

Summary

The apparent error in the reported melting points for monochloroacetylurea is clarified, and the melting point for monobromoacetylurea is reported.

Dichloro-, dibromo-, diiodo-, and triiodo-acetylureas have been prepared, thus completing the series of halogenoacetyl-monosubstituted ureas.

SEATTLE, WASH.

RECEIVED MARCH 20, 1939

[CONTRIBUTION NO. 54 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

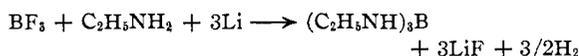
Organoboron-nitrogen Compounds. I. The Reaction of Boron Chloride with Aniline

BY REUBEN G. JONES AND CORLISS R. KINNEY

Two distinct types of organoboron-nitrogen compounds are known. One of these is the addition type in which the boron atom of a boron compound is attracted by the unshared pair of electrons belonging to a nitrogen atom in a molecule of ammonia, an amine, or a nitrile: $R_3B:NR_3$. Many of these compounds are surprisingly unreactive and thermally stable. The second type of boron-nitrogen linkage is the true covalent bond, known examples of which are very rare: $(R_2N)_3B$. The first of these was obtained by A. R. Johnson¹ in 1912, who found that boron bromide would form not only addition compounds with amines but also substitution products.



Recently, Kraus and Brown² have prepared the trisubstitution product by means of the reaction



Considering the work of Johnson and the reactivity of boron chloride and bromide, it appeared likely that the substituted amides of boric acid could be made directly from the halide and the various amines. Furthermore, Rideal³ in 1889 treated boron chloride with aniline and obtained a substance which he thought was $C_6H_5N=BCl$. This compound would be particularly interesting not only because of the possibilities for further synthesis but also because of the doubly bonded boron atom. With these points in view the study of the reaction of boron halides with amines was begun and in the present paper the work with aniline and boron chloride is presented.

The reaction of aniline with boron chloride is violent and it is desirable to moderate the reaction in some way. The first method tried was to depress the reactivity of the halide by converting it into an addition compound with a

tertiary amine. Upon treating dimethylaniline with boron chloride, the addition compound to be expected was obtained. This compound, however, did not yield the products desired when treated with aniline and the method was abandoned. The reaction rate is also lowered very markedly by using aniline hydrochloride instead of aniline; in fact, the reaction is too slow to be practicable. Thus, in one experiment, aniline hydrochloride and boron chloride were allowed to react at room temperature for a period of over three months. At intervals of two weeks the tube was opened and the hydrogen chloride produced allowed to escape, showing that a reaction was progressing. This procedure, while of interest in studying the reaction, also was abandoned. By far the best method is to dilute the reactants with an inert solvent such as benzene. Under these conditions no trouble was experienced in obtaining the addition compound of aniline and boron chloride and from that several other related derivatives. The reactivity of the addition compound was considerably greater and the thermal stability less than has been reported for many similar compounds. Thus, the substance reacts vigorously with water and readily with aniline, especially when heated in benzene, and, when heated alone in boiling benzene, decomposes into aniline and boron chloride.

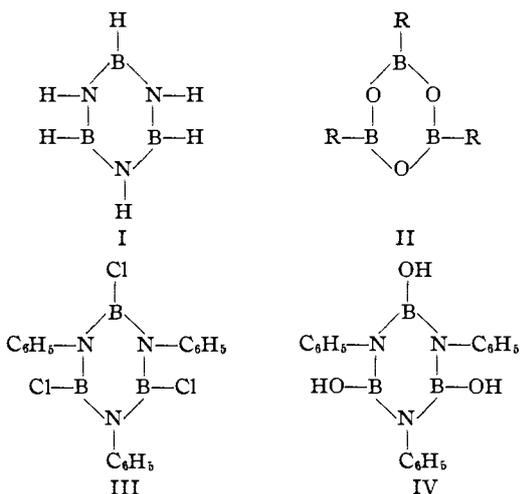
Using the addition compound as a starting point, several substitution products were obtained by further reaction with aniline. The analysis of the simplest of these corresponded to that of the primary substitution product plus a molecule of aniline, $C_6H_5NHBCl_2 \cdot NH_2C_6H_5$. Unfortunately, this compound was isolated in very small yields only and was not readily purified. However, no difficulty was experienced in obtaining the compound having the composition reported by Rideal,³ and in good yields. Upon determining the molecular weight, the compound

(1) A. R. Johnson, *J. Phys. Chem.*, **16**, 1 (1912).

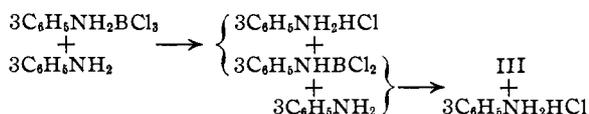
(2) Kraus and Brown, *THIS JOURNAL*, **52**, 4414 (1930).

(3) Rideal, *Ber.*, **22**, 992 (1889).

was found to be trimolecular. By analogy with Stock and Pohland's⁴ formula for $B_3N_3H_6$ and the structure for the organoboron oxides,⁵ the structure III below would be expected.



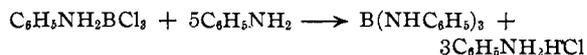
However, there are some differences in properties to be considered. The hydrogen derivative I is a low boiling liquid while the others are fairly high melting solids. The hydrogen compound reacts with water to form a trihydrate which, when treated with dry hydrogen chloride, evolves hydrogen and three chlorine atoms replace the hydrogens attached to the boron atoms. Compound III also reacts with water, but does not form a hydrate. Instead, the chlorine atoms are replaced by hydroxyl groups, giving the corresponding trihydroxide which is indicated by formula IV. This compound has weakly acidic properties and is easily hydrolyzed to boric acid and aniline. A sample of the trichloride III, which may be called triphenyltrichlorotriboronnitride for the present, has been sent to Mr. Stosick at the California Institute of Technology, working under the direction of Professor Pauling, for X-ray structural examination. The formation of this compound may be indicated by the following equations



By heating the addition compound of aniline and boron chloride with an excess of aniline, the trisubstitution product $B(NHC_6H_5)_3$ was obtained and in excellent yield.

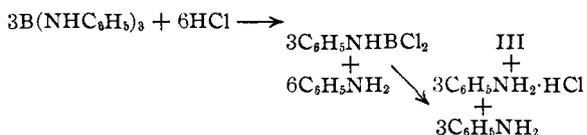
(4) Stock and Pohland, *Ber.*, **59B**, 2215 (1926).

(5) Kinney and Pontz, *THIS JOURNAL*, **58**, 197 (1936).



This substance should not be confused with Chaudhuri's boranilide⁶ which was shown to be the double salt of aniline and zinc chloride. The compound is easily hydrolyzed to boric acid and aniline, and, consequently, may be called boric trianilide. Kraus and Brown² named the ethyl analog mentioned in the introduction, $B(NHC_2H_5)_3$ tertiary boron ethylimine. This name does not indicate the relationship which these compounds bear to boric acid; and, therefore, it seems better to name them as derivatives of ortho boric amide, $B(NH_2)_3$. On that basis, the triethyl derivative would be called (ortho) boric triethylamide.

Since boric trianilide is easily hydrolyzed by water, it might be expected that the substance would be attacked by hydrogen chloride. Actually, it is attacked and triphenyltrichlorotriboronnitride results. Since the same compound is formed from boric trianilide as well as from the addition compound and aniline, it appears likely that the same intermediate is formed in each case. If this is true, then the following equations would account for the formation of triphenyltrichlorotriboron-nitride from boric trianilide and hydrogen chloride.



Considering the easily disturbed equilibrium which exists between the esters of carboxylic acids and the amides, it appeared possible that boric anilides could be made from esters of boric acid and aniline. However, no such reaction occurred between ethyl borate and aniline, even at the boiling point. Also, the possibility that boric trianilide might form an aniline addition compound was investigated with negative results.

Experimental Part

The anilides described in this paper were analyzed by modifying the usual procedure slightly because of the interference of the aniline in titrating both hydrochloric and boric acids. The compounds were first hydrolyzed. Those which were not hydrolyzed readily in pure water were dissolved in a few ml. of methanol and then diluted with water. The total acid content was then titrated to a phenolphthalein end-point with mannitol to strengthen the boric acid. The hydrochloric acid was determined by

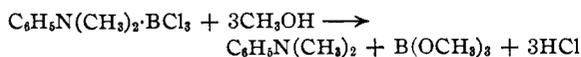
(6) Kinney and Pontz, *ibid.*, **57**, 1128 (1935).

a Volhard analysis for chloride ion in the neutralized solution. From the total acid value and the amount of hydrochloric acid obtained, the boric acid was determined by difference. From the boric acid concentration the per cent. boron was calculated and from the chloride ion value the per cent. of chlorine.

$C_6H_5N(CH_3)_2 \cdot BCl_3$, **The Addition Compound of Dimethylaniline and Boron Chloride.**—Twenty grams of pure boron chloride was dissolved in 30 g. of pure sodium-dried benzene and cooled to -15° . To this solution was added slowly, from a dropping funnel, 16.5 g. of freshly distilled dimethylaniline (20% less than the theoretical equivalent) dissolved in 30 g. of benzene. The solution was stirred constantly and about fifteen minutes taken for the addition. The reaction was vigorous, but not violent. The addition compound separated from the benzene solution and settled to the bottom. After standing for twelve hours at room temperature, the mixture was cooled to 0° and filtered through a Büchner funnel fitted with a stopper carrying a tube connected with a supply of dry air. The residue was washed four times with dry benzene and dried in the current of dry air. This colorless compound was fairly pure as the analysis below indicates. When heated in an open melting point tube it softened at $125-130^\circ$, but did not melt completely until 146° was reached. On cooling, the melt began to crystallize at $144-145^\circ$. When the solidified material was heated a second time similar results were obtained, indicating that no decomposition occurred.

Anal. Calcd. for $C_8H_{11}NBCl_3$: B, 4.53; Cl, 44.69. Found: B, 4.40; Cl, 44.45.

The substance appears to be stable when stored under dry benzene or over phosphorus pentoxide, but in contact with the air of the laboratory it rapidly loses its crystalline character and evolves hydrogen chloride. The substance does not dissolve in cold water, even on standing for three days, or in hot water when heated for a short time, apparently because of the formation of an insoluble coating. However, if benzene is present, the substance will react with water. It is readily soluble in methanol, probably reacting according to the equation



The compound is moderately soluble in benzene and carbon tetrachloride. It appears to react with aniline because heat is evolved and a white precipitate is formed which is undoubtedly a mixture of aniline and dimethylaniline hydrochlorides. After refluxing the mixture, a yellow tarry material was obtained which was insoluble in benzene, but soluble in water. The reaction was not studied further.

$C_6H_5NH_2 \cdot BCl_3$, **The Addition Compound of Aniline and Boron Chloride.**—Twenty-two grams of boron chloride, dissolved in 23 g. of sodium-dried benzene, was cooled to -15° and stirred constantly while 13.9 g. of freshly distilled aniline (20% less than the calculated amount) dissolved in 23 g. of dry benzene was dropped in, taking half an hour for the addition. The reaction was vigorous and a white precipitate of the addition product began forming at once. After two hours of standing the mixture was filtered in dry air as described for the dimethyl derivative.

The substance reacted violently with water in contrast with the dimethylaniline derivative and decomposed when exposed to the air in the laboratory for any length of time. When heated, it began to melt at about 100° and decomposed at about 120° . The relative instability of the compound is further demonstrated by its decomposition when heated with boiling benzene, in which it is quite insoluble. The vapors which escaped reacted with water, yielding hydrochloric and boric acids in the ratio of 3 to 1. This indicates that the compound decomposes into aniline and boron chloride. The compound is insoluble in carbon tetrachloride as well as in benzene and other anhydrous solvents and no satisfactory method was found for further purification. The crude product gave the following analysis.

Anal. Calcd. for $C_6H_5NH_2 \cdot BCl_3$: B, 5.14; Cl, 50.60. Found: B, 5.19; Cl, 49.28.

$C_6H_5NH_2 \cdot BCl_2NHC_6H_5$, **The Addition Compound of Dichloroboron Anilide and Aniline.**—To 7.2 g. of $C_6H_5NH_2 \cdot BCl_3$, 3.2 g. of freshly distilled aniline, dissolved in 40 g. of dry benzene, was added all at one time. Considerable heat was evolved and after shaking the mixture a few minutes a semisolid paste was formed. After standing for twenty-four hours, the mixture was heated to boiling and filtered hot. On cooling, 0.2 g. of fine needles separated which were filtered and dried in an atmosphere of dry air as described above. The substance reacted vigorously with water, producing aniline, and hydrochloric and boric acids, for all of which positive tests were obtained.

Anal. Calcd. for $C_6H_5NH_2 \cdot BCl_2NHC_6H_5$: B, 4.0; Cl, 26.6. Found: B, 3.3; Cl, 27.1.

$(C_6H_5N)_3B_3Cl_3$, **Triphenyltrichlorotriboron-nitride.**—Triphenyltrichlorotriboron-nitride was first found in the benzene filtrates from the preparation of the addition compound. The yields were small, but, by increasing the time of reaction and by heating the precipitated addition compound with benzene, the yield was increased very markedly. Twenty-eight grams of freshly distilled aniline dissolved in 190 g. of sodium-dried benzene was dropped slowly into a constantly stirred solution of dry benzene containing 42.7 g. of boron chloride dissolved in 205 g. of dry benzene, cooled to -15° . Considerable heat was evolved and at least forty-five minutes should be allowed for the addition. A white precipitate formed which was undoubtedly the addition compound. The flask was stoppered tightly and after standing for twenty-four hours at room temperature, the mixture was heated to boiling, and filtered hot. The filtrate was distilled until about 100 ml. remained. The distillate was mixed with the insoluble precipitate, again heated to boiling, filtered, and distilled with the 100 ml. remaining in the distilling flask. The process was repeated once more, distilling finally down to about 50 ml. or less. On cooling, 8 g. of needles was obtained. By extracting the precipitate twice again, 4.05 g. more was obtained. Basing the yield on the amount of aniline used and the following reaction, an 87.5% yield was obtained.



The substance crystallized from hot benzene in long thin needles. The solubility is 0.02 g. per gram of benzene at room temperature and about 20 times as much at the

boiling point. When heated, the compound sintered at 255–60° and melted with decomposition at 265–70°.

Anal. Calcd. for $(C_6H_5N)_3B_3Cl_3$: B, 7.88; Cl, 25.86; mol. wt., 411.9. Found: B, 7.91, 7.85; Cl, 25.79, 25.69; mol. wt., (in boiling benzene, av. 4 detns.) 419, (in boiling carbon tetrachloride, av. 6 detns.) 427.

Triphenyltrichlorotriboron-nitride may be made, also, from boron trianilide by the action of dry hydrogen chloride.

$(C_6H_5N)_3B_3(OH)_3$, **Triphenyltrihydroxytriboron-nitride**.—This compound was made from the trichloride by allowing the latter to stand in water for three hours. The white flocculent precipitate was filtered with suction and dried on the funnel. The product was very soluble in methanol at room temperatures and, unlike the chlorine derivatives described in this paper, would crystallize out again upon the addition of cold water. On the other hand, boiling alcohol rapidly decomposed the compound. The substance crystallized in fine needles. The melting point was not sharp. Softening began at about 95°, and complete liquefaction did not take place until 130° was reached. The substance is soluble in dilute sodium hydroxide.

Anal. Calcd. for $(C_6H_5N)_3B_3(OH)_3$: B, 9.09; N, 11.78; mol. wt., 356.4. Found: B, 9.03; N (Kjeldahl), 11.57; mol. wt. (in boiling absolute ethanol), 440, 397, 329, 278, 234, 212, 185, 162, 185, 187, 190.

The molecular weights given above were made upon a 0.1509-g. sample in 3.90 g. of ethanol and, in view of the small quantities employed, may be in some error. This may account for the high initial results. However, there seems to be no question that the compound undergoes decomposition in boiling alcohol and that an equilibrium is reached which has an average molecular weight of about 185.

$(C_6H_5NH)_3B$, **Boric Trianilide**.—Boric trianilide may be made from the addition compound of aniline and boron chloride by heating it with 5 equivalents of aniline. Also, considerable quantities may be recovered by heating the various boron containing residues obtained from the reaction described above with an excess of aniline. However, the following is a description of the best experiment for making this compound. To 13.4 g. of $C_6H_5NH_2 \cdot BCl_3$, 29.6 g. (5 eq.) of pure aniline was added, dissolved in 75 g. of benzene. The mixture was refluxed for an hour and then allowed to stand for forty-eight hours. A large quantity of aniline hydrochloride separated out during this time. Another 50 g. of benzene was added and the mix-

ture heated to boiling and filtered hot. The filtrate was distilled until only about 50 ml. remained. The distillate was mixed with the precipitate and refluxed for a few minutes. After filtering, the extract was mixed with the residue in the distilling flask and distilled until about 30 ml. remained. Upon cooling, 15.8 g. of colorless needles appeared, a yield of 86.5%. The pure compound soon turned yellow, even in a tightly stoppered tube and the odor of aniline developed. On the other hand, the compound could be kept indefinitely apparently, under dry benzene in a well-stoppered bottle. The melting point was 166–169° with decomposition. If heated slowly, the substance showed signs of softening at temperatures as low as 155°.

Anal. Calcd. for $(C_6H_5NH)_3B$: B, 3.77; mol. wt., 286.8. Found: B, 3.77, 3.78; mol. wt. (in diphenyl), 278.

Boric trianilide dissolves in aniline but there was no evidence that an addition compound was formed. The substance is readily hydrolyzed by water.

Hydrogen chloride reacts with boric trianilide with the formation of triphenyltrichlorotriboron-nitride in fairly good yields, as the following experiment indicates. Dry hydrogen chloride was passed into a solution of 8.5 g. of boric trianilide in 100 ml. of dry benzene, first at the boiling point and then at room temperature until saturated. A white precipitate of aniline hydrochloride formed. After standing for three hours the mixture was heated to boiling and filtered hot. The filtrate was concentrated to 20 ml. and upon cooling 1.9 g. of triphenyltrichlorotriboron-nitride separated, a yield of 46.5%.

Summary

The reactions of aniline with boron chloride have been studied and the following products obtained: (1) an addition compound, $C_6H_5NH_2 \cdot BCl_3$; (2) triphenyltrichlorotriboron-nitride, $(C_6H_5N)_3B_3Cl_3$ which may be a derivative of $B_3N_3H_6$; (3) the corresponding trihydroxide, $(C_6H_5N)_3B_3(OH)_3$ which has acidic properties; (4) boric trianilide, $B(NHC_6H_5)_3$; also, a small yield of an intermediate compound (5), $C_6H_5NH_2 \cdot BCl_2NHC_6H_5$ and the addition compound (6) of dimethylaniline and boron chloride were obtained.

SALT LAKE CITY, UTAH

RECEIVED MARCH 9, 1939