A STUDY OF ORGANIC BORO-NITROGEN COMPOUNDS

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Chemical Relationship of Boron and Nitrogen

A review of the binary compounds of boron thus far synthesized, and a study of the many unsuccessful attempts to form other compounds reveals the fact that there are but few elements which combine readily with this peculiar element. Though itself essentially a non-metal, boron combines under ordinary conditions, with but few metals to form metallic borides. As the number of strictly non-metallic elements is small compared with the number of metals named in the periodic system the number of binary compounds of boron appears quite limited. Among this limited number of compounds of boron with non-metals, which are fairly readily formed, we naturally recognize the preeminent importance and rôle of the oxide, B_2O_3.

But after the important oxygen compound, and also before the interesting halides, it appears that the strong mutual attraction between boron and nitrogen is of special interest and importance. By passing nitrogen over hot boron the nitride of boron, $B \equiv N$, forms. This is an extremely stable compound, as is evident from its behavior at high temperatures and toward the most powerful oxidizing agents. Not only do these elements combine directly, but boron nitride is one of the main products formed whenever a boron compound, like boric oxide or borax, is brought into intimate contact with almost any nitrogen compound at a fairly high temperature.

A glance at the periodic system shows that boron and nitrogen are in the same period—the first period (and only series) of the periodic system of the elements. Carbon, which is practically always tetravalent, stands in the middle group, with boron just preceding it. The latter is generally trivalent, though it has pentavalent possibilities. Nitrogen

immediately follows boron, with a valence that is usually three but probably five in many cases. In passing along the series from left to right there is as rapid a change in properties, both chemical and physical, as is found in any series in the periodic system. And so boron and nitrogen, two elements symmetrically placed in the periodic system with respect to each other nevertheless exhibit sufficient chemical and physical dissimilarities to insure their power to unite to form a firm chemical compound.

The above considerations caused the writer to look for so-called "molecular" compounds formed by the direct union of a boron compound with a nitrogen compound. Such molecular compounds would result from the "*residual attractions*" of boron and nitrogen. A review of the literature brought to light several addition-compounds of ammonia and certain halides of boron. These substances were, for the most part, prepared by Moissan's students. Following is a complete description of their work:

Compounds of BI_3 with NH_3.—There is at least one definite compound of ammonia and the iodide of boron (prepared by Besson[1]) which has the formula $BI_3 \cdot 5NH_3$. Dry gaseous ammonia combines directly with BI_3 with disengagement of much heat; and if the reaction is not moderated by cooling, there is formed as a secondary product, an insoluble substance, namely, BN. In practice the BI_3 is dissolved in CCl_4, and maintained at about 0°, while dry ammonia gas, also chilled to 0°, is slowly conducted through the solution. There is formed immediately a white solid on the surface of the CCl_4, and when the reaction is terminated, the solvent is expelled with a current of dry air at a temperature of 50°–60°. Thus an amorphous, white solid, corresponding to the composition above indicated, is obtained.

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[1] Besson: Comptes rendus, **110**, 80 (1890).

ANALYSIS

I	II	Theoretical for $BI_3 : 5NH_3$
NH_3 17.37	17.55	17.82
I 80.32	79.35	79.85
(Diff.) B 2.31	3.10	2.30

Properties of $BI_3.5NH_3$.—In light the compound slowly turns yellow and iodine is set free; it is also readily decomposed by water. When heated in a current of hydrogen, iodine is set free.

Other Compounds of BI_3 with NH_3.—Very interesting is the fact, also observed by Besson, that if the compound $BI_3.5NH_3$ is maintained in a current of dry ammonia gas, it absorbs the latter rapidly. The mass first becomes pasty, and if the process is continued to saturation at 0° the whole becomes liquid. It is stated that its composition is about $BI_3.15NH_3$ at 0° but no analytical figures are given. Even at 0°, this liquid substance is not stable; furthermore it loses gas in a current of dry hydrogen and after a time it attains the composition of $BI_3.5NH_3$.

Compounds of BBr_3 with NH_3.—There appears to be but one definite compound of ammonia and the bromide of boron. This has also been prepared by Besson. Dry, gaseous ammonia, conducted into a solution of BBr_3 dissolved in carbon tetrachloride, precipitates a beautiful snow-white mass, which, when treated as described for the iodine ammonia compound is found to have a composition corresponding to $BBr_3.4NH_3$.

ANALYSIS

I	II	Theoretical for $BBr_3 : 4NH_3$
NH_3 21.61	21.42	21.31
Br 74.35	74.60	75.23
(Diff.) B 4.04	3.98	3.46

When maintained at 10° in a current of dry ammonia gas, the compound absorbs a quantity of ammonia corresponding to $1/_2$ NH_3 for every $BBr_3.4NH_3$; but the absorption appears to be of a purely physical nature, because the ammonia is easily carried away again by a current of dry air. If the $BBr_3.4NH_3$ is heated progressively in a current of dry hydrogen, it begins to decompose at 150° and to sublime. The products of the decomposition are BN and ammonium bromide. Water or alkalies decompose $BBr_3.4NH_3$.

Compound of BCl_3 with NH_3.—The reactions between dry ammonia and the chloride of boron have been the object of several researches, first among which was Berzelius',[1] which indicated that the compound $2BCl_3.3NH_3$ is formed. Later the work of Berzelius was confirmed by that of Martius,[2] who formed a compound of the same composition. Martius conducted dry ammonia gas directly into well cooled liquid BCl_3, without the use of any solvent for the latter. He described the reaction as taking place with very great evolution of heat. When saturated with ammonia, there was obtained a fine, white, crystalline powder, *which did not fume in the air* (?). On heating the product in water, it decomposed into ammonium chloride, boric acid and hydrochloric acid, and when heated in a tube it sublimed unchanged. But if placed in a hot tube through which ammonia gas was conducted BN resulted as the principal product.

Martius' analytical results are as follows:

No. (1) 1.0420 gram of the compound gave 3.1335 gram *AgCl*, 74.33 percent *Cl*.

No. (2) 0.8646 gram of the compound gave 2.6032 gram *AgCl*, 74.49 per cent *Cl*.

0.8990 gram of the compound gave 2.086 gram of ammonium platinum chloride: representing 17.77 percent NH_3.

These figures correspond to the formula $2BCl_3.3NH_3$, which was also obtained by Berzelius.

Other Compounds of BCl_3 with NH_3.—It has already been

[1] Berzelius: Pogg. Ann., 2, 113–147 (1824).

[2] Martius: Liebig's Ann., 109, 80 (1859).

mentioned that in the case of the iodide of boron Besson obtained a liquid of high ammonia content by saturating BI_3 with ammonia at $0°$. Likewise, in operating at $8°$ he showed that two molecules of BCl_3 absorb nine molecules of ammonia, and concluded that the compound $2BCl_3.9NH_3$ is thus formed. Besson also claims that $2BCl_3$ react with $15NH_3$ to form NH_4Br and a mixture of amides and imides of boron. His evidence is based on manometric data for the dissociation tension of the products obtained at $-23°$. This work will be referred to again in the discussion further along under "Amides and Imides of Boron."

Compounds of BF$_3$ with NH$_3$.—After diligently searching the literature of boron and fluorine I have, as yet, failed to find any compound mentioned which has been formed by the interaction of the fluoride of boron and ammonia, nor does it appear that any attempts to prepare such compounds have been described.

Retrospect of Compounds of Boro-Halides with NH$_3$.—It is interesting to arrange these compounds of ammonia and the halides of boron in columns and series in the order of atomic weights of the halogens and content of ammonia or nitrogen, as follows:

Atomic weight of halogen	126.92	79.92	35.46	19.00
Series	BI_3	BBr_3	BCl_3	BF_3
I	$BI_3.5NH_3$	$BBr_3.4NH_3$	$BCl_3.^3/_2NH_3$	—
II	——	——	$BCl_3.^9/_2NH_3$	—
III	$BI_3.15NH_3$	——	$BCl_3.^{15}/_2NH_3$	—

This table shows that, in the series of simplest combinations, the capacity of the boro-halide for ammonia rapidly falls off with the decrease in the atomic weight of the halogen. While, of course, it is unsafe to attempt broad conclusions from such meager data, still, it appears that we might reasonably expect no compound of ammonia and the boride of fluorine, or at least, one containing but a very small proportion of ammonia.

That the foregoing molecular compounds offer problems in valency which are practically insoluble at the present time is quite evident; it is indeed remarkable how a single molecule like BI_3 with only two subordinate valencies, so far as we know, can bind to itself so many molecules of another compound. There is without doubt an exercise of deep mutual *residual* attractions, perhaps mainly between boron and nitrogen.

The Amides and Imides of Boron.—In those compounds of the halides of boron with several molecules of ammonia it would seem quite possible to obtain amides and also imides by cleverly splitting off the halide of hydrogen. While no one appears to have attempted this by ordinary chemical means, still Joannis[1] seems to have obtained evidence through manometric measurements of the dissociation pressures of the reaction products of boro-halides and ammonia at various temperatures that such amides and imides may actually exist. However, none have been isolated by Joannis as definite, separate, chemical compounds and analyzed.

Joannis allowed dry ammonia gas to act on BBr_3, chilled to —10°, and obtained not an ammonical compound of BBr_3 (as indicated by the different experiments mentioned above), but a decomposition into the imide of boron and ammonium bromide. He claims that if the reaction is carried on at 0° the following equation represents the actual change:

$$2BBr_3 + 27NH_3 = 6(NH_4Br.3NH_3) + B_2(NH)_3$$

This formula demands 27 molecules of ammonia for 2 molecules of BBr_3 (Joannis' data are 27.04 and 27.40). He also states that if one allows the temperature to rise to 20°, NH_4Br, whose dissociation tension is higher than one atmosphere at this temperature, decomposes under atmospheric pressure, and there parts with 9 molecules of ammonia for one molecule of BCl_3. He obtained 8.77 and 8.93 experimentally.

In carrying out the experiments with ammonia and BCl_3 Joannis operated as follows: Into a tube (full of air)

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[1] Joannis: Comptes rendus, **135**, 1106 (1902).

there was introduced a known weight of BCl_3, contained in a small vial, which was opened by heating, and to this outer tube was puttied a lead tube leading to a chamber containing dry, liquefied ammonia. The ammonia vaporized and gradually penetrated to the BCl_3 maintained at a little below 0°. The presence of the air helped to moderate the action of the ammonia. The statement is made that under these conditions the imide of boron $B_2(NH)_3$ is obtained; however, if the temperature is lowered to —78° the amide of boron $B(NH_2)_3$ is obtained, which decomposes slowly when the temperature is elevated.

The volatility of BBr_3, which is notably less than that of the chloride, did not permit of exactly the same sort of procedure, nor use of so low a temperature as to yield the amide. The imide of boron decomposes in its turn with the disengagement of ammonia.

Borimide may also be prepared by heating the additive compound $B_2S_3.6NH_3$[1] to 115–120° in a stream of ammonia, when it decomposes, giving borimide and sulphur, the latter being removed by continued heating in ammonia. It is a white powder which is decomposed by water with evolution of heat, yielding ammonium borate. On heating, boron nitride and ammonia are formed. When shaken with liquid HCl, it forms a white hydrochloride $B_2(NH)_3.3HCl$.

Boro-Nitrogen Organic Compounds. (Action of BBr₃ on Amines and Nitriles).—The interesting boro-halide-ammonia compounds described in the preceding paragraphs very naturally suggest the possibility of preparing a whole series of organo-boron compounds by the reaction of a boro-halide with an organic-radicle derivative of ammonia, *i. e.*, in general with the chain and cyclic amines. However, a search of the literature reveals the fact that, while several compounds have been made by using halides of silicon, arsenic and phosphorus, almost none at all have been prepared with the halides of boron. I consequently decided to attempt the

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[1] Basarow: Comptes rendus, **78**, 1698, 4698 (1874).

preparation of a series of new amino-boron compounds of the most typical and characteristic classes.

As BBr_3 is more readily prepared and preserved than BI_3 and more easily handled at room temperature than BCl_3 it was chosen in this work. Furthermore, one would naturally expect the compounds formed with BBr_3 to present about average properties for the halide compounds in general on account of the position of bromine with respect to chlorine and iodine in the periodic system.

The typical amines selected include examples of primary, secondary and tertiary amines from both the aliphatic and the aromatic series, as well as some mixed and heterocyclic compounds of the pyridine class. For the sake of brevity and system in the discussion of the results the particular examples are classified in tabular form as shown in table following. In the first column are placed examples of primary aliphatic and aromatic amines, in the order of their complexity. The next column contains examples of secondary amines, the third tertiary amines and the fourth nitriles.

TABLE OF REPRESENTATIVE AMINES AND NITRILES

Primary	Secondary	Tertiary	Nitriles
$(CH_3)NH_2$ $(C_2H_5)NH_2$	$(CH_3)_2NH$	$(CH_3)_3N$ $(C_2H_5)_3N$	$(CH_3)CN$ $(C_2H_5)CN$
	$(C_3H_7)_2NH$		
i-$(C_5H_{11})NH_2$	i-$(C_5H_{11})_2NH$	C_5H_5N (Pyridine)	
	$C_5H_{10}\cdot NH$ (Piperidine)		
		C_9H_7N (Quinoline)	
$(Ph)NH_2$	$(Ph)_2NH$	$(Ph)(CH_3)_2N$	$(Ph)CN$ $Ph.CH_2.CN$

General Method of Procedure

Boron-tribromide, the reagent common to all the subsequently described reactions, was usually prepared by passing bromine over pure boron contained in a Jena combustion

tube. The details of methods for preparing boron-tribromide, and also descriptions of the most important physico-chemical properties of this substance, will appear in a separate publication in the near future. The samples used were always very carefully purified and appeared as colorless as water. They boiled at a constant temperature, usually about 91°.

In all cases the amines not gases at room temperature, were distilled from lime or sodium hydroxide immediately before using, the fraction from 3° below to 3° above the boiling point as given in chemical hand-books being taken whenever the boiling point was not constant. In all experiments it was always made certain that the amine was perfectly dry, the compound being allowed to stand over calcium chloride or lime for some time before using.

The liquid reagents were placed in graduated burettes protected with drying tubes at the top. Extensive preliminary work had shown that most of the compounds were almost insoluble in CCl_4 and CS_2. Of these two CCl_4 was usually the better medium, as the CS_2 in some cases gave slightly jelly-like masses, when used as a reaction medium. An Erlenmeyer flask of 250 cc capacity was provided with a two-hole stopper. Into one of these holes was inserted a small drying tube filled with $CaCl_2$ and into the other the delivery point of the burette. The reaction flask was partly submerged in ice water during the reaction whenever the heat evolution was great.

It was usually found most satisfactory to first dissolve the BBr_3 in about two to four times its own volume of CCl_4, then allow the amine, likewise dissolved in CCl_4, to drop into the former solution. However, in several instances pure BBr_3 was added drop by drop to the solution of the amine in CCl_4 until the reaction ceased. (Of course where the amine was a solid it had to be first dissolved in CCl_4.) The products in the different cases were compared with one another.

With the lower members of the series of aliphatic amines, of which about 30 percent alcoholic solutions were at hand, the solution of the amine was placed in a flask containing

NaOH and attached to a reflex condenser. A return tube led from the upper end of the condenser down into the reaction flask, which was usually a small distilling flask containing a solution of BBr_3 in CCl_4. The side tube of the distilling flask was provided with a Bunsen valve. On gently heating the flask containing the amine the latter was driven up the condenser as a gas and finally bubbled into BBr_3 solution where chemical action occurred.

   Treatment of the Precipitates.—Usually the precipitates initially formed were readily decomposed by moisture, and also dissociated at temperatures but little above room temperature; hence the necessity of an arrangement for handling the precipitate in such a manner as to eliminate both of these sources of disturbance if necessary. The apparatus depicted in Fig. 1 served the purpose admirably. After a reaction
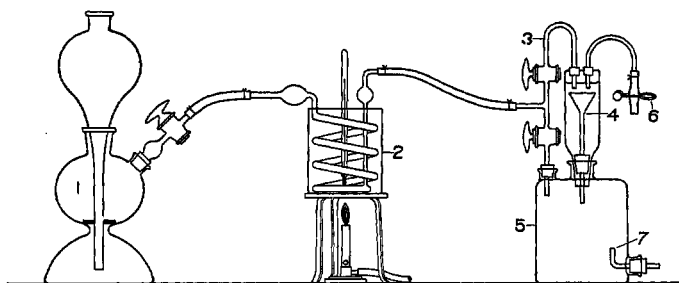
Apparatus for Filtering, Washing and Drying Boron Compounds

Fig. 1

was completed in the CCl_4 or CS_2, the precipitate was allowed to settle, the medium poured off and replaced with a fresh lot. After shaking and allowing to settle, the decantation was repeated several times. The precipitate was then placed in the funnel (4) provided with common filter paper and filtered rapidly by suction (when needed) applied at (7), dry hydrogen, or air being supplied to the apparatus after passing through a sulphuric acid dryer (2) which could be maintained at any common temperature. When sufficiently washed with CCl_4 or CS_2, or both, taken in at (6), the current

of gas was drawn through the material until quite dry. It was then transferred to small containers and kept in a desiccator.

Method of Analysis.—In all the following work it was deemed sufficient to determine quantitatively the nitrogen and halogen only. Boron is exceedingly difficult to determine directly with consistent results when working with different kinds of compounds, hence its presence in the substances was ascertained qualitatively only. The halogen was determined gravimetrically as AgBr, and the nitrogen was determined by the Kjeldahl method, P_2O_5 and H_2SO_4 being used for digestion.

Action of BBr_3 on Primary Amines

Methyl Amine and BBr_3.—The methyl amine obtained from a 30 percent alcoholic solution, prepared by Merck, was heated under a reflux condenser as described above and the gas passed directly into a CCl_4 solution of BBr_3 until no further precipitate was formed. Even on the slow introduction of the gas into the solution there was a very decided rise of temperature. The snow-white precipitate is practically insoluble in CCl_4. After being thoroughly washed and dried, there remains a very fine powder which is crispy under the spatula, but appears on examination under the microscope to be practically devoid of a definite crystalline form. When the substance is introduced into water there occurs a violent reaction, and complete solution of all of the products. In the air of the laboratory the material gradually dissociates, fumes of $B(OH)_3$ and HBr escaping. An analysis of the powder gave the following results:

	N	Br
Calculated	18.55	53.00
Found	18.47	53.20
Formula	$(CH_3)_2 : (NH)_2 : BBr$	

Ethyl Amine and BBr.—This next higher member of the series was prepared in exactly the same manner as described

above. However, the product obtained, in spite of much washing with CCl_4 was not quite so pure white. This product, like its next lower homologue, was quite amorphous. The following figures obtained from an analysis:

	N	Br
Calculated	6.52	74.45
Found	6.61	73.91
Formula	$C_2H_5.NH.BBr_2$	

Mono-Iso-Amyl-Amine and BBr_3.—A little over 5 grams of the dry amine, boiling between 95° and 98°, was dissolved in dry CCl_4. Approximately a molecular equivalent amount of BBr_3 was likewise dissolved in CCl_4, and then run drop by drop into the amine solution, cooled by ice water on the outside and always shaken after each addition. Though the reaction was apparently not violent, still, much heat was evolved. At first, considerable of the precipitate appears to partially dissolve in the CCl_4 warmed up by the heat of the reaction, giving a yellow, oily solution rising to the upper portion of the CCl_4 medium, and growing more of an orange color until $1/_2$ mol of BBr_3 has been added; but from this point on, there forms a white, voluminous precipitate until one mol of amine has been added.

Examined under the compound microscope, the precipitate appears perfectly amorphous and exceedingly fine-grained, in fact, the grains were not as large as butter-fat globules with which they were directly compared. After several decantations and washings and then drying in the apparatus already described, the material may be handled with considerable impunity on a porcelain plate in the laboratory. It rubs down perfectly smooth under the spatula, does not dissociate very rapidly below 40°, turns light yellow in sunlight, and reacts with water, especially when alkaline. with NaOH, with considerable energy. If warmed up rapidly on a piece of platinum it appears to melt and decompose at once. It will ignite and burn furiously, coloring the flame intensely deep green.

ANALYSIS

	N	Br
Calculated	4.14	70.81
Found	4.16	70.73
Formula	$(C_5H_{11}).NH_2.BBr_3$	

The composition of the oily product first formed is probably $[(C_5H_{11})NH_2]_2BBr$, though, thus far no attempts have been made to purify and analyze the product.
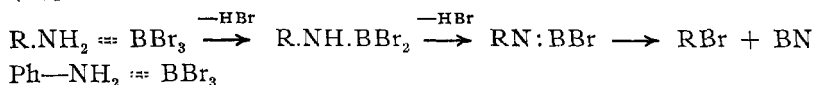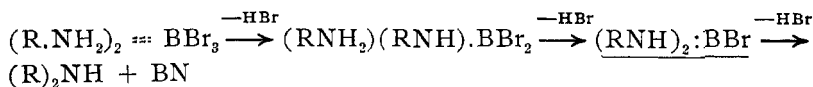
Mono-Phenyl-Amine (Aniline) and BBr₃.—The mode of procedure for the preparation of a compound of these two substances was in all details the same as for the amyl-amine compound. The best grade of aniline was used and twice distilled immediately before use, an almost perfectly colorless liquid being obtained. No matter whether the aniline is added drop by drop to the BBr₃ solution, or the BBr₃ to the aniline, if the reaction is too fast, a deep yellow precipitate results at first. But if the addition is slow and the vessel well cooled, there is obtained a perfectly white, amorphous precipitate. After being washed and dried and taken into air it fumes strongly, and moisture rapidly converts it into boric acid and aniline hydrobromide. In alkaline solution aniline oil appears. An analysis of the product obtained (quickly dried and prevented as much as possible from decomposing) gave the following results:

	N	Br
Calculated	4.07	69.80
Found	4.03	69.92
Formula	$(C_6H_5).NH_2BBr_3$	

Conclusions Regarding the Nature of the Reaction of a Primary Amine with BBr₃

Fairly general conclusions may be drawn from a survey of the formulae of the above described compounds as to the formula of the compound that may be expected when any primary amine reacts with BBr₃. It will be noted that in the case of the lower members of the series, the BBr₃ reacts with more than one molecule of amine, but also splits off hydro-

bromic acid very readily to form a compound which is not so rich in halogen and more stable. Higher homologues have a greater tendency to combine with the BBr_3 molecule for molecule, and less tendency to part with halogen. Compounds with five or more carbon atoms appear to form addition products which are quite stable at room temperature and pressure if moisture is absent. We may represent the foregoing facts very well by the following series of formulae:

$$(R.NH_2)_2 \rightleftharpoons BBr_3 \xrightarrow{-HBr} (RNH_2)(RNH).BBr_2 \xrightarrow{-HBr} \underline{(RNH)_2:BBr} \xrightarrow{-HBr}$$
$$(R)_2NH + BN$$

$$R.NH_2 \rightleftharpoons BBr_3 \xrightarrow{-HBr} R.NH.BBr_2 \xrightarrow{-HBr} RN:BBr \longrightarrow RBr + BN$$
$$Ph—NH_2 \rightleftharpoons BBr_3$$

R = Alkyl group.
Ph = Phenyl group.

From these formulae and series it is evident how a great number of products are possible. The possibility of the formation of any particular type depends on the place of the amine in the homologous series and the conditions of the experiment. The formulae underscored represent types which have actually been formed. The writer hopes to be able to follow out by experiment these series of possible products to the final halogenless decomposition products.

Action of BBr₃ on Secondary Amines.

Di-Methyl-Amine and BBr₃.—As this substance is a gas under ordinary laboratory conditions, its alcoholic solution had to be used and the amine distilled off by heat as in the case of mono-methyl-amine already described. Here too, the precipitate formed from the reaction of di-methyl-amine and BBr_3 appears so much like that from mono-ethyl-amine that the same description will answer for both. The former is slightly more stable in presence of moisture, and its dissociation does not appear to be so great under common conditions. The white, dry material readily reacts with water, alcohol and ether.

ANALYSIS

	N	Br
Calculated	6.52	74.25
Found	6.57	74.31
Formula	$(CH_3)_2 = N - BBr_2$	

Di-Propyl-Amine and BBr₃.—A quantity of di-propyl-amine, boiling between 108° and 111° was dissolved in CCl_4. Into this solution was dropped a solution of BBr_3 in the same solvent. The first half of the BBr_3 added (about $1/_2$ mol) formed an oily, light layer above the main portion of the CCl_4 solution, in which it seemed but slightly soluble. Further addition, however, brough down a white precipitate and when a trifle more than one molecule was added, there was only a suspension of a fine white precipitate in the reaction medium, the latter being discolored but slightly. This precipitate, when washed and dried, like the previous ones, proved to be a soft, pure white powder of no definite crystalline form. Much heat is evolved during the formation of the compound and the reaction flask must be well cooled. The product isolated is only fairly stable at ordinary temperature if kept from moisture.

ANALYSIS

	N	Br
Found	5.19	59.18
Calculated	5.108	59.22
Formula	$(C_3H_7)_2: N.BBr_2$	

Di-Amyl-Amine and BBr₃.—Not unlike the action of BBr_3 on dipropyl-amine is its action on di-iso-amyl-amine, only here the oily layer which is first formed appears to become almost gelatinous on continued addition of the BBr_3. But when a whole molecular equivalent quantity has been added with constant shaking, there forms a creamy to granular precipitate which is exceedingly hard to filter off and wash. Much better results are obtained when the precipitate is allowed to stand in the reaction medium two or three days after the reaction before attempting to separate it. The product dissolves to some extent in CCl_4 and may be slowly

crystallized from the same. The pure white substance reacts with water, yielding di-iso-amyl-amine-hydrobromide and boric acid. At ordinary room temperature it readily yields a hydrobromic acid and boric acid fumes.

<div align="center">ANALYSIS</div>

	N	Br
Calculated	4.28	48.81
Found	4.16	48.65
Formula	$(C_5H_{11})_2.N : BBr_2$	

Piperidine and BBr₃.—In connection with the investigation of the action of BBr_3 on the secondary amines, piperidine seems of especial interest. We must regard this compound as a type of secondary amine, for it has the group: N.H, only here the two nitrogen bonds are satisfied by carbon bonds of the same nucleus, thus forming a closed figure instead of an open one as is the case in the ordinary secondary amine.

The samples of piperidine used for different trials were all taken from an ounce bottle of material by Merck. The substance boiled sharply at 105.5°. After drying and redistilling the piperidine, as in all preceding work, it was dissolved in CCl_4, which was also perfectly dry and pure. In some trials the piperidine was added to a slight excess of BBr_3 and in others BBr_3 was added to an excess of piperidine, but in either case the same final product was obtained. The reaction takes place with great violence, much greater than with ordinary secondary amines and there is a great disengagement of heat, necessitating careful cooling of the reaction system, even when the materials are brought together very slowly, in order to ensure a good product. Such precautions give a very light yellow precipitate, which can be washed thoroughly with CCl_4 and dried in a current of dry air or hydrogen. Under ordinary conditions the product gives off abundant fumes of HBr, rapidly undergoing transformation into a stable product which dissolves readily in several organic solvents, apparently without decomposition, yielding greenish yellow solutions of fluorescing properties.

This latter substance is best obtained from the initial precipitate by spreading it out in a thin layer in a desiccator containing fused calcium chloride and solid sodium hydroxide. Analysis of the initial product gave the following figures:

	N	Br
Calculated	8.31	47.34
Found	8.37	47.21
Formula	$3(C_5H_{10}NH) = BBr_3$	

Analysis of second product obtained by splitting off HBr:

	N	Br
Calculated	9.88	37.49
Found	9.83	37.54
Formula	$C_5H_{10}N.BBr_2 : (C_5H_{10}NH)_2$	

Di-Phenyl-Amine and BBr_3.—Seven grams of di-phenyl-amine prepared by Merck, melting at 52.0° and boiling at 311° were dissolved in CCl_4 and to the solution was added a solution of BBr_3. A voluminous, snow-white precipitate forms instantly with only moderate evolution of heat. As compared with the other compounds of the secondary amines this product is much more stable under ordinary room conditions. An analysis of the substance gave the following results:

	N	Br
Calculated	5.54	31.60
Found	5.59	31.57
Formula	$((Ph)_2NH)_3 : BBr_3$	

General Type of Reaction between Secondary Amine and BBr_3.—A review of the meager number of compounds of the three different types of secondary amines at hand would appear to indicate that the aliphatic amine compounds are generally the simplest—molecule of amine for molecule of brom-boride—and that the lone hydrogen atom quickly drops off with a halogen atom, leaving a compound which is more stable under ordinary conditions. If the series were followed to its termination BN would probably be the final product.

Not so simple, however, is the case of piperidine and other cyclic aromatic amines. Here as high as three molecules of amine will unite with one molecule of BBr$_3$, and still the new substance will not split off HBr so readily that they cannot be handled in dry air at ordinary temperature and pressure, though they decompose readily on slight rise of temperature. We see in this case that the gradual splitting off of HBr would not be so likely to yield BN.

$$\begin{array}{ccccc}
& \xrightarrow{-HBr} & & \xrightarrow{-RBr} & & \xrightarrow{-RBr} \\
(R)_2NH = BBr_3 & \longrightarrow & (R)_2N{\equiv}BBr_2 & \longrightarrow & R.N{\equiv}BBr & \longrightarrow & BN
\end{array}$$

$$\begin{array}{ccc}
\xrightarrow{-HBr} & & \xrightarrow{-HBr} \\
(Ph_2NH)_3 = BBr_3 \longrightarrow (Ph_2NH)_2(Ph_2N){\equiv}BBr_2 \longrightarrow (Ph_2NH)
\end{array}$$

$$\xrightarrow{-HBr}$$
$$(Ph_2N)_2{\equiv}BBr \longrightarrow (PH_2N)_3{\equiv}B$$
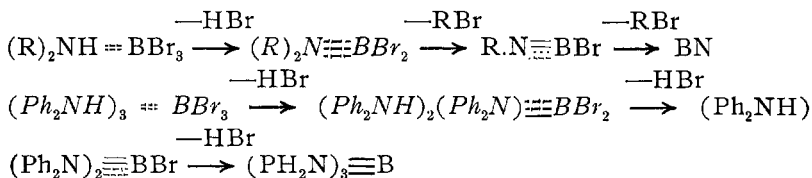
Action of BBr$_3$ on Tertiary Amines

Trimethyl Amine and BBr$_3$.—The trimethyl amine was driven from an alcoholic solution in the manner already described and passed into a small flask containing BBr$_3$ and CCl$_4$. When the gaseous amine reached the flask, action took place immediately with evolution of heat, but only a slight precipitate formed and copious white fumes were evolved from the liquid. It was quite apparent that a general decomposition was going on and perhaps a dissolution of the initial product. No success was met with in attempting to crystallize out a definite compound; the amount of precipitate formed was small, and qualitative tests showed that it contained no halogen.

Tri-Ethyl-Amine and BBr$_3$.—A considerable quantity of tri-ethyl-amine which boiled at 87–90° was on hand. It was therefore determined, in view of the above results obtained with tri-methyl amine, to investigate its action with BBr$_3$. A CCl$_4$ solution of BBr$_3$ was prepared, and into this while well cooled there was slowly dropped a dilute solution of the amine in CCl$_4$. Heat was evolved, and at first a white precipitate formed which soon disappeared because of its solubility in warm CCl$_4$. On cooling the solution, fine crystals were deposited. These formed during the rapid cooling of

the liquid. Under the microscope they appeared as long, slender prisms, readily forming large, irregular, translucent masses. When, however, a CCl_4 solution was allowed to stand for a long time, bunches of "cotton-batting-like" crystals formed and floated about in the liquid. Examination of these crystals under a microscope showed them to be exceedingly thin, long needles; in fact, many were observed whose length was at least 200 times the diameter. After washing and drying, this substance was found to be relatively unstable, especially at temperatures from 50° up. It is readily, though not violently decomposed by water.

ANALYSIS

	N	Br
Calculated	3.98	68.20
Found	3.47	67.88
Formula	$(C_2H_5)_3N.BBr_3$	

Di-Methyl-Aniline and BBr$_3$.—One of the most important, and most interesting of the tertiary amines is di-methyl-amine. This substance also reacts readily with the boride of bromine, with considerable evolution of heat, forming masses of small, translucent crystals which are somewhat soluble in CCl_4. The masses of partially crystalline material appear under the microscope much like camphor gum. It is difficult to handle the substance in the air, for as soon as the CCl_4 evaporates off, the residue becomes hygroscopic and decomposes; hence, in drying the precipitate, the air must first be passed through concentrated H_2SO_4. In cold water, the decomposition of this unstable compound proceeds rapidly though not violently, as one might expect, forming an oil, and a white, insoluble material, and also a small quantity of gas. An analysis of the camphor-like substance gave the following results:

	N	Br
Calculated	3.76	64.44
Found	3.80	63.78
Formula	$(CH_3)_2NBBr_3.C_6H_5$	

Some of the above camphor-like substance was placed with fused NaOH and $CaCl_2$ in a desiccator and kept in the vicinity of a common steam radiator until no more gases came off. The product was then washed with CCl_4, dried and analyzed. The sample for analysis was introduced into hot alkali solution where it was quickly decomposed with the formation of a white, insoluble powder. The latter was filtered off in a Gooch crucible and weighed. It showed every property of BN. The halogen content of a sample and also the nitrogen were determined as usual.

ANALYSIS

	N	Br	BN[1]
Calculated	5.04	57.50	9.03
Found	4.96	57.13	8.89
Formula	$(CH_3) - N = (C_6H_5) - (BBr_2)$		

Pyridine and Quinoline

The strongly basic organic compounds of the hetero-cyclic nitrogen-carbon type, of which pyridine is regarded as the prime representative may be regarded as tertiary-amines, or ammonia derivatives, all of whose hydrogen atoms have been replaced, the nitrogen bonds being satisfied by the three different carbon atoms. However, though each carbon atom, satisfying nitrogen in the ordinary tertiary amines, is in a separate nucleus or radicle, in pyridine, on the other hand, all three carbon atoms are in the same complex (assuming the centric formula for pyridine).

Pyridine and BBr_3.—Boron tribromide and pyridine dissolved in CCl_4 combine with great energy and evolution of heat. The precipitate is snow-white, light and perfectly amorphous. After driving off the CCl_4, it may be worked under the spatula in the open air for some time before decomposing appreciably, but the dissociation tension increases very rapidly as the temperature rises. At 120° the compound turns brown and crispy. Analysis of the material gave the following figures:

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[1] This is probably the first time boron has been determined directly gravimetrically in the form of BN.

	N	Br
Calculated	4.25	72.64
Found	4.29	71.96
Formula	$(C_5H_5N) = BBr_3$	

If, however, this compound is allowed to remain in a desiccator containing solid NaOH and $CaCl_2$, a powder more stable under ordinary conditions is obtained, which after being washed with CCl_4, yields the following results upon analysis:

	N	Br
Calculated	5.62	64.20
Found	5.57	64.75
Formula	$\overline{(C_5H_4)N}.BBr_2$	

Quinoline and BBr_3.—As with pyridine so with quinoline and BBr_3, reaction occurs readily, though apparently there is not quite so much heat evolved. Nevertheless, the analogous product is much more stable under laboratory conditions of temperature and pressure; in fact it may be handled with impunity, and worked on a porcelain plate with a spatula, without fuming to any extent. It also decomposes relatively slowly in cold alkaline solution. This pure white initial product, according to analysis, has the formula $(C_9H_7N) : BBr_3$.
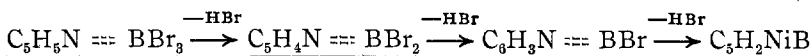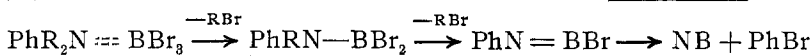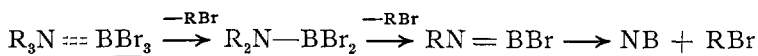
	N	Br
Calculated	3.69	63.03
Found	3.71	63.20

Correlation of Tertiary Amine-Brom-Boride Compounds

Facts thus far accumulated from work with the four kinds of tertiary amines would appear to show that there is usually first formed a simple addition-product. In the case of quinoline this compound is very permanent under ordinary working conditions, thus pointing to the general conclusion that the larger the aromatic nucleus the more stable these addition products are. Alkyl, or mixed alkyl-phenyl-amine addition compounds are much less stable and have a great

tendency to split off alkyl halide progressively to substances more permanent—even going as far as $B \equiv N$.

Pyridine offers an interesting fact in that its addition compound, initially formed with BBr_3, very readily splits off HBr. The hydrogen in this case must be detached from a carbon atom, thus making it evident that the boron atom becomes attached directly to carbon as well as the nitrogen.

$$R_3N \doteq BBr_3 \xrightarrow{-RBr} R_2N-BBr_2 \xrightarrow{-RBr} RN = BBr \longrightarrow \underline{NB + RBr}$$

$$\underline{PhR_2N \doteq BBr_3} \xrightarrow{-RBr} \underline{PhRN-BBr_2} \xrightarrow{-RBr} \underline{PhN = BBr} \longrightarrow \underline{NB + PhBr}$$

$$\underline{C_5H_5N \doteq BBr_3} \xrightarrow{-HBr} \underline{C_5H_4N \doteq BBr_2} \xrightarrow{-HBr} \underline{C_5H_3N \doteq BBr} \xrightarrow{-HBr} \underline{C_5H_2NiB}$$

Action of BBr_3 on Nitriles

Nitriles, or organic compounds which may be regarded as esters of hydrocyanic acid of the structural formula $HC - \equiv N$, are known to act basic in the presence of various acids, including HCl and even H_2S, forming salts of the formulae $R.CN.HCl$ and $R.CN.H_2S$[1] respectively. We see here manifested a weak basic property, and perhaps the occurrence of the pentavalence of the nitrogen atom. Indeed a not exceedingly farfetched view is to regard a nitrile as ammonia all of whose hydrogen atoms have been displaced, the nitrogen bonds being satisfied by one and the same carbon atom instead of by three distinct carbon atoms as in the case of the tertiary amines and pyridine bases. On this basis we should expect to find in the nitrile some of the properties characteristic of amines in general.

Hydrocyanic Acid and BCl_3.—A review of the literature reveals the fact that Martius[2] attempted to bring about a reaction of HCN and BCl_3 by passing the former as a dry gas into well cooled liquid BCl_3. He states that at first a solid substance forms, but that at room temperature this soon decomposes yielding a brown liquid. No analysis is given but it is assumed that the solid first formed was $HCN.BBCl_3$.

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[1] Comptes rendus, **63**, 923 (1866).

[2] Liebig's Ann., **109**, 80 (1859).

Chloro-Cyanogen and BCl₃.—Martius met with much more success in conducting chloro-cyanogen in well cooled liquid boron-trichloride. The chloro-cyanogen gas is absorbed readily, with great development of heat and the formation of a white, crystalline precipitate, consisting of small prisms. The substance smells of chloro-cyanogen gas, and fumes somewhat in damp air. In water it is decomposed instantly, forming chloro-cyanogen gas, boric acid and hydrochloric acid. Similar action occurs in absolute alcohol. At higher temperature it sublimes with partial decomposition, leaving behind a white substance.

0.5736 gram of the substance, analyzed for halogen in the chlorocyanogen gas gave 1.8505 gram AgCl, representing 79.7 percent chlorine.

0.685 gram of substance analyzed for the halogen bound to the boron gave 1.7032 AgCl, representing 61.3 percent chlorine.

The formula of the compound is then $BCl_3.ClCN$.

Gautier[1] claims to have formed a compound of ethyl-cyanide and BCl_3, but, as no details are given and no analytical results, I determined to prepare, if possible, several typical alkyl and aromatic cyanide compounds with BBr_3 as a part of the scheme already outlined.

Methyl-Cyanide and BBr₃.—A quantity of methyl-cyanide was redistilled several times after being dried. The fraction taken which came over between 80° and 82°, as with amines so in this case a known quantity was dissolved in CCl_4, and an excess of BBr_3 in the same solvent was added gradually while the reaction vessel was cooled. A beautiful, flaky, snow-white precipitate separated. The substance is slightly soluble in CCl_4 and may be crystallized slowly from the same. At low temperature the dry powder is quite stable, but at 30° the dissociation proceeds rapidly. In water it is quickly decomposed. Upon analysis this compound gave the following results:

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[1] Comptes rendus, **63,** 923 (1866).

	N	Br
Calculated	4.81	82.00
Found	4.86	81.72
Formula	$CH_3CN : BBr_3$	

Ethyl-Cyanide and BBr₃.—The compound formed between these two substances is in every way similar to the preceding, except that it is less slowly acted upon by moisture, and does not dissociate at so low a temperature. Much heat is developed during the reaction.

ANALYSIS

	N	Br
Calculated	4.58	78.21
Found	4.57	78.23
Formula	$(C_2H_5)CN : BBr_3$	

Phenyl-Cyanide and BBr₃.—The phenyl-cyanide used was a sample prepared in my laboratory. It boiled sharply at 189°. When treated with BBr₃ it yielded a substance which was quite soluble in CCl₄, but good. Crystals were obtained with some difficulty. The compound is pure white powder when dry, attracts moisture readily, and decomposes quickly in H_2O.

ANALYSIS

	N	Br
Calculated	3.96	67.62
Found	3.87	67.57
Formula	$(C_6H_5)CN : BBr_3$	

Benzyl-Cyanide and BBr₃.—This homologue of phenyl-cyanide is of interest in connection with compounds of nitriles with boro-halides, as a methylene group stands between the (C_6H_5) and (CN), and thus we might expect the substance to have properties lying between those of the methyl cyanide and phenyl cyanide. Like with the phenyl compound the reaction proceeds with the development of comparatively little heat. A sample of the product taken directly from the reaction medium and examined under the microscope showed an almost amorphous, translucent mass, although around the edges of the field there were found a few clusters of small
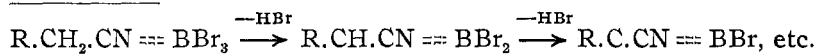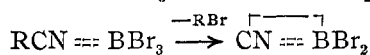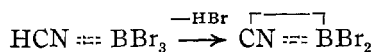
needles. Later it was observed that the dried material would absorb considerable CCl_4, and dissolve to some extent in it; but it was difficult to get well formed crystals from the solution. Carbon bisulphide was even a worse solvent in some respects. When purified as far as feasible by the use of both CS_2 and CCl_4, the final product still had a faint, yellow color, which is probably characteristic. It fumes in the air and may be melted down, but not without some decomposition.

ANALYSIS

	N	Br
Calculated	3.81	65.00
Found	3.73	64.81
Formula	$(C_6H_5.CH_2)CN : BBr_3$	

General Type of Reaction between a Nitrile and BBr_3

Nitriles, like tertiary amines, form simple addition products with boro-halides. But the addition products with the nitriles do not split off HBr nor yield BN as readily under the *same experimental conditions* as the addition products with amines. Carbon and nitrogen are known to form a powerful union. Boron and nitrogen also form an exceedingly stable compound. In these compounds there probably is a combination of these three elements in which they are held together by mutual powerful affinities and which makes for the stability of the molecule as a whole. However, at fairly high temperatures, it is likely that BN would be formed, especially in view of the general method of forming BN as given in the opening paragraphs of this work.

The following formulae indicate the typical reactions between nitriles and boron bromide:

$$HCN \equiv BBr_3 \xrightarrow{-HBr} \overline{CN \equiv BBr_2}$$

$$RCN \equiv BBr_3 \xrightarrow{-RBr} \overline{CN \equiv BBr_2}$$

$$R.CH_2.CN \equiv BBr_3 \xrightarrow{-HBr} R.CH.CN \equiv BBr_2 \xrightarrow{-HBr} R.C.CN \equiv BBr, \text{ etc.}$$

In addition to the general conclusions already stated, it may be added that in carrying on the preceding work the

great mutual attraction of boron and nitrogen, and the fact that either element may function as a trivalent or pentavalent element, have been kept steadily in mind as fundamental and guiding facts. And all the compounds of nitrogen used in this work may be regarded as derivatives of ammonia.

As might be expected, most of these new organic boro-nitrogen compounds decompose instead of melting when heated in a melting point tube. Sublimates also form in several instances. In fact, they closely resemble ammonium compounds in many ways. As a rule the compounds of the nitriles with BBr_3 are far more stable toward heat than those of the amines with BBr_3. Some of these may be heated to nearly 200° before decomposing. Of the amine products those of pyridine and quinoline are the most stable.

The various graphic formulae given were determined, not alone from valence considerations and the results of the analyses of the compounds, but also from the action' of the compounds toward weakly alkaline solutions and various reagents. In the case of many of the products initially formed (least stable) the relative proportions of BBr_3 and the amine were roughly determined from readings of the burette from which a solution of one of the reagents was dropped into a solution containing a known amount of the other until a precipitate no longer formed.

The actions of a number of the more stable compounds prepared upon about twenty common organic solvents were noted. For the sake of brevity in discussing the results these solvents may be classified as: those containing oxygen; hydrocarbons; and halogen derivatives of hydrocarbons. As representatives of the first group were selected absolute alcohol, amyl alcohol, acetaldehyde (para), acetone, acetic ester, amyl acetate, ether, glacial acetic acid, nitrobenzene. Representatives of the second group were petroleum ether, benzol, toluol, xylol. In the third class, chloroform, carbon tetrachloride, bromoform, ethyl bromide and phenyl bromide. Each of the boro-nitrogen compounds studied showed, of course, its specific and characteristic action toward any

particular solvent, but still, certain fairly general rules may be drawn from the data at hand. Both the amine and nitrile compounds, as a rule, react violently with absolute alcohol, acetaldehyde, and acetic acid. Boric acid was formed in all cases, and alkyl bromide, bromaldehyde and acetyl bromide in alcohol, aldehyde, and acetic acid respectively. Fumes of hydrobromic acid were often evolved. The action of both amine and nitrile compounds upon acetone, the esters, and ether, was usually far less violent than in the hydroxyl solvents. Indeed, in several cases the compounds appear to merely dissolve, and after evaporating spontaneously, crystalline products appear which contain carbon and boron....... Almost without an exception both the nitrile and amine compounds were found quite insoluble in the hydrocarbons. But if the compound under test was left in contact with the hydrocarbon for several hours, it became colored red to brown, and the solution assumed a "bromine color." The action was enhanced by sunlight, and was most noticeable in benzol, then petroleum ether, then toluol and least apparent in xylol. However, the action was sufficient in all cases to discourage the use of the hydrocarbons as media for precipitations and crystallizations.......The third group gave by far the most satisfactory results as solvents, or media for carrying out precipitations. In no case could it be said that the boro-nitrogen compound was copiously soluble in any one of the solvents, yet in a few instances crystallization could be carried out without decomposition taking place. Carbon tetrachloride and carbon tetrabromide are the most satisfactory media for precipitations, as the solubility is usually slight at room temperature and no reactions occur with these solvents. But chloroform and bromoform presented complications. At first they are apparently good solvents for several of the compounds, but after a few hours or days discoloration sets in and a gel separates. Perhaps the lone hydrogen atom in these solvents has a tendency to enter chemical reaction with the halogen of the boro-nitrogen compounds.

To Dr. L. Kahlenberg is due my most sincere thanks for the hearty encouragement which he has given me ever since the inception of my work on the chemistry of boron. He has aided me, not only by giving freely valuable suggestions, but also by supplying me with many samples of expensive amines and nitriles.