[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO BORON. II. ACTION OF LITHIUM ON ETHYLAMMINO BORON TRIFLUORIDE

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As was stated in a preceding paper,[1] ammino boron trifluoride is appreciably ammonolyzed when dissolved in liquid ammonia. This is conclusively shown by the fact that when sodium is added to a solution of the trifluoride in liquid ammonia, hydrogen is evolved. It was at first thought that ethylammino boron trifluoride might dissolve in ethylamine without aminolysis. However, on adding lithium to a solution of this compound in ethylamine, three atoms of hydrogen were evolved per mole of boron trifluoride, thus showing that aminolysis went to completion.

The reaction between lithium and boron trifluoride in ethylamine may be expressed by the equation

$$BF_3 + 3C_2H_5NH_2 + 3Li = B(C_2H_5NH)_3 + 3LiF + 3/2H_2$$

Experiment has shown that the reaction proceeds practically quantitatively. The various products of the reaction have been isolated and identified.

Preparation of Tertiary Boron Ethylimine.—On adding lithium to an ethylamine solution of ethylammino boron trifluoride, hydrogen is evolved and a precipitate, consisting of lithium fluoride, is formed. This reaction is due to aminolysis of the boron trifluoride, the resulting ethyl ammonium fluoride reacting with lithium to form lithium fluoride and hydrogen. The reaction proceeds until all the fluorine atoms have been aminolyzed.

Four reactions were carried out for the purpose of determining the nature of the various reaction products. The apparatus employed was substantially as is shown in Fig. 1. The reactions were carried out in a weighed tube A. A known quantity of ethylammino boron fluoride was introduced into the bottom of the reaction tube and a weighed quantity of lithium into the introduction tube B. The reaction tube was attached to the system at T by means of de Khotinsky cement. After exhausting the apparatus, a bath of ammonia was placed around the auxiliary chamber M, into which a quantity of lithium had previously been introduced, and, by opening the valve O of the cylinder L, containing ethylamine, the desired quantity of solvent was condensed in M. After closing stopcock K, the bath surrounding M was removed and placed around the reaction tube A. Stopcocks C, D and H were opened, allowing the solvent evaporating in M to condense in the reaction tube. When condensation was completed, any hydrogen present was removed with a pump and the lithium in the addition tube B was introduced as needed by turning this tube through a suitable angle about its axis. In the meantime, the stirrer Z, suspended from a spring Y, was set in motion by an intermittent current passing through the solenoid X. Lithium was added slowly, piece by piece, the evolved hydrogen passing through stopcocks C, D and F and through a sul-

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[1] Kraus and Brown, THIS JOURNAL, 51, 2690 (1929).

furic acid trap W into the chambers V and U containing sulfuric acid and phosphorus pentoxide, respectively. The acid and oxide served to remove ethylamine carried over with the hydrogen.

The addition of lithium was continued until the solution remained permanently blue. All the hydrogen was carried over into the drying tubes by the amine vapor. After standing, it was removed by means of a Töpler pump, J, and transferred into a graduated buret Q. After determining the volume of the hydrogen, it was introduced into a bulb R of known volume and its density determined from the weight and pressure of the gas.

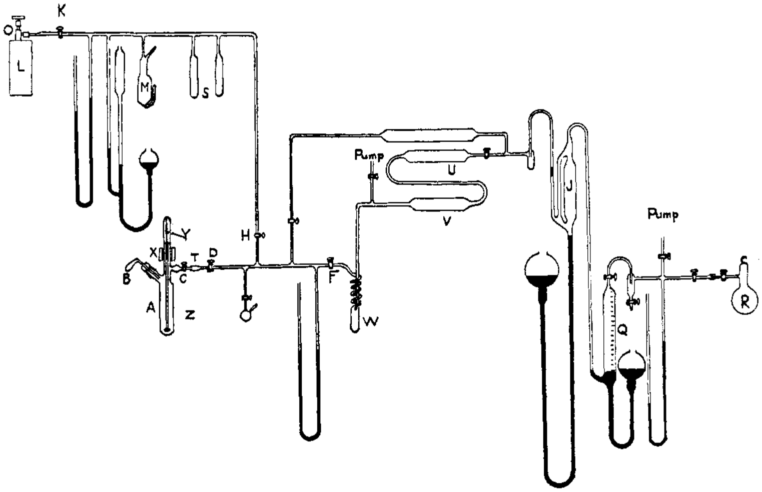

Fig. 1.—Apparatus used in aminolysis of boron trifluoride.

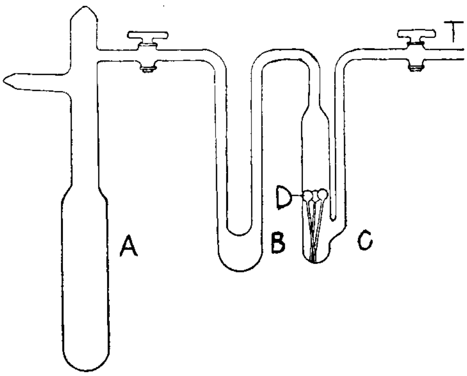

Fig. 2.—Apparatus used in preparing boron triethylimine.

The excess solvent was distilled from the reaction tube into the recovery tubes, S, which were then sealed off from the system. Dry nitrogen was introduced into the reaction tube, the addition tube B was removed and the amount of lithium remaining, determined. The reaction tube A was then pumped to constant weight.

On weighing, it was found that the weight of the contents was less than that of the materials used. This led to the inference that one of the products of the reaction was a more or less volatile liquid or solid.

Accordingly, in a third experiment, a two-legged reaction tube was used in place of that illustrated in Fig. 1. Before distilling off the amine at the end of the reaction, the tube was detached from the system, the precipitate was allowed to settle and the clear liquid decanted into the second limb of the tube. The solvent was then distilled back into the first leg for the purpose of washing the solid residue. This process was repeated nine times. The tube was then again attached to the system and the excess amine recovered. It was found that a quantity of liquid remained in the second limb of the reaction tube which was much less volatile than ethylamine. The two limbs of the reaction tube were sealed and separated from each other, and the limb A containing the liquid product was attached to two U-tubes, B and C, as shown in Fig. 2. The tube T was attached to T of the apparatus as shown in Fig. 1. The apparatus was exhausted through T while a bath of liquid ammonia was placed around tube B. Under a pressure of about 0.1 mm., the liquid distilled rapidly from A into the cooled tube. The ammonia bath was then removed and placed around tube C and the liquid was redistilled from B to C. When this process was completed, nitrogen was slowly introduced into the apparatus, forcing the liquid through the capillaries into the previously weighed bulbs D. Tube C was then opened, the bulbs were removed and the capillaries sealed and weighed. The solid residue left in the first limb of the original two-legged reaction tube was treated with sulfuric acid in a platinum crucible and the weight of lithium determined as lithium sulfate.

A fourth reaction was carried out with a tube of the form shown in Fig. 3. Tube A′ was attached, by means of T to tube T of Fig. 1 in place of the reaction tube A. The reaction was carried out as already described and, when completed, stopcock D was closed and tube X was attached to a pump. On placing a liquid ammonia bath around tube B (containing the weighed bulbs) and exhausting the system through C, the volatile product distilled rapidly from the reaction tube A′ into B. This liquid was then forced through the capillaries into the bulbs under a pressure of nitrogen. The known samples in the bulbs were employed for analyses and molecular weight determinations.

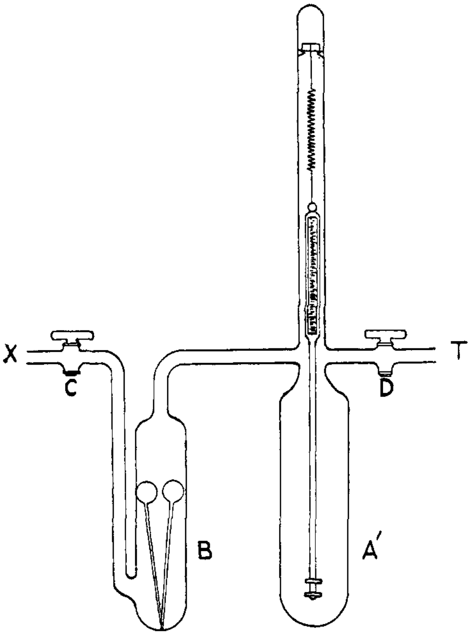

Fig. 3.—Improved apparatus for preparing boron triethylimine.

Determination of Products of Reaction

Hydrogen.—The relation between the volume of hydrogen collected and the weights of material used is summarized in the following table for Expts. 1, 2 and 3.

TABLE I

DATA RELATING TO HYDROGEN EVOLVED

Expt. no.	Mole of BF_3	Mole Li	H_2, cc.	Atoms H_2
1	0.0095	0.037	266	0.0238
2	.00681	.0217	240	.0214
3	.00626	.0187	197.2	.0176

The density of the gas evolved in Reaction 1, was 3.36, which clearly indicates that it consisted essentially of hydrogen. As is shown by the figures in the last column, the volume of hydrogen collected in Expts. 2 and 3 was approximately three atoms per mole of boron trifluoride.

The Insoluble Solid Product of Aminolysis.—The solid product of the reaction, which was insoluble in ethylamine, was assumed to be lithium fluoride. After washing with ethylamine, various samples were analyzed for lithium and fluorine without further purification.

Anal. Lithium subs., 0.0621, 0.1898, 0.2413: Li_2SO_4, 0.1206, 0.3882, 0.4965. Calcd. for LiF: Li, 26.75. Found: Li, 24.51, 25.82, 25.87.

The solid was also analyzed for fluorine by the lead chlorofluoride method.

Anal. Subs., 0.0322: PbClF, 0.3119. Calcd. for LiF: F, 73.4. Found: F, 70.32.

The results show that the insoluble product of reduction was slightly impure lithium fluoride.

Analysis of Liquid Product $B(C_2H_5NH)_3$.—Samples of the liquid product, prepared as described above, were analyzed for nitrogen by hydrolyzing the material, distilling the ethylamine with water vapor and titrating the distillate with hydrochloric acid of known concentration.

Anal. $B(C_2H_5NH)_3$ subs., 0.0777, 0.0712: cc. of 0.1083 *N* HCl, 15.11, 13.78. Calcd. for $B(C_2H_5NH)_3$: N, 29.30. Found: N, 29.20, 29.36.

A quantity of the material was hydrolyzed by means of a small quantity of water vapor and the amine resulting was collected and its vapor density determined. The vapor density corresponded to a molecular weight of 44.8, as against 45.1 for ethylamine.

Analyses for boron were carried out by the titration method, as described in the preceding paper. In a number of instances the ethylamine was boiled off from an alkaline solution, while in others, the amine was first titrated with 0.1 *N* HCl. Samples of material from which the amine had been removed by the boiling of an alkaline solution yielded, in three determinations, 8.11, 8.27 and 8.16% of boron. In another series of determinations, in which the amine was neutralized with 0.1 *N* HCl, there were obtained the following values: 8.00, 7.96, 8.02 and 7.96% of boron. The boron content of $B(C_2H_5NH)_3$ is 7.67%. The value found for boron was slightly high. This discrepancy was due to inadequacy of the analytical method rather than to lack of purity of the compound.

Properties.—The properties of tertiary boron ethylimine, which is an ammono boron ethyl ester, were not extensively studied. It is fairly volatile at ordinary temperatures and, except for its sensitiveness to moisture, it is quite stable. It is readily soluble in ethylamine.

Summary

Ethylammino boron trifluoride is aminolyzed when dissolved in ethylamine. When a solution of this compound is treated with three atoms of metallic lithium, boron triethylimine, $B(C_2H_5NH)_3$, is formed. This ammono boron ethyl ester is a liquid readily soluble in ethylamine, ap-

preciably volatile at ordinary temperatures and readily hydrolyzable by water vapor.

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COBALT COMPLEXES OF THIOGLYCOLIC ACID

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For reasons understandable from some preceding papers,[1] it seemed important to enhance our knowledge of metal complexes of sulfhydril compounds which also contain a carboxyl group. Though the behavior of various representatives of this group toward cobalt has some common aspects, there are individual differences. This paper is restricted to the simplest of these compounds, thioglycolic acid.

Compounds of cobalt and thioglycolic acid have been described by Rosenheim and Davidsohn.[2] Attempts to repeat their work did not yield readily crystallizable compounds and furthermore these authors were not aware of the fact that the formation of their brown compounds requires free oxygen and does not take place in the absence of air.

Another brief notice is given by Myers[3] but he evidently did not obtain a pure compound and was also unaware of the oxidation which takes place in its formation. Much more nearly related to the compounds described in this paper is Cremer's[4] observation of a complex established with cysteine and cobalt in the absence of air and in the presence of carbon monoxide. This complex, according to Cremer, contains two molecules of cysteine and one molecule of carbon monoxide for each atom of cobalt. The color of this complex is olive-green, more intense than the color of the cobaltous complex of cysteine without carbon monoxide. This author does not mention the fact that this cobalto complex in contact with air undergoes a considerable change and intensification of color, a fact which will be the starting point for our investigation. Cremer also describes an analogous complex of ferrous iron. One atom of iron combines with two molecules of cysteine and two molecules of carbon monoxide, so differing from the cobalt complex. This ferrous complex is highly optically active, is orange-yellow in color, and reversibly dissociates the carbon monoxide on being illuminated.

Closely related to the present work is the attempt of Cannan and Rich-

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[1] L. Michaelis and E. S. Guzman Barron, *J. Biol. Chem.*, **83**, 191 (1929); L. Michaelis. *ibid.*, **84**, 777 (1929).

[2] A. Rosenheim and J. Davidsohn. *Z. anorg. Chem.*, **41**, 231 (1904).

[3] C. N. Myers, *J. Lab. Clin. Med.*, **6**, 359 (1921).

[4] W. Cremer, *Biochem. Z.*, **206**, 228 (1929).