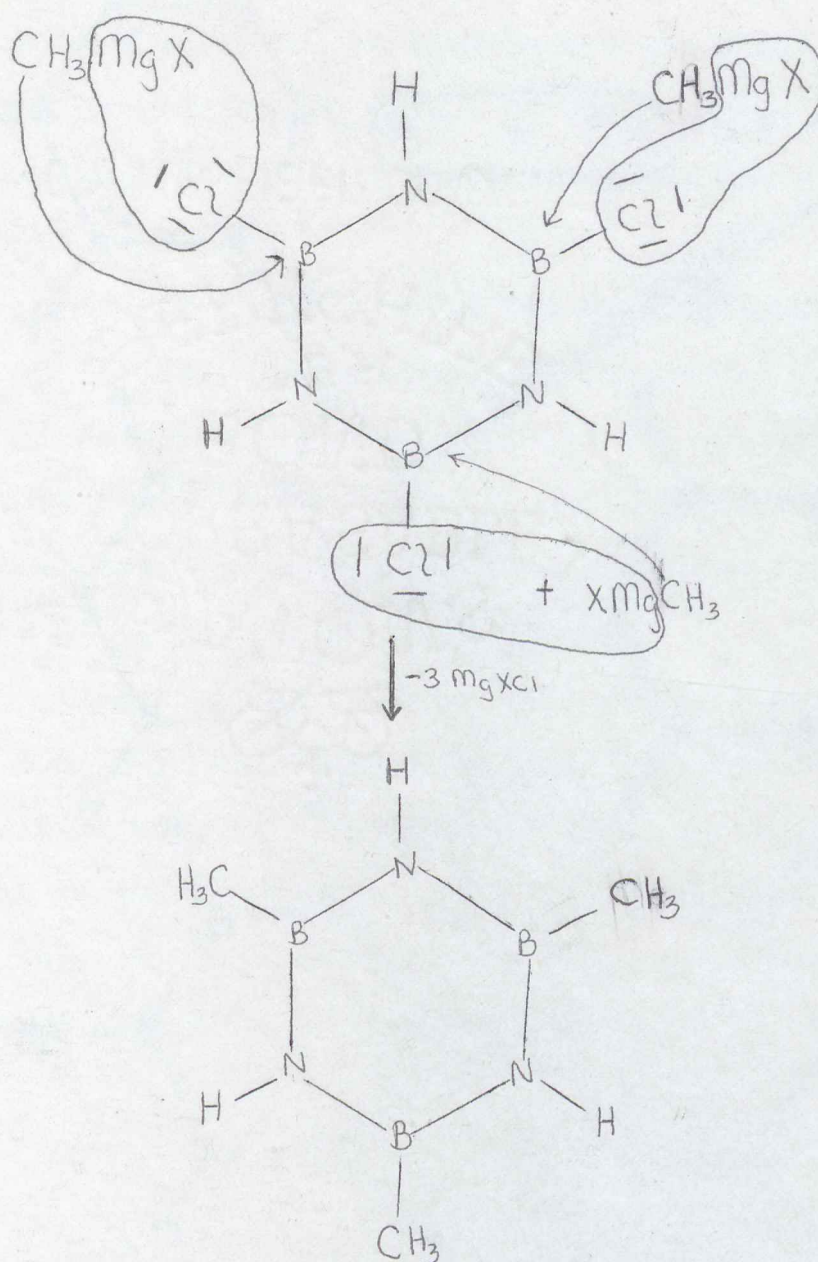


Figure XX Mechanism of Grignard Attack on
 Structure A of B-trichloroborazine

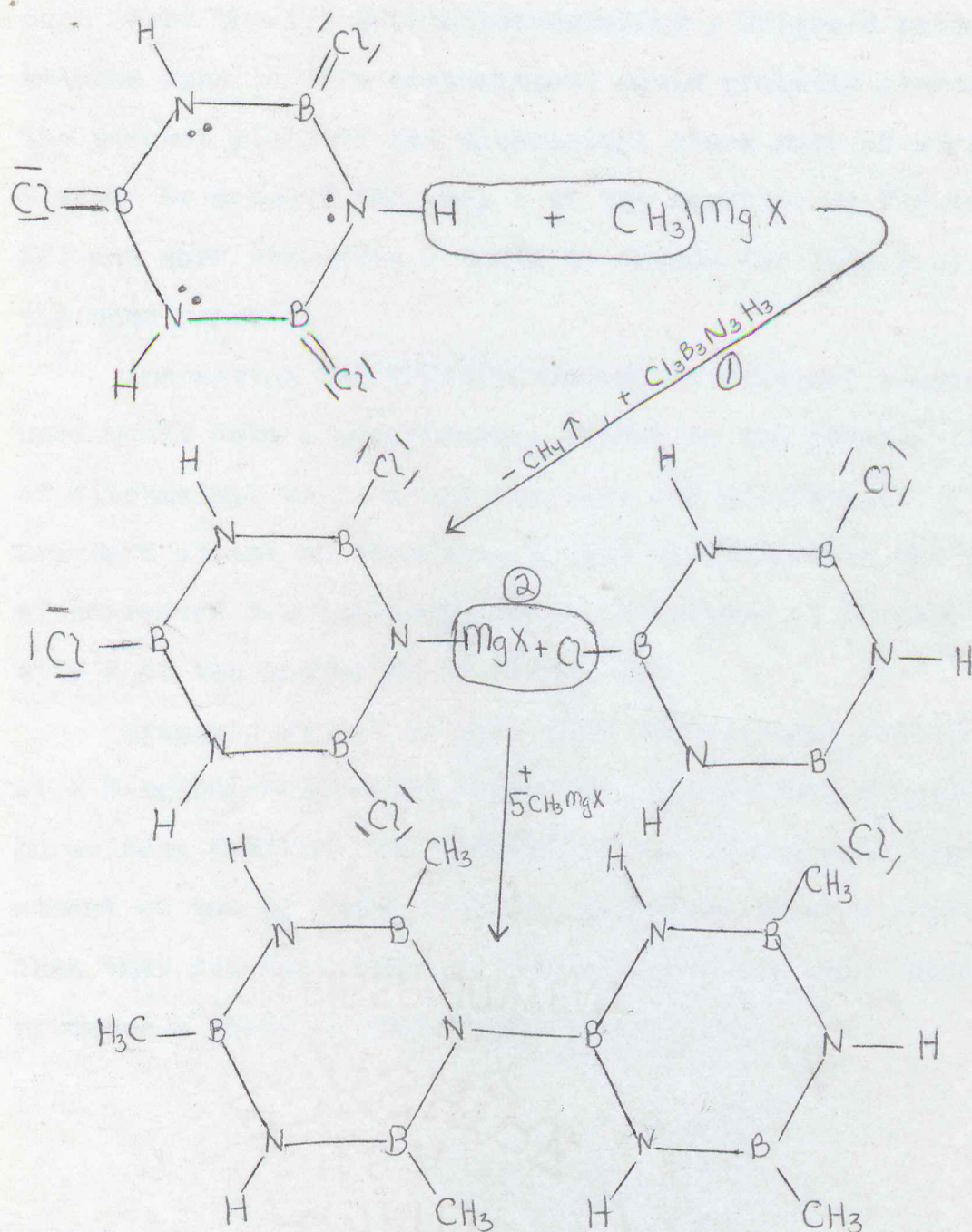


Figure XXI

Mechanism of Grignard Attack on Structure B of B-trichloroborazine in the Synthesis of 2,4,4',6,6'-pentamethyl-1,2'-diborazinyl

Increasing the relative amount of B-trichloroborazine used (over the 1:3 B-trichloroborazine : Grignard ratio of amounts used in this preparation) would probably increase the percent yield of the diborazinyl since more of structure B would be present for step 1 of the reaction in Figure XXI and more structure A would be around for step 2 of the same reaction.

Increasing the relative amount of Grignard reagent used would have a questionable effect on the percent yield of diborazinyl as it would increase the possibility of Grignard attack on structure B, but also decrease the amount of unreacted B-trichloroborazine (structure A) present for step 2 of the mechanism in Figure XXI.

Grignard attack at more than one nitrogen position of a B-trichloroborazine molecule could produce polycyclic borazines; however, the probability of such a simultaneous attack at two or three nitrogen positions is much smaller than that for the attack at one nitrogen position (which produces a yield of only 0.39% diborazinyl).

PREPARATIONS

III. PREPARATIONS

3.1 MATERIALS

A. Chemical Reagents

Diethyl ether was used as the reaction solvent in all of the liquid phase reactions. Absolute ether (MCB, Reagent) was stirred (Vogel, p. 140) over anhydrous magnesium sulfate (MCB, Reagent) for one day. The MgSO_4 was filtered from the MgSO_4 -ether mixture, and the pre-dried ether was refluxed for 48 hours over P_2O_5 (Matheson, Coleman and Bell, Reagent) in a one-meter vacuum-jacketed, fractionating column. The ether was then distilled through the column into a sealed flask. (This ether shall, in the future, be referred to as "dry ether".)

Hexane (MCB, Technical) was used as an extraction solvent. It was dried by refluxing for 24 hours over P_2O_5 and then distilling into a sealed flask. (It will henceforth be referred to as "dry hexane".)

Benzene (MCB, Technical) was also used as an extraction solvent. It was dried by stirring over anhydrous magnesium sulfate for 24 hours, refluxing over P_2O_5 for 48 hours and distilling into a sealed flask. (It will henceforth be referred to as "dry benzene").

All solid reagents were dried in the oven at $100-110^\circ\text{C}$. Ammonium chloride (MCB, Reagent) and asbestos (MCB, medium, acid-washed) were both dried at

110°C for 10 hours (longer heating decomposes the NH_4Cl) to remove any water present. Magnesium turnings (MCB, "For Grignard Prep") were dried for 2 days at 110°C, washed with untreated absolute ether and dried for 12 hrs. before use in a drying oven at 110°C.

Methyl iodide (MCB, Reagent) was used without further treatment in the Grignard preparation.

Trichloroborane (Airco, Technical, 99.0%) was used directly from the cylinder during the 2,4,6-trichloroborazine preparation.

Nitrogen gas (Matheson, dry preparative) was also used directly from the tank for flushing systems and producing an anhydrous (<0.001%) and anaerobic (<0.001%) atmosphere.

B. Other materials and glassware

All glassware used was first washed, rinsed with acetone and dried in an oven at 110°C.

Air-sensitive chemicals were handled in a glove bag (I^2R , polyethylene bag). The bag was filled with dry nitrogen at atmospheric pressure and flushed when opened to add or remove materials from the bag.

Two kinds of vacuum greases were used: Dow-Corning High Vacuum Silicone Grease and Apiezon N Grease. Apiezon greases are paraffin oil residues and are especially suited for use in stopcocks. However, they are quite expensive. Therefore, the silicone grease, stable over a wider

temperature range (-40 to +200°C) and slightly more stable against dissolution by organic solvents, was used in the majority of joints and stopcocks involved in the preparations.

3.2 Preparation of B-trichloroborazine

Wiberg and Bolz first prepared B-trichloroborazine by the thermal decomposition of the addition product of $B_3N_3H_6 \cdot 3HCl$. Attempts at production by the reaction of BCl_3 and NH_3 resulted in no trace of the desired product.

The synthesis of B-trichloroborazine done here follows the "Hot Tube" procedure first reported by Brown and Laubengayer⁴ and described in detail by Johnson¹⁵. The yield reported by Johnson to be the greatest possible was 35% but by increasing the tube temperature to 200°C and expanding (lengthening) the cool region, the yield could climb as high as 50%. The hot tube used was constructed by Johnson¹⁵ and consisted of a 60x5-cm. Pyrex tube, wrapped tightly for half its length with nichrome wire and asbestos tape. The temperature was controlled by varying the current through the nichrome wire with a rheostat.

A diagram of the Hot Tube apparatus (Figure IV) is shown below. Bubbler A is a monitor of the gas flow (bubbles/min.) through the tube. Bubbler B serves as a safety valve; if, for any reason, the tube clogs or the tygon tubing pinches, the gas mixture will pass out through Bubbler B into the hood. The release pressure in Bubbler B is equal to the height of the mercury above the tip of the tube extending into the bubbler.

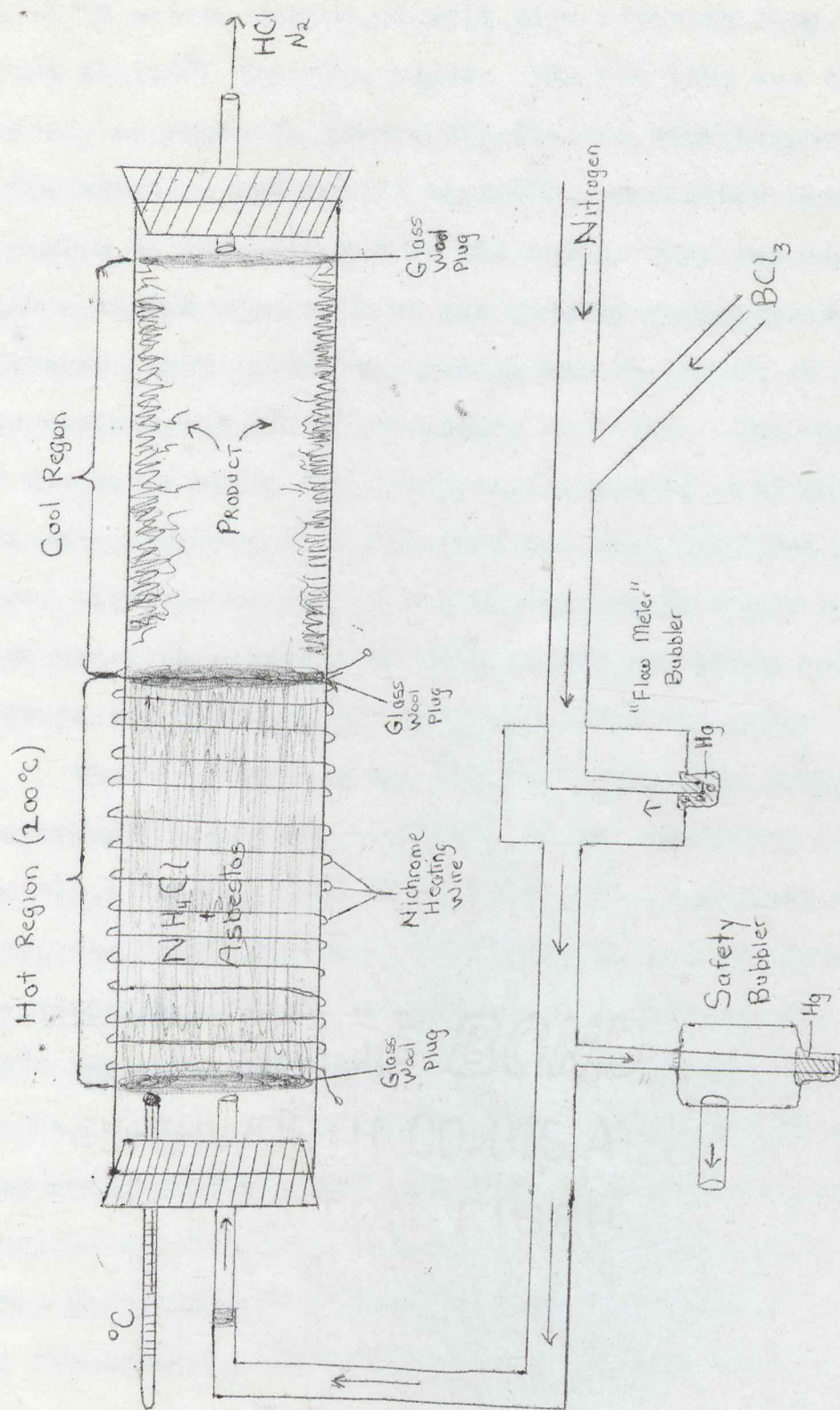


Figure IV Setup for Hot Tube Preparation of B-trichloroborazine

In this preparation, ammonium chloride (75.0-80.0gm, 1.43-1.52 moles) was mixed well with asbestos (40g.) and dried at 110°C for nine hours. The hot tube was then loaded, as shown in Figure IV, flushed with nitrogen for a few minutes, and heated to 200°C. Condensed water vapor appeared in the cool end of the tube. This was wiped off with a tissue and the tube was quickly restoppered. The nitrogen flushing and the wiping was an effort to attain the maximum anhydrous conditions possible. The appearance of the water vapor was not at all expected and, hopefully did not interfere with the reaction that followed in the tube. (The source of this condensed water vapor may have been water used as a lubricant in making tubing connections between the nitrogen and BCl_3 tanks and the tube).

When the temperature reached 210°C, the nitrogen flow was stopped and the BCl_3 flow rate was regulated at approximately 1 bubble/sec. The nitrogen flow was then increased until the total flow was 2 bubble/sec. Almost immediately, the temperature began to drop and in 5 minutes was down to 170°C (this demonstrated that the reaction was endothermic). One hour later, the temperature remained at 170°C while the same heating of the tube continued. Four and one-half hours later, the BCl_3 and the power (heating) were turned off. The stopper at the cool end of the tube was then removed and the contents of this region of the tube were scraped

into a large, clean, brown-glass bottle already containing unpurified B-trichloroborazine (P_1). The mass of the raw yield was not recorded.

The following observations and suggestions for a better yield were made at this point:

1) Grind up the NH_4Cl in a mortar and pestal before mixing with the asbestos. This would divide more finely the NH_4Cl and thus allow for more efficient drying and for more complete reaction with the BCl_3 .

2) The NH_4Cl should have been better dispersed in the asbestos. The use of more asbestos, perhaps even fine fiber asbestos (especially if the NH_4Cl is to be finely divided) might facilitate this increased, homogeneous dispersion throughout the "hot region".

3) During this first preparation, the glass wool plug nearest the cool region developed into a hard cake. This cake could have been composed of partially unreacted reactants, which might be avoided by limiting the asbestos/ NH_4Cl mixture more within the "hot region" to ensure more complete reaction. Another possible component of the cake could have been ~~overreacted~~, polymerized product. This might be avoided by more finely dividing the NH_4Cl in the hot region of the tube.

3.3 Purification of the B-trichloroborazine

The raw product (P_1) was vacuum sublimated to purify it before use. The sublimator was washed and dried in an

oven at 65°C overnight. When the sublimator had cooled, the stopcock was greased, put back on the sublimator and then the entire sublimator was evacuated.

The sublimator was then brought into the glove bag along with the bottle of raw product. Some of this product was put into the sublimator (enough to cover the bottom with 2 mm of P_1). The sublimator was then assembled and evacuated. After being removed from the glove bag, the sublimator was placed on a hotplate ($60-80^{\circ}\text{C}$) and ice was put into the cold finger (Figure V).

After four days of sublimation, the ice was removed from the cold finger and the sublimator was carefully moved into the glove bag. Upon allowing the glove bag atmosphere to enter the sublimator, the sublimator was slowly disassembled. Great care was taken to avoid touching the cold finger to the walls of the sublimator and thereby knocking sublimed product from it. The sublimed product (P_2) was very hard to chip off of the cold finger. (No cause for this has been suggested, save that possibly the long period (4 days) of sublimation might have allowed the P_2 to become caked onto the cold finger.) This P_2 was put into a clean, dry bottle and stored in the glove bag. The remaining raw product was similarly purified, except that it was sublimed for only two days. In this case, the P_2 came off the cold finger easily. The total mass of the P_2 thus obtained was 25.8 ± 0.2 g.

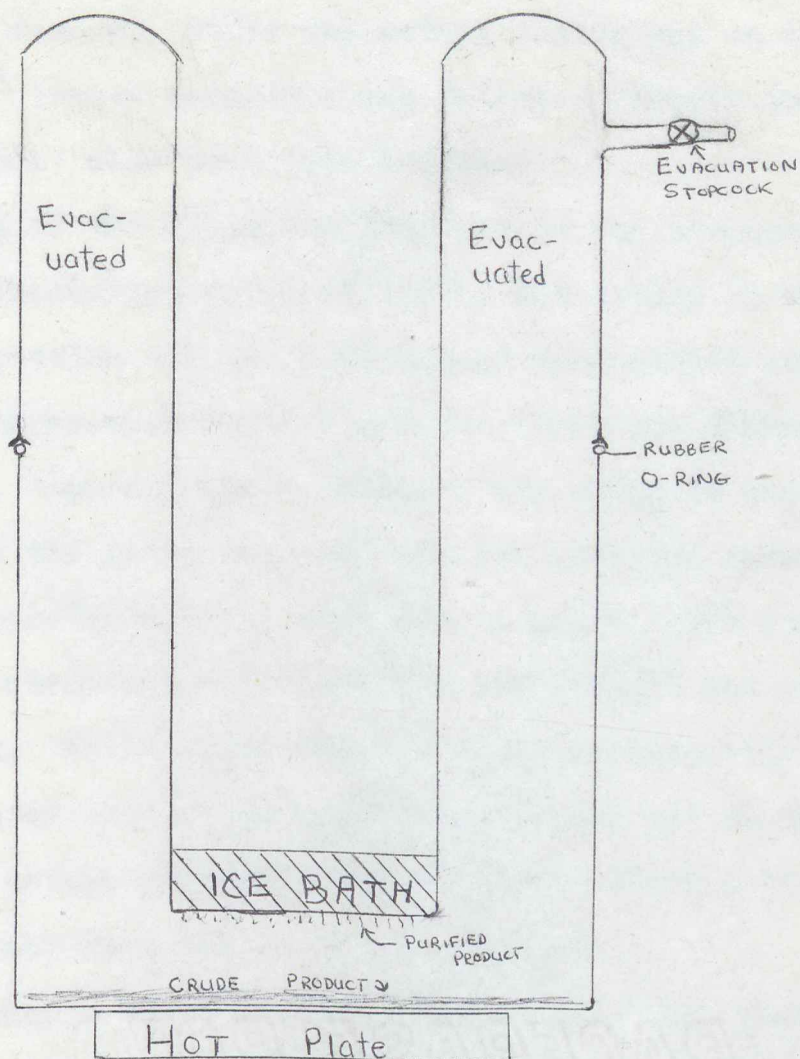


Figure V Vacuum Pyrolysis Apparatus

3.4 First Grignard Reagent Preparation

Methyl magnesium iodide (MeMgI) was chosen as the Grignard reagent, since the methyl iodide was on hand and Johnson¹⁵ (whose procedure was followed closely in this preparation) also used this Grignard.

All of the glassware involved in the preparation were washed thoroughly, dried at 110°C , and cooled in the glove bag. Magnesium (23.3g., 0.96 moles) was weighed into a 500-ml. three-necked flask and the flask was flushed with nitrogen. Approximately 100ml of dry ether is added to the flask (in the glove bag) and the two addition funnels, their stopcocks closed, were put in place. The center neck was stoppered and the flask was brought out of the glove bag. While being flushed with nitrogen, the flask was incorporated into other apparatus already set up in the hood. When the entire apparatus was assembled (Figure VI), ice and salt were put in the cold finger.

A couple small iodine crystals were then added to the ether, and they immediately reacted mildly with the magnesium. Five minutes later magnetic stirring was begun (it should have been started right away). Water flow through the condenser was started and some ether and CH_3I were added. The solution boiled rapidly, and condensed ether vapor dripped extensively from the cold finger.

The reaction mixture had now become more and more brown in color. The CH_3I was added in small amounts (each

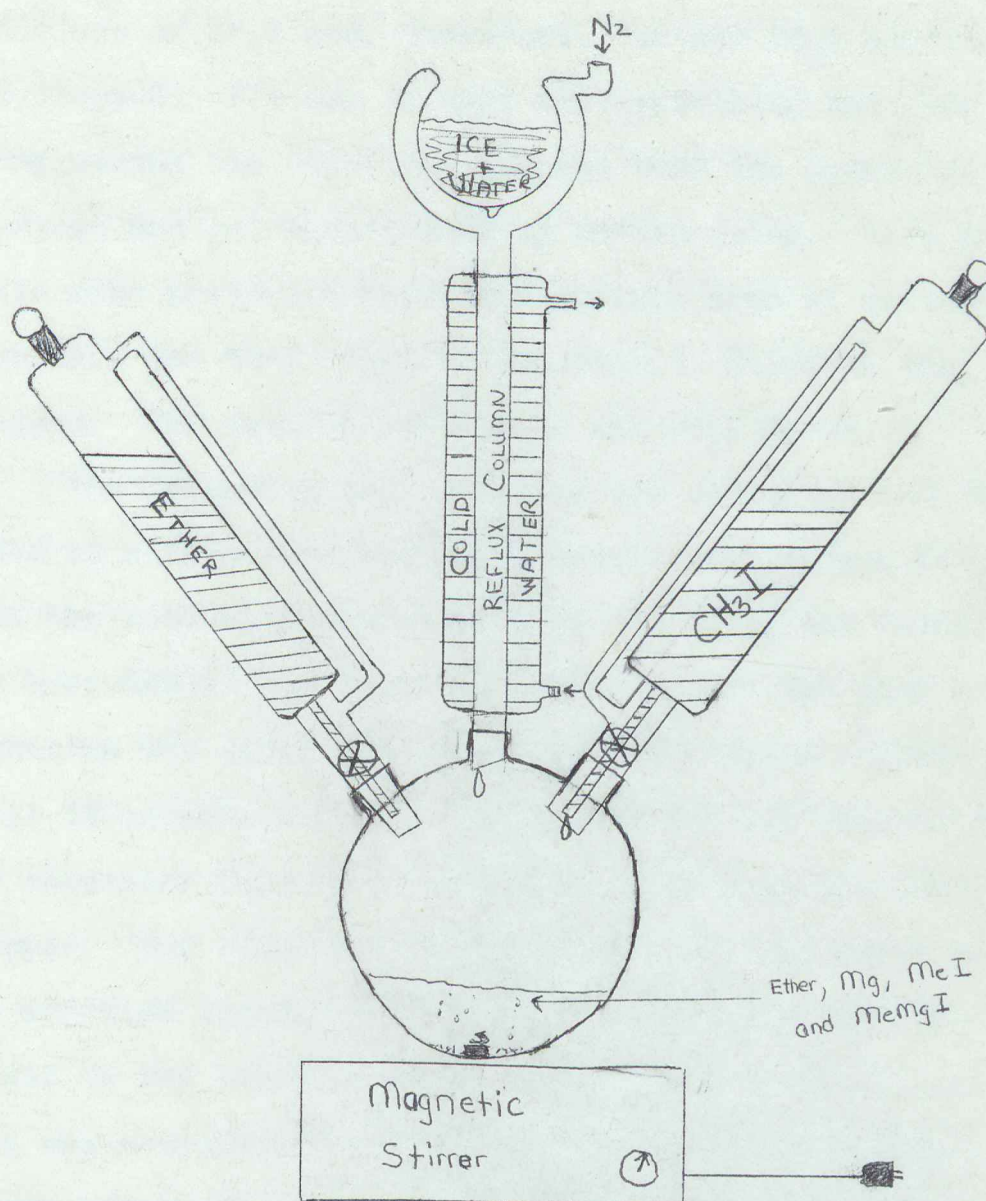


Figure VI Apparatus for Grignard Preparation

addition being followed by less vigorous boiling) until half (50g) of the CH_3I had been added. At this point, no boiling (sign of the reaction) was observed with new additions of CH_3I and, therefore, further CH_3I addition was stopped. (It was thought that something had gone wrong during the reaction; perhaps that the magnesium turnings had not been ground up before using. This grinding would make available much more surface area of unoxidized magnesium for more complete reaction.) Stirring was stopped. The supernatant liquid was dark brown.

The following day, stirring was continued and CH_3I added at a rate such that mild boiling was maintained. When the remainder (approximately 50 g.) of the methyl iodide had been added, the reaction flask was hot and much of the magnesium was gone. The reaction was stirred rapidly until it cooled, at which time the flask was removed from the condenser column and stoppered with a ground glass stopper. The flask was then brought into the glove bag, the addition funnels were removed, and the supernatant liquid in the reaction flask was decanted into a clean flask that was greased and stoppered. This liquid (volume=150ml) ~~was~~ the ether solution of the Grignard reagent, CH_3MgI . (The brown color was due possibly to dissolved magnesium salts or some iodine complex dissolved in the ether.) The Grignard reagent was not treated further before use.

3.5 First Preparation of 2,4,6-trimethylborazine

The apparatus used in this preparation is shown in Figure VII. The addition funnel delivering the CH_3MgI solution has been fitted with an extension tip so that the Grignard reagent will drip directly into the reaction mixture. The setup and procedure were chosen so that the volume of methane evolved during the reaction could be measured.

A clean, dry 500-ml reaction flask was taken (stoppered) into the glove bag along with the B-trichloroborazine (P_1). Enough of the P_1 ($4.7 \pm 0.1\text{gm}$, 0.026 mole) was measured out to react with all of the CH_3MgI available (about 0.078 mole) in a 3:1 ratio ($\text{MeMgI} : \text{P}_1$). The stoppered flask was then removed from the bag and attached to the apparatus shown in Figure VII. (The addition funnels were, at this point, replaced by ground-glass stoppers.)

Dry nitrogen was introduced through stopcock 2 (stopcocks 1 open and 3 closed) and the reaction apparatus was flushed for a few minutes through one of the side necks. Thirty ml of dry ether were put into an addition funnel and this funnel was put onto the apparatus while flushing continued. Likewise, 50 ml of Grignard reagent were, in the glove bag, poured into an addition funnel and the funnel put on the apparatus. At this point, stopcock 2 was closed and the vacuum line evacuated up to stopcock 3.

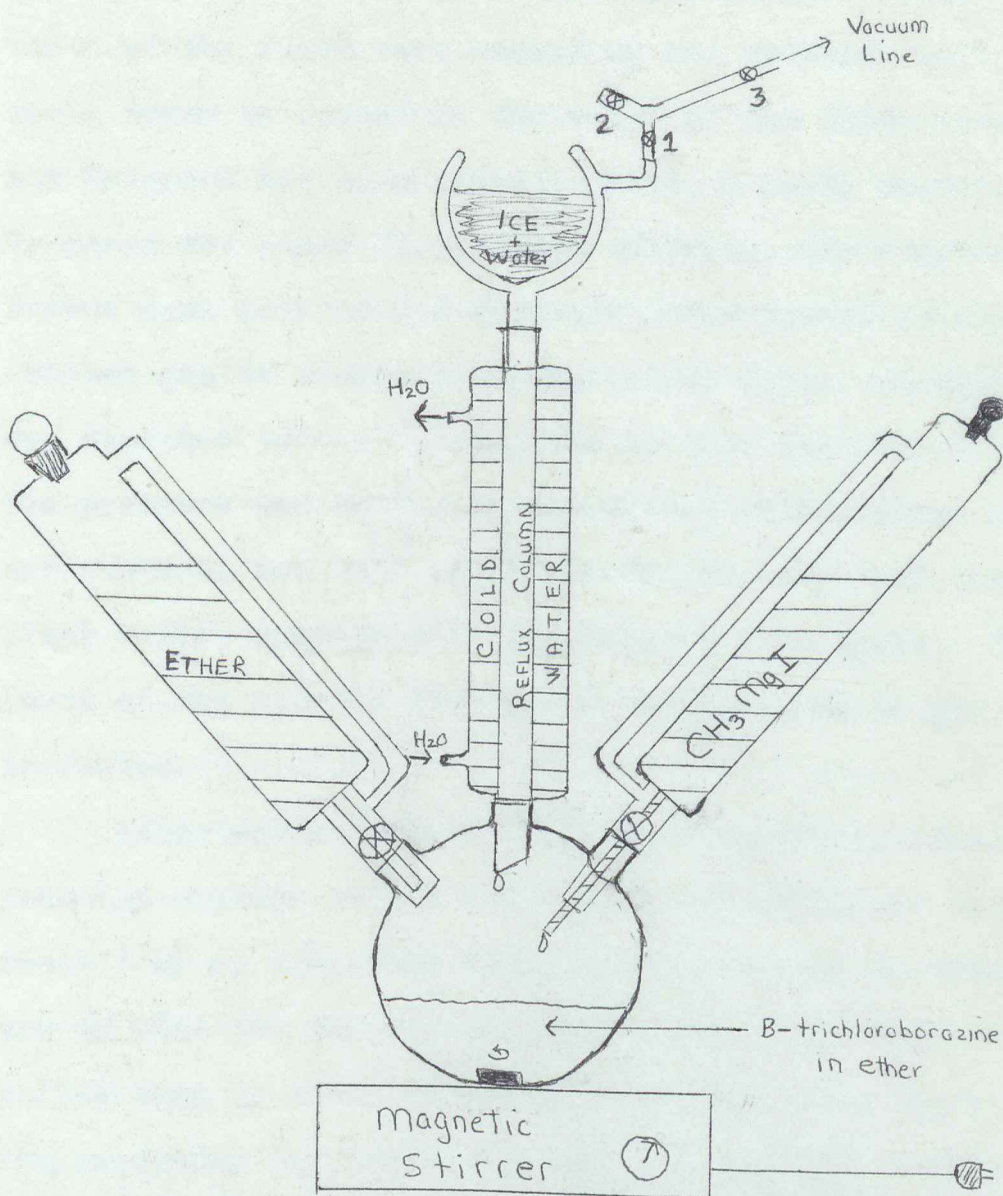


Figure VII

Apparatus for B-trimethylborazine
Preparation and the Measurement
of Noncondensable Gases Evolved

Ten ml of ether was then added to the P_1 , and the reaction flask was frozen with liquid nitrogen and evacuated. Ice and salt were then added to the cold finger. While the contents of the flask were warmed up and stirred, white splash spots began to appear on the walls of the flask (even before any Grignard had been added). Next, a small amount of the Grignard was added slowly with stirring. The reaction showed some boiling and stopcock 3 was opened to allow the evolved gas to escape into the vacuum line. (A manometer was attached to the vacuum line so that one had an idea what the pressure was in the vacuum line.) Ether vapor also was evolved, but this was to be frozen back into the reaction flask before pumping with the Toepler pump began. The level of the mercury dropped as the pressure in the line increased.

After adding about 20 ml of Grignard solution, the reaction mixture became very thick and difficult to stir. About 5 ml of ether was added to the mixture in order to try to make the slurry easier to stir. This ether turned yellow when it make contact with the reaction mixture. Stirring continued for twenty minutes and then the rest of the Grignard solution was added. No real boiling (apparent reaction) occurred. (It was noted at this time that all of the ether in the addition funnel had been sucked around the teflon stopcock, although it was greased, into the reaction flask.) The reaction mixture was stirred vigorously.

One hour later the contents of the reaction flask had turned light brown and the mercury level in the manometer had dropped to within a few centimeters of the Hg reservoir. This would indicate that the combined pressures of the methane and ether vapor was a little less than atmospheric pressure. Stirring was stopped and the reaction flask was frozen with liquid nitrogen in order to recondense all of the ether in the line before pumping the remaining, noncondensable gas(es) out of the line and reaction apparatus with the Toepler pump. However, the mercury level in the manometer rose only very slowly so that after two hours of condensing, over 30cm of pressure still remained in the line. The problem was either that the volume of the line was so big (2 liters) that it took a long time to condense out all of the vaporized ether or that a leak had developed, allowing other noncondensable gases (i.e., nitrogen and oxygen) to enter the system. In either case it was decided that it would be more expedient, for reasons of time and available liquid nitrogen, to forego trying to measure the amount of gas evolved by the reaction.

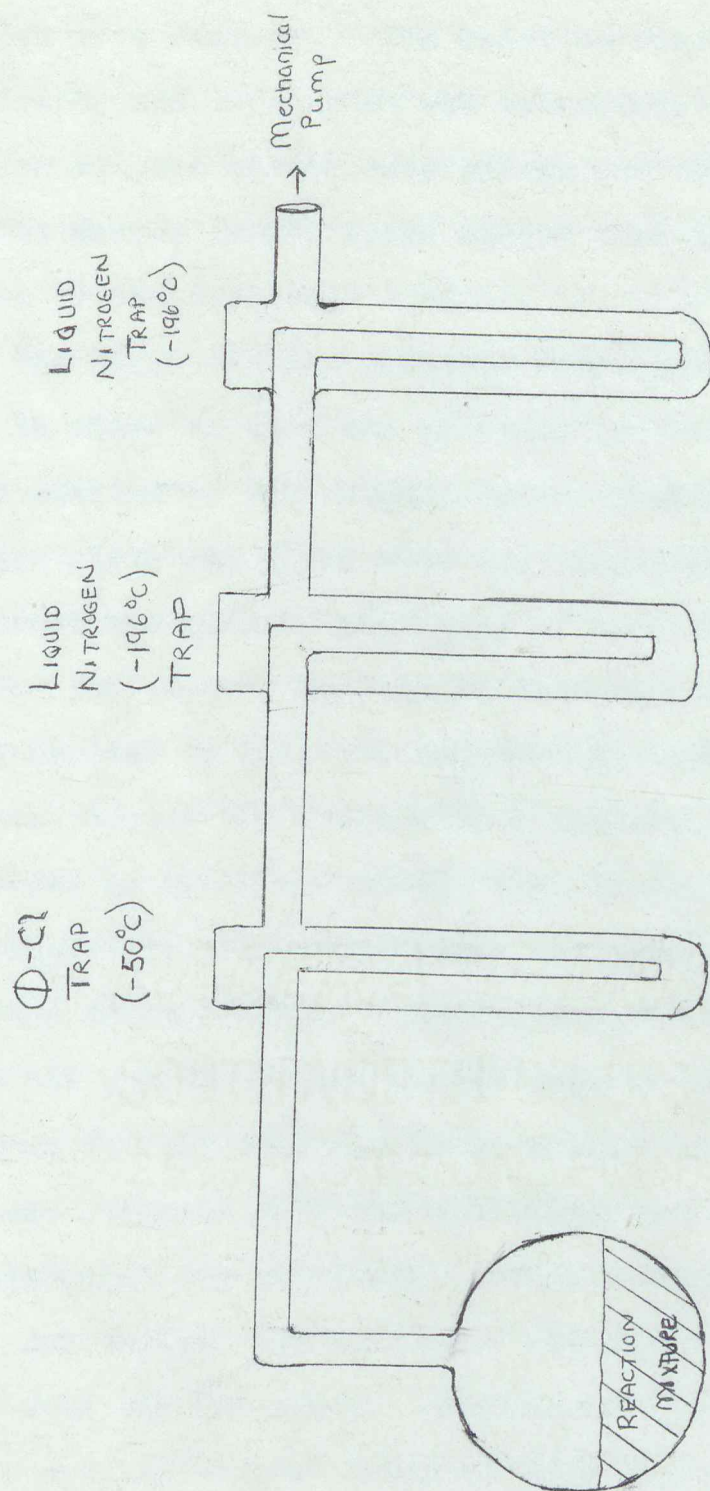
3.6 Isolation of Products of 2,4,6-trimethylborazine preparation.

The entire vacuum line, up to stopcock 1, was then pumped out through a liquid nitrogen trap (to protect the pump). The reaction flask then was pumped through a chlorobenzene trap, at -48°C , and two liquid nitrogen traps, at -196°C . After 18 hours of pumping and stirring, two-thirds

of the reaction mixture still remained and had become too thick to stir. When the reaction mixture was pumped on, it would foam up with tiny bubbles and fill the entire reaction flask.

The reaction flask was removed from the apparatus, quickly stoppered, and brought into the glove bag. Here the addition funnels were removed, the necks were cleaned and greased, and ground glass stoppers were put in their place. All of the apparatus shown in Figure VII, save the reaction flask itself, was then removed from the line and the reaction flask attached directly to the line (Figure VIII). Upon pumping on the product solution in the flask, foam built up again, filling up the flask.

During the next three weeks time, no further efforts were made to extract product from the reaction mixture. This was due to a loss of power in the building during this period. The reaction flask remained sealed, on the line, as in Figure VIII. When power was restored, pumping was again begun through two liquid nitrogen traps and a chlorobenzene trap. The sound of a noncondensable gas being pumped suggested that some gas had leaked into the line or, more probably, the reaction flask during the three-week interval. (This could be checked by closing all of the stopcocks leading from the pump to the reaction flask, waiting about 30 minutes and then opening each stopcock sequentially, beginning at the pump and working toward the



Apparatus for Vacuum Distillation
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Figure VIII

reaction flask. By listening to the pump, one could locate the leak more closely). The reaction mixture now boiled very nicely and more ether was extracted. However, the reaction mixture became very syrupy and thick, so much so that the bubbles formed would hardly rise through the reaction mixture to the surface.

The flask and its contents were heated with a hair dryer in order to make the contents less viscous. A large vacuum sublimator was washed, dried, evacuated, and put into the glove bag along with the stoppered reaction flask. An attempt was made to pour some of this reaction product into the sublimator, but the process was such a slow one that it was decided to help the reaction mixture (like very thick molasses) out of the flask with a spatula. The substance had become so thick and sticky that it was very difficult to transport it and to extricate the spatulas from it when done transporting. Finally, enough of this substance was in the sublimator and packed down to begin sublimation. The setup in Figure VIII was used, except that the reaction flask was replaced with the sublimator and a hot plate was put underneath the sublimator. When a vacuum was created in the sublimator, the substance expanded, as it did when heated with the hot plate. Ice was put in the cold finger; yet, after four hours of sublimation, no product had crystallized onto the cold finger. Crystals had,

however, condensed in the chlorobenzene trap and about 5 ml of ether had condensed in the liquid nitrogen trap. The crystals in the chlorobenzene trap melted and vaporized when brought to room temperature and, therefore, were probably B-trimethylborazine (m.p.= 31.5°C ⁵, vapor pressure (31°C) = 17.5cm^2 ²³). The substance remaining in the sublimator was discarded and the sublimator washed and dried, as it was apparent that no more B-trimethylborazine (and more importantly, no 2,4,4',6,6'-pentamethyl-1,2'-biborazinyl) was to be extracted from this sample of reaction product.

It was decided to try to extract the product borazines from the reaction mixture. A nonpolar solvent (hexane) was used with the hope that the polar magnesium salts would not dissolve along with the borazines. Dry hexane (230 ml) was added to the remaining reaction mixture (in the glove bag) and stirred with a spatula. The whole flask was shaken vigorously and allowed to stand overnight. However, no noticeable amount of the reaction product dissolved in the hexane, which, by now, had become whitish in color. The hexane was then decanted off (in the glove bag) and discarded.

Dry ether (200ml.) was now added to the reaction mixture. The thick mixture, when shaken with the ether, dissolved and stirred easily. After allowing to stand overnight, one could observe three distinct layers in the ether solution of the reaction products. The upper layer was gray in color; the middle layer was light brown and the bottom layer very

dark brown. The upper two layers were decanted off and the remaining layer discarded.

The upper of these two extraction layers was put into the clean, dry sublimator and pumped on through a trap in a chlorobenzene slush bath ("chlorobenzene trap") at -48°C and two traps at liquid nitrogen temperature (-196°C). (The cold finger always contained ice during sublimation). The solvent bubbled off nicely, leaving a solid residue. This residue was (in a glove bag) transferred into a flask, dissolved in 15 ml of dry benzene and the solution filtered. The filtrate was put into the clean sublimator and the benzene removed until the solution became very thick. The following day, the sublimator was heated on a hotplate ($70-90^{\circ}\text{C}$) and the solution was pumped on for 4 hours: at which point about one-half of the surface area of the bottom of the sublimator was dried out. By the following morning the color of the solution remaining was orange (indicating significant decomposition) and the contents of the sublimator were discarded.

The lower of the two benzene extraction layers was also vacuum distilled in the sublimator until it became very thick. It was then heated ($80-100^{\circ}\text{C}$) on a hot plate and pumped on until the thick mass began to expand and reached the cold finger of the sublimator. This mass was then dissolved in benzene and filtered, the filtrate being yellow. Four days later, this same filtrate was orange in color with

a precipitate. The solution was again filtered (in the glove bag). The filtrate was put in the cleaned sublimator and vacuum distilled (through a chlorobenzene trap and two liquid nitrogen traps) until a white solid remained on the bottom. Three days later, this solid had turned yellow, could not be purified by vacuum sublimation and was discarded.

3.7 Second Preparation of Grignard Reagent

The magnesium (19-20gm, 0.8 mole, freshly ground) was put into a triple-necked reaction flask and the apparatus (Figure VI) assembled and flushed with nitrogen. About 20 ml of ether was added and the ether-magnesium mixture stirred. Over a two hour period, the MeI was added slowly while vigorous stirring was maintained. The reaction mixture was stirred rapidly for 3 hours while a ~~cap of nitro-~~ nitrogen gas pressure kept the ether vapor from escaping from the reaction system. The stirring was then stopped and the Grignard solution (dark gray) was decanted and used without further treatment.

3.8 Second Preparation of B-trimethylborazine

(This preparation was, in this experiment, really an attempt to prepare the pentamethyl-biborazinyll, which is a side product in the B-trimethylborazine preparation.)

B-trichloroborazine ($4.5 \pm 0.1\text{g}$, 0.024 mole) and the Grignard reagent prepared in section 3.7 were reacted by a procedure similar to that described in section 3.4

except that no attempt was made to collect non-condensable gases released in the reactions. Hence, the reaction could be carried out on the benchtop, independent of the vacuum line. Also, no freezing of reactants in the reaction flask was necessary. The Grignard reagent was added gradually (over a two-hour period) with stirring and bubbles were seen to form. When all of the Grignard had been added, the reaction mixture was stirred overnight.

3.9 Attempts to Isolate the Diborazinyl

When stirring was ceased, two layers could be seen in the flask; the upper one clear and the lower one slightly whitish. An attempt to filter this reaction solution failed (the liquid would not pass through the filter paper (Whatman, qualitative)), and the solution was simply poured into a 500-ml single-necked flask and this attached to the vacuum line. The solution was pumped on through one chlorobenzene trap and two liquid nitrogen traps until it began to get thick and viscous. Dry benzene (50 ml) was then added to this solution and it dissolved (liquified) immediately. An attempt to vacuum filtrate this redissolved reaction mixture failed, as the solution was again too thick to pass easily through the filter paper and the benzene began to boil out of the solution.

It was decided to dissolve the reaction mixture in a large volume of benzene in the hopes that the separation of the more polar magnesium salts might have been facilitated.

Thus, 375 ml of dry benzene were added to the reaction mixture solution in a 500-ml separatory funnel (in the glove bag). The contents (total volume=550 ml) were shaken vigorously and the resulting "solution" allowed to stand. Two days later, a clear layer extended from the surface down to the 300-ml mark. In order to expedite the separation of the magnesium salts from the benzene solution, the entire volume in the separatory funnel was centrifuged in 50-ml aliquots at 2900 r.p.m. for 30 minutes. The supernatant liquid (clear, colorless) was decanted off and the thick residue (containing predominantly the magnesium salts) saved in a greased, stoppered flask.

The supernatant liquid (benzene extract) was filtered (in the glove bag) and the flask containing the filtrate attached to the vacuum line. A carbon tetrachloride (CCl_4) slush bath was calculated (using vapor pressure data²⁷) to yield a trap temperature (-23°C) at which B-trimethylborazine had a vapor pressure of about 1 mm (low enough to retain it in the trap) and benzene would have a vapor pressure of 5.8 mm (not low enough to keep the benzene in the trap). Thus the benzene extract of the reaction mixture (second B-trimethylborazine preparation) was pumped on through the CCl_4 trap (-23°C) and two liquid nitrogen traps (-196°C) until about 100 ml of benzene had been removed and the extract had become syrupy. The extract was then transferred (in the glove bag) into the sublimator. The sublimator

was then attached to the vacuum line, ice was put into the cold finger and more benzene was pumped out of the extract. Soon, (8 hrs.), the extract became thick and bubbles formed in it, rising only slowly through the liquid. At this point, the bottom of the sublimator was heated to 100°C using a boiling water bath. This caused the extract to eventually foam up and dry out (lose most of its remaining benzene) and form kind of a honeycomb, nearly reaching up to the cold finger. (In the center of the surface of this honeycomb layer, all of the benzene had not yet been driven off.) There was also a small amount of white solid (not crystalline) on the bottom of the cold finger.

The sublimator was now brought into the glove bag (always after drying out the cold finger), opened and the substance from the dry honeycomb region, the soft honeycomb surface layer and the cold finger removed and stored in separate containers in the glove bag.

Three days later, the solid from the cold finger and the soft honeycomb surface had turned yellow-orange in color (indicative of some decay) but the dry honeycomb part was still white. The dry, honeycomb solid was then ground with a mortar and pestal (in the glove bag) and put into the cleaned sublimator which was then evacuated. Ice was kept present in the cold finger as the sublimator was lowered 5cm into an oil (corn oil) bath and the temperature increased

to 50°C. (This was in the hopes of sublimating the diborazinyll onto the coldfinger.) Some globules formed in the solid and gradually all of the solid became thick and syrupy as the temperature of the oil bath reached 120°C. The temperature was held there for 3 hours. Next, the temperature was raised to 165°C and bubbles began to form in the thick syrup now in the sublimator. The sublimator contents were pumped on for 15 minutes until no further bubbling occurred and the contents of the sublimator appeared quite dry (of benzene). The sublimator was removed from the oil bath and allowed to cool. The following day, the dried solid was removed from the sublimator in the glove bag and stored in a stoppered, greased flask. No crystals were found on the cold finger.

A similar procedure was carried out on the solid found on the cold finger above the honeycomb solid. Again the temperature was held at 140°C for 4 hours (with ice in the cold finger). Solid material was found on the cold finger but it was orange in color and not crystalline in structure so it was discarded. Water was added to the residue remaining in the sublimator and some of it reacted with the water, although a white solid material remained in the water. This solid was filtered out of the water, washed with distilled water and dried initially in the air and finally in the glove bag. A melting point determination revealed no melting point (up to 300°C), which indicates

that the solid must be impure.

* Vacuum sublimation of the soft, honeycomb surface layer yielded no crystals and an orange residue in the sublimator.

DISCUSSION

IV. DISCUSSION

Since no pentamethyldiborazinyll was isolated, no data was collected in this experiment that would further the goals of this experiment as stated earlier. The problem lay in isolating the diborazinyll (and, for that matter, the B-trimethylborazine) from the reaction mixture. Although traces of the B-trimethylborazine were seen in the chlorobenzene trap, no significant amount was isolated.

Several workers have suggested that the product borazines are complexed with the magnesium salts (magnesium halides) formed from the Grignard reagent (Haworth and Hohnstedt⁵, 1960; Smalley and Stafiej²⁵, 1959). The results of this experiment would support the conclusion that if this complex is not broken, the product borazines cannot be isolated on the basis of their volatility.

One method for breaking this complex is described by Groszos and Stafiej²⁶ and Smalley and Stafiej²⁵. The method employs aqueous ammonium chloride to displace the product borazine-magnesium salt complex, thereby dissolving the magnesium salts in the aqueous layer and liberating the borazine into the ether layer. The borazines are then easily isolated from the ether solution and recrystallized (usually in hexane). One wonders as to the advisability of this method when one considers the fact that most borazines are highly sensitive to water. However,

the borazine derivatives (B-trialkyl-N-triphenylborazines) prepared by Groszos and Stafiej and isolated using this method were all stable against moisture and high yields (65-85%) were obtained.

Another method for breaking this complex is described by Haworth and Hohnstedt⁵ and involves refluxing the reaction mixture for 12 hours after which the ether is distilled away by vacuum distillation, leaving a white residue. This white residue is then vacuum sublimated at about 150°C with the product crystallizing out on the cold finger of the sublimator.

The method used in this experiment resembled closely the latter of the two outlined above except that the reaction mixture was not refluxed before vacuum distillation was begun. Actually, that part of the reaction mixture that contained the magnesium salts (and, therefore, probably most of the product borazines as well) was never vacuum sublimated. It was thought that the magnesium salts were complexed to the solvent ether only and not to the product borazines as well. For this reason, there was no attempt made to isolate the product diborazinyll from that part of the reaction mixture containing the magnesium salts.

The failure to isolate the product borazines in this experiment does not shed doubt on the effectiveness of the vacuum pyrolysis method of breaking the borazine-magnesium

complex but does support the conclusion that most of the product borazines are tied up in this magnesium salt complex and, as such, are very difficult to isolate.

FUTURE WORK

V. FUTURE WORK

The preparation of the B-trimethylborazine (and, thus, the pentamethyldiborazinyll) should be repeated. The possibility of running this preparation in benzene or carbon tetrachloride might be investigated. (The Grignard reagent would, of course, have to be made up in ether.) The presence of the benzene or CCl_4 might prevent the formation of the magnesium-borazine complex by providing a nonpolar medium in which the product borazine would be soluble whereas the magnesium salts would not be.

There are a variety of isolation methods available to be tried, working from the product reaction mixture. One would be to add CCl_4 or benzene to the reaction mixture while continuously distilling off the ether. (This would remove the agent that is apparently making the magnesium salts soluble in nonpolar organic solvents.) Another method would be to vacuum distill ether from the reaction mixture until it begins to get thick and syrupy. This syrup can then be transferred to the sublimator for further vacuum distillation and eventual vacuum sublimation (at temperatures up to 150°C). A third method would be to attempt removal of the magnesium salts using a saturated ammonium chloride solution as described by Groszos and Stafiej²⁶. Johnson¹⁵ noted that the pentamethyldiborazinyll is quite stable against water so that this method for

isolating the diborazinyl might be safe as far as product hydrolysis is concerned.

Vapor pressure data on the pentamethyldiborazinyl will be very valuable as it can be used to deduce some thermodynamic properties of the diborazinyl. A good gas-phase infrared spectrum of the diborazinyl will tell us more about the bond strength of the B-N bond connecting the two borazine rings.

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