extremely slow after about 60% of the fluoride has been released. Some of the runs were followed for as long as 4 months; others were heated to speed up the reaction in order to obtain an effective infinite time reading. Values obtained at different acidities were 64.45, 65.11, 64.35, 65.60, and 64.92% of fluoride released. Although these values are within experimental error equal to 66.67, which would correspond to a final product containing F and Sb in a ratio of 2:1, the resolution of each kinetic curve was begun by subtracting a value of 35.0% fluoride remaining.

The residual curves resulting from this subtraction could be resolved satisfactorily into two linear components. The intercepts indicate that these linear portions correspond to the hydrolysis of $[SbF_5(OH)]^-$ and $[SbF_4(OH)_2]^-$. According to this interpretation the following steps of hydrolysis have been measured

$$SbF_6^- + H_2O \xrightarrow{\text{fast}} SbF_5(OH)^- + H^+ + F^-$$

$$SbF_5(OH)^- + H_2O \xrightarrow{k_2} SbF_4(OH)_2^- + H^+ + F^-$$

$$SbF_4(OH)_2^- + H_2O \xrightarrow{k_3} \text{final product}$$

The pseudo-first-order rate constants, k_2 and k_3, and the corresponding half-times are given in Table I. The success of the resolution is due to the marked difference in rates for these steps; $[SbF_5(OH)]^-$ disappears over the period of hours, while $[SbF_4(OH)_2]^-$ disappears over the period of days.

Attempts to resolve the residual first-order plots into three linear components, corresponding to the hydrolysis of $[SbF_5(OH)]^-$, $[SbF_4(OH)_2]^-$, and $[SbF_3(OH)_3]^-$, provided a much less satisfactory fit of the data than did the resolution into two components. More positive support for the proposed three-step hydrolysis has been provided by experiments in which the antimony species present in the reaction mixture are separated by chromatography on cellulose columns.[7] Only three species (corresponding to $[SbF_5(OH)]^-$, $[SbF_4(OH)_2]^-$, and the final product), rather than four, are observed.

The rate of release of hydrogen ion is equal to the rate of release of fluoride ion during the first two stages of hydrolysis, but during the third stage the ratio of hydrogen ion released to fluoride ion released is 1.17:2. A small amount of a fine solid was also observed at this stage in some of the reactions. These observations suggest that the final product is not an anion as simple as $[SbF_2(OH)_4]^-$, but is instead a polymeric anion which contains F and Sb in a ratio very close to, but not necessarily equal to, 2:1. There is considerable evidence that antimony(V) forms polymeric anions in acid solution, with most of the evidence suggesting a hexaantimonate.[8]

In solutions more basic than pH 12 the hydrolysis was complete and all six fluorides were lost quite rapidly. The reaction in 1 M NaOH was so rapid that a fine white precipitate, probably $NaSb(OH)_6$, formed before the first aliquot could be taken. In 0.1 M NaOH the rate was measurable and could be followed both by the fluoride titration and by titration with HCl. In aqueous ammonia at pH 10.2 after 1 month of reaction 17% of the fluoride still remained complexed.

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[7] These experiments were performed by Mr. Jesse H. Hall.

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CONTRIBUTION FROM THE U. S. BORAX
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Polycyclic Borazines[1]

BY J. L. BOONE AND G. W. WILLCOCKSON

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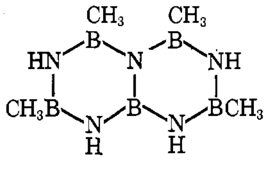
The yield of B-trimethylborazine from B-trichloroborazine and methylmagnesium bromide has never exceeded 34% in this laboratory. In every case, large amounts of residue remained which had infrared spectra that strongly resembled the spectrum of B-trimethylborazine. Some trimethylborane and methane were also formed. It appears from the present work that ring opening occurs followed by condensation which gives as the second principal product a B-methylborazine (I) analogous to naphthalene. Elemental analyses checked closely for this compound but were also consistent with a structure analogous to biphenyl. However, cryoscopic determination of the molecular weight in benzene gave values which were consistently within 0.5–1.5% of the value calculated for structure I.



I

A similar reaction using butylmagnesium halides has been reported by Harris to yield the B-butyl derivative analogous to biphenyl.[2] Laubengayer and co-workers have reported both the naphthalene and biphenyl analogs of the borazine system from the pyrolysis of borazine,[3,4] and Wagner and Bradford have reported the biphenyl analogs of hexamethylborazine from the condensation of N-lithioborazines and B-chloroborazines.[5]

Further workup of the products of the B-trichloroborazine–methylmagnesium bromide reaction gave two more boron–nitrogen compounds which were appar-

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[1] Presented in part to the Inorganic Division, 142nd National Meeting of the American Chemical Society, Sept. 11, 1962, paper No. 16.

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[4] A. W. Laubengayer and O. T. Beachley, Jr., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, pp. 281–289.

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ently also polycyclic borazines. They have not been well characterized, however. One of these, with a melting point of 250–257° and referred to as condensed borazine A, had an analysis consistent with any of several condensed boron–nitrogen compounds such as those analogous to anthracene, naphthacene, the terphenyls, etc., in which the hydrogen atoms on the borons are replaced with methyl groups. The other was a viscous oil distilling at 115–122° (0.2 mm.) and is referred to as condensed borazine B. The elemental analyses gave a nitrogen–boron atomic ratio of 1.18, which suggests a structure such as would be formed by fusing three borazine rings together in one plane with each ring sharing a common nitrogen atom. This structure would contain seven nitrogen and six boron atoms, giving a ratio of 1.17. The actual boron and nitrogen contents and the molecular weight were only in fair agreement with this compound, however. Although only four borazine-type materials were isolated, there are apparently others which remained in the residues.

The B^{11} n.m.r. spectrum of a hexane solution of B-trimethylborazine gave a single band at -34.7 p.p.m. (measured against $BF_3 \cdot (C_2H_5)_2O$ and $B(C_2H_5)_3$ as external standards) with a half-width of approximately 9 p.p.m. The bands due to the different borons in a hexane solution of the naphthalene analog (I) apparently merged in a single broad band at -34.5 p.p.m. with a half-width of approximately 19 p.p.m. These shifts are consistent with other reported B^{11} shifts for B-trialkylborazines.[6,7]

The possibility of hydrogen chloride elimination from B-trichloroborazine with formation of condensed B-chloroborazines before the alkylation procedure was eliminated by recrystallizing B-trichloroborazine just prior to the Grignard reaction. The results were essentially the same as those obtained from other sources of B-trichloroborazine, proving that the condensation reactions actually occurred during the Grignard reaction.

Experimental Section

Reaction of B-Trichloroborazine with Methylmagnesium Bromide. (1) Isolation of B-Trimethylborazine.—B-Trichloroborazine (184.0 g., 1.00 mole) was dissolved in 475 ml. of anhydrous diethyl ether and stirred constantly while a diethyl ether solution of methylmagnesium bromide (1.00 l., 3.0 *M*) was added dropwise at the reflux temperature during an approximately 3-hr. period. Sufficient trimethylborane was formed in the process to cause spontaneous ignition of the effluent gases. The mixture was refluxed and stirred vigorously for an additional 0.5 hr. and then held for 16 hr. at room temperature with no stirring. Benzene was then added continuously as the ether was removed by distillation. Approximately 3 l. of mixed solvents was distilled through a short Vigreux column before the head temperature reached 80°. The remaining benzene slurry was filtered at room temperature and the insolubles washed with benzene. A significant but undetermined amount of boron–nitrogen material was lost with this insoluble fraction. Most of the benzene was removed from the filtrate by distillation at atmospheric pressure. The residual benzene and the borazine forerun were distilled at 49–95° (258 mm.). B-Trimethylborazine (30.85 g., 25.2%) was collected at 95.2–95.8° (258 mm.). After draining off a small liquid phase in contact with the crystalline B-trimethylborazine and distilling off the most volatile portions during 15 min. under vacuum, the melting point of the product was 31.4–32.4° (lit.[8] m.p. 31.5°).

(2) Isolation of $(CH_3)_4B_5N_5H_4$.—A small intermediate liquid phase (3.8 g.) was taken and then the next pure cut (13.4 g.) was collected at 138–139° (25 mm.). This material ($(CH_3)_4B_5N_5H_4$, I), m.p. 58–61°, was recrystallized from a small amount of anhydrous pentane by dissolving at room temperature and cooling slowly to 0° to give a crystalline product, m.p. 60.0–61.5°. A second recrystallization from pentane raised the melting point only slightly (60.5–61.4°).

Anal. Calcd. for $C_4H_{16}B_5N_5$ (the naphthalene analog): C, 25.51; H, 8.56; B, 28.73; N, 37.19; mol. wt., 188.3. Calcd. for $C_5H_{20}B_6N_6$ (the biphenyl analog): C, 26.20; H, 8.80; B, 28.33; N, 36.67; mol. wt., 229.2. Found: C, 26.05; H, 8.61; B, 27.61 (Parr bomb); N, 36.82 (Kjeldahl); mol. wt. (cryoscopic in benzene), 187.9, 187.0, 191.7, 189.8.

Fractional sublimation gave a material with a maximum melting point of 60.5–61.5°. The boron analysis and molecular weight were unchanged.

(3) Isolation of Condensed Borazine A.—On completion of the distillation of the first polycyclic borazine at 138° (25 mm.), a large amount of residue remained in the flask; this material had an infrared spectrum similar to that of the previously isolated borazine fractions. In addition, the upper part of the distillation flask was filled with long, needle crystals. There were obviously other distinct borazine-type materials remaining which had not been previously isolated. The next most volatile components were distilled from the flask under vacuum (0.1–0.2 mm.; maximum temperature 225°) without fractionation. The distillate was dissolved in 50 ml. of refluxing toluene and then cooled slowly to 25°. The precipitate (fraction A, 4.64 g.) was separated from the soluble part (fraction B) by filtration and dried under high vacuum at room temperature (m.p. 210–223°). It was then fractionally sublimed under vacuum at 145° (0.1–0.2 mm.) (m.p. 244–252°) and again recrystallized from toluene (m.p. 250–257°). The compound is referred to as condensed borazine A.

Anal. Found: C, 23.11; H, 8.05; B, 28.60; N, 38.39; mol. wt. (ebullioscopic in benzene), 300–350.

(4) Isolation of Condensed Borazine B.—The toluene was removed from fraction B by distillation under vacuum at room temperature. The remaining viscous oil was then fractionally distilled at 115–122° (0.2 mm.). It is referred to as condensed borazine B.

Anal. Found: B, 27.98 (Parr bomb); N, 42.81 (acid hydrolysis and steam distillation of ammonia from basic solution); mol. wt. (cryoscopic in benzene), 238.2.

Isolation of Pyridine Trimethylborane from the Reaction of B-Trichloroborazine with Methylmagnesium Bromide.—B-Trichloroborazine (184.0 g., 1.00 mole) was dissolved in 500 ml. of benzene and the ether solution of methylmagnesium bromide (1.00 l., 3.0 *N*) was added during a 45-min. period. Although the flask was immersed in a 0° bath, the reaction mixture heated to the reflux temperature. Workup of the products as indicated above gave 41.73 g. (34.0%) of B-trimethylborazine and 14.96 g. of I. The trimethylborane was trapped from the exit gases in a toluene solution of pyridine (50–50 mixture) as the pyridine–trimethylborane complex and purified by sublimation under vacuum (6.60 g., 0.05 mole). The melting point (51.55°; lit.[9] m.p. 53.8–55.1°) and boron analysis (7.91; calcd. 8.02) confirmed the composition. The gas emerging from the toluene–pyridine trap burned when ignited but without a green flame. This indicated methane formed from Grignard attack on the N–H bonds.

Reaction of B-Trichloroborazine with Methylmagnesium Bromide at Reduced Temperature.—Several attempts to increase

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TABLE I

INFRARED ABSORPTION BANDS OF REPORTED BORAZINES (CM.$^{-1}$)

$(CH_3BNH)_3$	$(CH_3)_4B_6N_5H_4$	Condensed borazine A	Condensed borazine B
3440	3450	3450	3470
2960	2960	2960	2960
1605			
1490	1470	1490	1470
	1410	1446	
1336		1342	1334
1300	1316	1310	
	1200	1230	
	1185		
	1160		1162
	1122	1120	1103
1082	1080	1087	
893	893	893	893
	827	827	
784	806	775	
720	720	715	
		685	698

the yield of B-trimethylborazine by running the Grignard reaction in diethyl ether at low temperature were not successful. Below −45° the formation of solids prevents stirring. If mixed at −45° and warmed slowly to about −38°, an exothermic reaction occurs which rapidly heats the mixture to the reflux temperature. Several such experiments, starting with one mole of B-trichloroborazine in each case, gave 17.90 g. and 20.35 g. of B-trimethylborazine and 8.00 g. and 4.80 g. of I.

Reaction of Highly Purified B-Trichloroborazine with Methylmagnesium Bromide.—In order to be sure that the borazine condensation was occurring during the Grignard reaction and not prior to it the B-trichloroborazine was very carefully purified by recrystallization from carbon tetrachloride. The chloride analysis (57.4%; calcd. 57.85%) and the melting point (83.9–84.6°; lit.[10] m.p. 83.9–84.5°) were indicative of high purity. The yields of B-trimethylborazine (30.30 g.) and the bicyclic borazine I (15.46 g.) were essentially the same as those resulting from other preparations.

Infrared Spectra.—The infrared absorption bands of these four borazines were obtained using a Perkin-Elmer Infracord and are recorded in Table I. The first two rows obviously arise from the N–H and C–H absorptions. However, the placement of bands in the other rows is merely intended to indicate similarity and not necessarily the correlation of any specific energy transitions.

Acknowledgment.—The research reported in this publication was supported by Wright Air Development Division, Air Research and Development Command, United States Air Force, under Contract AF 33(616)-7303.

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Assignment of Optical Spectra for Vanadyl Complexes[1]

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Recently there have been a number of experimental and theoretical discussions of the energy levels and optical spectra of vanadyl complexes from which several alternate assignments of the optical spectra have been made.[2–6] In this note we wish to present an empirical correlation between e.s.r. hyperfine splittings and values of the ratio of axial to equatorial charge obtained from optical spectra which makes possible a consistent set of optical assignments. This was suggested by our previous work on the e.s.r. spectra of substituted copper(II) acetylacetonates[7] in which it was found that two dissimilar copper(II) complexes which had similar e.s.r. *A* values also had similar optical absorption spectra.

From crystal field theory and an ionic model it is possible to determine the ratio ρ of the axial charge to the equatorial charge[8] defined as

$$\rho = \frac{\rho_4^{+z} + \rho_4^{-z}}{2\rho_4^{xy}} \qquad (1)$$

where ρ_4^{+z} is the field strength along the V=O axis, ρ_4^{-z} is the field strength *trans* to the V=O position, and ρ_4^{xy} is the in-plane field strength[9]; ρ is obtained from the experimental optical spectra by use of the equation[8]

$$\rho = \frac{3(E_{xy\rightarrow z^2}) - 4(E_{xy\rightarrow xz,yz})}{2(E_{xy\rightarrow x^2-y^2})} - {}^1/_2 \qquad (2)$$

The optical band for vanadyl compounds which normally lies between 18,000 and 26,000 cm.$^{-1}$ has been variously assigned as the $d_{xy} \rightarrow d_{z^2}$ transition[8] or as a charge-transfer band.[3,6] If it is uniformly assigned as the d–d transition, and if the values of ρ computed on this basis are plotted against the e.s.r. hyperfine splittings *A* for the vanadium nucleus for a series of vanadyl compounds (Figure 1), the points fall close to a straight line. Since this series (Table I) covers a wide range of vanadyl–ligand bond types, from the more ionic $[VOF_5]^{-3}$ to the more covalent $[VO(NCS)_5]^{-3}$, the excellent correlation appears to be significant. If this is so one may then use the observed e.s.r. *A* values to obtain ρ from Figure 1 as a check on future vanadyl optical assignments or to determine the position of the $d_{xy} \rightarrow d_{z^2}$ transition if it is buried under the shoulder of an intense charge-transfer band. The data and assignments chosen in drawing Figure 1 are summarized in Table I and two extensions, to the largest known e.s.r. *A* value, $VOSO_4$, and the smallest, $VO(CN)_5^{-3}$, are discussed below.

However, before discussing the two extensions we wish to point out that the relative changes in ρ are those expected from a consideration of other data and the physical model of the complexes. The increase in ρ value in going from vanadyl sulfate to vanadyl acetylacetonate is consistent with the decrease in the

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