

of *o*-aminobenzylamine in 10 g. (0.075 mole) of 50% hypophosphorous acid was added 10 ml. of water (solution A). Solution B was made up by mixing a cold solution of 5.4 g. (0.075 mole) sodium nitrite in 15 ml. of water and 20 g. of cold 50% hypophosphorous acid (0.15 mole). Solution B was cooled to  $-5$  to  $0^{\circ}$  and, with stirring, solution A was slowly added simultaneously with 9 ml. of 15% aqueous hydrochloric acid (0.045 mole).

After an hour at  $0^{\circ}$  the reaction mixture was permitted to come to room temperature and stand for twelve hours. The product was extracted with four 5-ml. portions of ether and these were washed with 5% aqueous sodium hydroxide, with water and then dried over anhydrous sodium sulfate. The solvent was removed on a steam-bath and the residue vacuum distilled. One gram of benzyl chloride was obtained; the colorless product boiled at  $80^{\circ}$  (8 mm.);  $n_{20}^{D}$  1.5373; lit. value<sup>46</sup>  $n_{20}^{D}$  1.5391. The benzyl chloride thus obtained gave a positive Beilstein test and did not give a 3,5-dinitrobenzoate upon treatment with 3,5-dinitrobenzoyl chloride. In contrast, a 50-mg. sample when refluxed for two hours in dry benzene containing dry silver 3,5-dinitrobenzoate gave the ester; m. p. and mixed m. p. with authentic benzyl 3,5-dinitrobenzoate, 112–113 $^{\circ}$ .

The acid reaction mixture from which the benzyl chloride had been extracted was made alkaline and exhaustively extracted with ether. Removal of the solvent yielded one drop of brown residue which gave a negative arylamine test and did not have an amine odor.

**Attempted Reaction of Benzylamine with Nitrous Acid.** (a)—To 660 g. of 25% aqueous hypophosphorous acid (2.5 moles) was added 21.4 g. (0.2 mole) of benzylamine. The solution was cooled to  $0^{\circ}$  and, while stirring, 21.5 g. (0.3 mole) of 97% sodium nitrite was added. After fifteen hours at  $0^{\circ}$  and twenty-four hours at room temperature the reaction product was extracted with four 60-ml. portions of ether. These extracts were combined, dried over sodium sulfate, and concentrated on a steam-bath. The few drops of brown liquid which remained were soluble in concentrated sulfuric acid, gave a negative ceric nitrate test<sup>47</sup> for alcohols, and a negative fuchsin-aldehyde test.

The aqueous layer was made alkaline and extracted with four 100-ml. portions of ether. These were combined, dried over potassium hydroxide, concentrated and the residue vacuum distilled. A 92% recovery of benzylamine was obtained; 19.7 g., b. p. 41–42 $^{\circ}$  (4 mm.);  $n_{20}^{D}$  1.5424.

Experiments employing 50, 35 and 15% aqueous hypophosphorous acid also failed to give either toluene or

benzyl alcohol. Instead, benzylamine was recovered in 90–93% yield.

(b)—When 8.0 g. of benzylamine was subjected to the conditions described in part c of the "Attempted Selective Deamination of *o*-Aminobenzylamine," 7.1 g. (89%) was recovered; b. p. 179–181 $^{\circ}$ .

**Deamination of *o*-Aminobenzyl Alcohol**<sup>11</sup> (a)—Upon treating 1 g. of *o*-aminobenzyl alcohol in the manner described in part a of the "Attempted Selective Deamination of *o*-Aminobenzylamine," 0.47 g. (54% yield) of benzyl alcohol was obtained;  $n_{20}^{D}$  1.5388; lit. value<sup>48</sup>  $n_{20}^{D}$  1.5387. The 3,5-dinitrobenzoate had m. p. and mixed m. p. 110–112 $^{\circ}$ .

(b)—When 5 g. of *o*-aminobenzyl alcohol was deaminated according to part b of the "Attempted Selective Deamination of *o*-Aminobenzylamine," 1.95 g. (45% yield) of benzyl alcohol was produced;  $n_{20}^{D}$  1.5399. The 3,5-dinitrobenzoate melted 110–112 $^{\circ}$  alone and when mixed with an authentic sample.

### Summary

Aliphatic primary amines are not attacked by nitrous acid below pH 3. In contrast, aromatic primary amines are readily diazotized in comparatively strongly acidic solutions (pH below 1). Consequently, by maintaining the pH below 3 selective diazotization of the aromatic primary amino group is easily achieved. The resulting diazonium salts are susceptible to the usual reactions of diazonium compounds; in the present investigation replacement of the diazo group by hydrogen was accomplished by reduction with hypophosphorous acid.

The over-all result is a simple method for replacing an aromatic primary amino group by hydrogen without affecting any aliphatic amino group which may be present. The generality of this selective deamination reaction has been demonstrated by its successful application to thirteen aromatic-aliphatic diamines in which the side chains are ortho, meta and para to the aromatic amino group. The only diamine which fails to undergo the selective deamination reaction is *o*-aminobenzylamine; the reasons for this are discussed.

WEST LAFAYETTE, INDIANA

RECEIVED DECEMBER 13, 1948

[CONTRIBUTION OF THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## The Preparation of Trimethylamine-borine, N-Trimethylborazole and N-Dimethylaminoborine

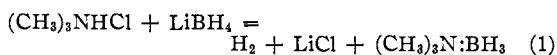
BY GEORGE W. SCHAEFFER<sup>1</sup> AND ELAINE R. ANDERSON<sup>2</sup>

An investigation of the reactions of lithium borohydride and the methylammonium chlorides in ether solution has led to the development of excellent methods for the preparation of trimethylamine-borine,  $(\text{CH}_3)_3\text{N}:\text{BH}_3$ ; N-dimethylaminoborine,  $(\text{CH}_3)_2\text{NBH}_2$ ; and N-trimethylborazole,  $\text{B}_3\text{H}_3\text{N}(\text{CH}_3)_3$ . Previously, these compounds have

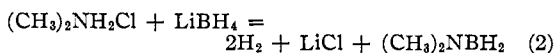
(1) Present address: St. Louis University, St. Louis 4, Missouri.  
(2) Taken in part from a thesis submitted by Miss Elaine R. Anderson to the Department of Chemistry, the University of Chicago, in partial fulfillment of the requirements for the degree of Master of Science.

been prepared by the reaction of diborane with the appropriate anhydrous amine in sealed tubes, employing high vacuum techniques. The experimental difficulties inherent in this type of reaction and the necessary limitations on the quantities of materials used, have made these substances available only in millimole quantities. By the methods described herein, these compounds can be prepared from readily available reagents, in reasonable yields, using the usual techniques of organic synthesis.

Trimethylammonium chloride and lithium borohydride react rapidly and smoothly in diethyl ether at room temperature to produce trimethylamineborine

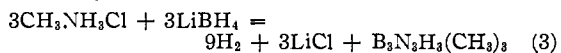


Under similar conditions, dimethylammonium chloride and lithium borohydride give N-dimethylaminoborine



In both cases, the products may be isolated from the reaction mixture by removal of the ether by distillation, and by subsequent sublimation, in vacuum, of the boron compound from the solid residue. Alternately, the reaction mixture may be filtered and the products, which are soluble, recovered from the ether solution by evaporation of the ether, then purified, if necessary, by sublimation. Yields between 65 and 90% based on equations (1) and (2) and the quantity of lithium borohydride taken have been obtained in both reactions; the principal loss appears to be mechanical.

The reaction of monomethylammonium chloride and lithium borohydride ultimately gives N-trimethylborazole



This reaction is, however, somewhat more complex than those of the tri- and dimethylammonium chlorides in that it proceeds in at least two definite steps. At room temperature in diethyl ether solution, only part of the hydrogen expected from equation (3) is evolved. At this stage of the reaction, the intermediate boron-nitrogen compound is non-volatile. The solvent may be removed by distillation and, the non-volatile residue being heated to 250°, additional hydrogen is produced and N-trimethylborazole is recovered from the volatile products in good yield. If the reaction is carried out in hexyl ether (b. p. 210°) both steps of the reaction may be done in a single process and the product recovered from the reaction mixture by distillation to 134°.

The preliminary experiments described in the present paper and other experiments in progress indicate that the reaction between metallo borohydrides and ammonium halides affords a general method for the establishment of a boron-nitrogen bond. A comprehensive study of the reaction to determine its synthetic value, to define optimum condition of yield and to clarify the mechanism is being undertaken in this Laboratory.

### Experimental

The boron-nitrogen compounds are somewhat sensitive to air and moisture; consequently it is necessary to take precautions to ensure strictly anhydrous conditions. The outlets of the reaction system were protected with drying tubes or mercury bubblers and the systems were swept with oxygen-free, dry nitrogen for several hours before use. The reagents and products were handled either in a nitrogen-filled dry box or under a blanket of dry nitrogen.

Although the amounts of reactants used in the experiments described below were drastically limited by the available supply of lithium borohydride there seems to be no inherent limitation placed on these quantities either by the reaction or by the experimental methods employed. All yields are calculated on the basis of the lithium borohydride taken.

(1) **Trimethylamine-borine.** (a) **Preparation.**—The reaction of 1.68 g. of trimethylammonium chloride and 0.42 g. of lithium borohydride in diethyl ether was carried out in a 100-ml., three-necked flask equipped with a stirrer, a condenser and a dropping funnel. The trimethylammonium chloride was introduced into the flask, then a diethyl ether solution of the lithium borohydride was added through the dropping funnel. The reaction was allowed to proceed, with vigorous stirring, at room temperature until the evolution of hydrogen had ceased; then the mixture was refluxed for an hour to ensure completion. The solvent was distilled away from the solid reaction products. These were then transferred to a vacuum sublimation apparatus and 1.05 g. of trimethylamine-borine, a yield of 86% based on equation (1), was recovered from the residue.

(b) **Identity of Product.**—The product of the reaction was identified as  $(\text{CH}_3)_3\text{N}:\text{BH}_3$  by its melting point, 93°, and by its vapor tension, 5.3 mm. at 50.0°, as compared with the calculated<sup>3</sup> value of 5.2 mm. The identity of the product was further confirmed by hydrolysis of two unmeasured samples with concentrated hydrochloric acid in sealed tubes for ten hours, and by measurement of the hydrogen and titration of the boric acid. The first sample gave 1.40 millimoles of boron and 4.27 millimoles of hydrogen, a ratio of 1/3.05, and the second gave 1.18 millimoles of boron and 3.58 millimoles of hydrogen, a ratio of 1/3.01, results which are in accord with the formula  $(\text{CH}_3)_3\text{N}:\text{BH}_3$ .

(2) **N-Dimethylaminoborine.** (a) **Preparation A.**—An excess, 8.99 g., of dimethylammonium chloride was introduced into a reaction flask provided with a stirrer, condenser and dropping funnel. Lithium borohydride, 0.78 g. in diethyl ether solution, was run into the methylammonium chloride. After the evolution of hydrogen had ceased the reaction was allowed to reflux at the boiling point of ether for two hours. The apparatus was arranged for distillation and the solvent was removed. The water condenser employed for the ether distillation was exchanged for a short air condenser, and the temperature of the reaction flask raised until, at 76 to 77°, 1.53 g. of the product N-dimethylaminoborine was collected, a 91% yield.

(b) **Preparation B.**—Lithium borohydride, 11.5 g. was mixed with 35 g. of dimethylammonium chloride in a 600-cc. flask fitted with a mercury sealed stirrer, a reflux condenser and a dropping funnel. Diethyl ether, 150 cc., was added through the dropping funnel and, after the initial reaction had subsided, the mixture was refluxed for three hours. The resulting suspension was filtered through a porous plate under nitrogen pressure, and the residue was washed once with 50 cc. of dry ether. The ether was removed from the combined filtrate and washings by distillation in vacuum, the N-dimethylaminoborine being trapped in a bath kept at -63°. The crude product, trapped at -63°, was again sublimed into a -63° trap to effect final purification. The yield was 16 g. or 65%.

(c) **Identity of Product.**—The product was identified as N-dimethylaminoborine<sup>4</sup> by its melting point, 73°, its boiling point of 76 to 77°, and its vapor tension of 10 mm. at 23°, and 80 mm. at 55°.

(3) **N-Trimethylborazole.** (a) **Procedure A.**—Methylammonium chloride, 4.033 g., was introduced into a reaction flask provided with a condenser, stirrer and dropping funnel. Fifty cc. of a 0.476 molar solution of lithium borohydride in diethyl ether was added through the funnel, the mixture was allowed to react until the evolution of

(3) A. B. Burg and H. I. Schlesinger, *THIS JOURNAL*, **59**, 780 (1937).

(4) E. Wiberg and A. Bolz, *Ber.*, **73B**, 209 (1940).

hydrogen had ceased, and was then refluxed for three hours. The diethyl ether was removed by distillation and the residue in the reaction flask was slowly heated to 250° and maintained at this temperature for four hours. During this stage of the reaction efficient operation of the condenser is essential, for the product may be lost in the stream of hydrogen that is produced. At this time the reaction flask was made to communicate to an oil pump through a trap maintained at -196°. The volatile reaction products were distilled from the flask and condensed in the trap. This trap was then removed from the reaction system, attached to a vacuum apparatus, and the product purified by fractional condensation at -45°. A yield of 0.95 g., 98%, as calculated from equation (3), was obtained.

(b) **Procedure B.**—Monomethylammonium chloride, 16.5 g., and 5.3 g. of lithium borohydride were mixed in a 500-cc. reaction flask arranged as in the former experiments. di-*n*-Hexyl ether, 125 cc., previously dried over sodium hydride, was slowly added through the dropping funnel. After the initial reaction had ceased, the mixture was refluxed for half an hour. The apparatus was arranged for distillation and the mixture was distilled until the products boiling below 134° were collected. The crude product was transferred to a vacuum apparatus and

purified by fractional condensation at -45°. A yield of about 7 g., or 70%, was obtained.

(c) **Identity of Product.**—The product was identified<sup>5,6</sup> by its boiling point, 132° (obs. 132-133°), its melting point, -9° (obs. -8 to -7.5°), and by its vapor pressure, 27 mm. at 37° (obs. 28 mm.), 163 mm. at 85° (obs. 158 mm.).

**Acknowledgments.**—The authors wish to express their gratitude to Mr. Riley Schaeffer and to Mr. M. Berger who assisted in several experiments.

### Summary

A simple method for the preparation of N-dimethylaminoborane, trimethylamineborane and N-trimethylborazole by the reaction of lithium borohydride with the appropriate alkylamine chloride is described.

(5) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *THIS JOURNAL*, **60**, 1297 (1938).

(6) E. Wiberg, K. Hertwig and A. Bolz, *Z. anorg. Chem.*, **236**, 177 (1938).

CHICAGO, ILL.

RECEIVED DECEMBER 8, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

## The Effect of Inorganic Electrolytes upon the Conductivity of Aqueous Solutions of Dodecylammonium Chloride<sup>1</sup>

By A. W. RALSTON, D. N. EGGENBERGER AND F. K. BROOME

The general effect of the presence of inorganic electrolytes in enhancing the colloidal properties of colloidal electrolytes is well recognized and reference to some of the prior work upon this subject has been given in our former paper.<sup>1a</sup> In our previous work, which was also concerned with the effect of inorganic electrolytes upon the electrical conductivity of aqueous solutions of dodecylammonium chloride, an attempt was made to compare the effects at similar specific conductivities and, as a consequence, the concentrations of inorganic electrolytes varied over a wide range. Although our results were in substantial agreement with those expected from previous work, the procedure employed led to the masking of several significant facts. The present paper constitutes an extension of our former work upon this subject and compares the effects of various salts and acids at similar concentrations upon the electrical conductivity of aqueous solutions of dodecylammonium chloride.

### Experimental

The dodecylammonium chloride was of the same quality as that used in our former work.<sup>2</sup> The conductivities were determined in the manner and with the equipment previously described.<sup>3</sup> The calculation of the conductivity by difference was similar to that employed previously.

(1) Presented in part before the Colloid Division, 114th Meeting, American Chemical Society, Portland, Oregon, September, 1948.

(1a) Ralston and Eggenberger, *THIS JOURNAL*, **70**, 980 (1948).

(2) Ralston and Eggenberger, *ibid.*, **70**, 436 (1948).

(3) Ralston, Hoerr and Hoffman, *ibid.*, **64**, 97 (1942).

### Results and Discussion

Figure 1 compares the conductivity of dodecylammonium chloride in pure water with its conductivity by difference in 0.0025, 0.005, 0.01 and 0.02 *N* sodium chloride solutions. It is apparent that progressive increases in the concentration of sodium chloride lower the conductivity attributable to the colloidal electrolyte and materially decrease its critical concentration. A similar effect was noted for 0.0025, 0.005, 0.01 and 0.02 *N* barium chloride solutions, Fig. 2.

In our previous work<sup>1a</sup> concerned with the effect of the presence of hydrochloric acid upon the conductivity of aqueous solutions of dodecylammonium chloride, the conclusion was drawn that although the presence of hydrochloric acid materially lowers the equivalent conductivity it has only a negligible effect upon the concentration at the critical point. Figure 3 shows this latter conclusion to be in error, since the presence of hydrochloric acid lowers both the conductance and the concentration of colloidal electrolyte at the critical point.

The effect of sodium chloride, barium chloride or hydrochloric acid upon aqueous solutions of dodecylammonium chloride may be attributed to two factors, which are, first, the depression in the ionization of the colloidal electrolyte caused by the increase in the common chloride ion and second, the salting-out effect of the strong electrolyte. Randall and Failey<sup>4</sup> have published

(4) Randall and Failey, *Chem. Revs.*, **4**, 285 (1927).