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REACTIONS OF CYANIDES WITH BORAZINES

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THESIS

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APPROVED

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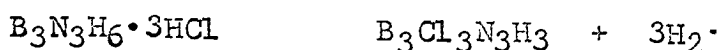
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## ABSTRACT

B-trichloro-N-trimethylborazine in a dry tetrahydrofuran solution was reacted with potassium cyanide, and sodium cyanide. On analysis of this reaction mixture, the precipitate was shown to contain both potassium chloride, and potassium cyanide when reacted with the potassium cyanide, and sodium chloride and sodium chloride when reacted with sodium cyanide. On repeated runs of these reactions, it was shown that the percentages of the chloride to cyanide was approximately the same.

## INTRODUCTION

In the years previous to 1940, very little work was done in the field of borazine chemistry. Around 1940, B-trichloro borazine was first prepared<sup>1</sup>. This was accomplished by the thermal decomposition of borazine and hydrochloric acid.



A short time later other borazine compounds were prepared by various methods. In 1947 N-trimethyl-B-trichloro-borazine was synthesized by the reaction of borontrichloride and methylamine hydrochloride.<sup>2</sup>

This preparation tended to indicate that substituted borazines could be prepared by other methods besides the thermal decomposition method. Then in 1955 B-trichloroborazine was prepared by refluxing a mixture of ammonium chloride in the presence of boron trichloride vapor.<sup>3</sup>

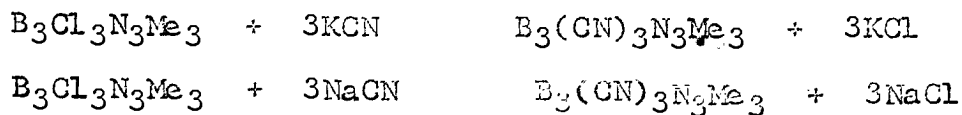
Later this method was improved, until it was possible to get an almost quantitative yield of pure product.<sup>4</sup>

Since that time, much has been done in the preparation of these substituted borazines. In 1960, B-tricyanoborazine was prepared by Bremnan, Dahl, and Schaeffer by the reaction of B-trichloroborazine and silver cyanide in acetonitrile.<sup>5</sup> This reaction went as follows:



This method yielded a good cyanoborazine, but it could not be purified to less than 5% silver presence.

The method I intend to use will replace the B-trichloroborazine with B-trichloro-N-trimethylborazine, the silver cyanide with both potassium cyanide, and sodium cyanide, and the acetonitrile with tetrahydrofuran. The reactions are as follows:



## MATERIALS AND APPARATUS

Tetrahydrofuran (dried)  
B-trichloro-N-trimethylborazine  
Nitrogen (dry, high pure)  
Reaction apparatus (diagram #1)  
Dry box (diagram #2)  
Silver nitrate  
Potassium Cyanide  
Sodium cyanide  
Potassium Chloride  
Potassium Chromate  
Filter system (diagram #3)

## EXPERIMENTAL

The apparatus was set up as shown in diagram #1. Following this, the reactions are given in a step by step order in which they took place.

### A. Reaction apparatus set up.

All the glassware was thoroughly cleaned before use, and the reaction line was set up as follows

A hose line was taken from a tank of highpure dry nitrogen into a mercury bubble tube. From this tube, the nitrogen line went into a phosphorous pentoxide drying tube, and then into reaction flask #1. This flask was a 1000ml three neck flask in which the gas inlet is in one neck, the stirring apparatus in the center neck, and the gas outlet in the third neck. From this outlet neck, the line goes through a calcium chloride drying tube, and into the inlet neck of reaction flask #2 which is set up as flask #1. Reference to diagram #1 will show how this line was set up. All ground glass joints in the apparatus were greased to prevent air leakage from the outside, as all moisture must be kept out of the system due to the reactivity of both the products and reactants of the reaction to water.

### B. Preparation of samples for the two reactions. (1a, and 2a)

Five grams of B-trichloro-N-trimethylborazine was weighed out in a weighing bottle. This was placed in the dry box (diagram 2) to keep it free from moisture.

Five grams of potassium cyanide was dried, ground up to



a fine powder, and weighed out in a weighing bottle. This was placed in the dry box to keep it free of moisture.

A large bottle of tetrahydrofuran was dried by placing pieces of sodium metal in the bottle, and waiting until no more hydrogen gas was released.

250 ml. of this dry tetrahydrofuran was measured out and set aside for the reaction.

These three constituents are the reactants to reaction 1a.

Five grams of B-trichloro-N-trimethylborazine was again weighed out and placed in another weighing bottle, and placed in the dry box as before.

Twenty five grams of Potassium cyanide was dried, ground, and weighed out in a fourth weighing bottle, and placed in the dry box.

Another 250 ml. of tetrahydrofuran was measured out and set aside for the start of the reaction.

These three constituents are the reactants to reaction 2a.

C. Run of reactions 1a. and 2a.

In flask #1 of the reaction apparatus was placed the first of the five gram samples of B-trichloro-N-trimethylborazine, the five gram sample of potassium cyanide, and 250 ml of tetrahydrofuran. The stirrer was then put in operation, causing the reaction mixture to be stirred constantly.

In flask #2 the second sample of the B-trichloro-N-trimethylborazine was placed along with the twenty five gram sample of potassium cyanide, and the other 250 ml of tetrahydrofuran. The stirrer was put into operation on this flask as with flask #1 for the period of the reaction.

The dry nitrogen was then passed through the two atmospheres above the reactions for a period of one hour. The reaction was then allowed to run for two weeks, with a flushing of nitrogen each day.

It was noticed that the solution turned from a clear solution to a light brown solution, and the solid went from a white powder to a brown powder. This occurred in both flask #1 and flask #2.

At the end of the two week period, the two flasks were taken down and placed in the dry box to allow the precipitate to settle.

#### D. Set up of dry box filter system.

For The filtration of the two reaction systems, a special filter system had to be set up in the dry box to keep all moisture away from the products. This was set up as shown in diagram 3.

Here the filter flask, and filter was set up inside the dry box. The suction line then led to a vapor trap submerged in a dry ice acetone bath. This was done to prevent any solvent vapors from getting into the suction pump which runs from the trap. At the top of the dry box was hooked an in-

let tube that allowed dry air to enter the dry box, so a suction would not exist in the dry box causing the rubber gloves to expand in the box.

#### E. Filtration of the reaction products.

The reaction precipitates in the two reaction flasks were then filtered. The collected precipitate was then washed with the clear mother liquid until the precipitate appeared to get no cleaner on rinsing. It was noted that the precipitate was a very fine white to gray powder in flask #1, and a mixture of the very fine powder plus a large amount of crystalline solid in flask #2. In both cases, the liquid was a clear brown color.

#### F. Analysis of precipitate of the ratio of cyanide to chloride.

A method of analysis was set up which would allow for the determination of cyanide and chloride in the reaction product. This was done by titrating a sample of the reaction precipitate with silver nitrate solution which has been previously standardized with potassium chloride, potassium cyanide, and potassium chromate. This was done by noting that the  $K_{sp}$ 's for silver cyanide, silver chloride, and silver chromate are  $1.6 \times 10^{-14}$ ,  $2.8 \times 10^{-10}$ , and  $1.9 \times 10^{-12}$  respectively. Therefore the silver cyanide will show first, then the silver chloride, and finally the silver chromate. By this method, we could determine the amount of chloride and cyanide in the precipitate, and from this, the percentage of conversion of B-trichloro-N-trimethylborazine to

B-tricyano-N-trimethylborazine can be determined.

G. Calculation of the percent cyanide and percent chloride in the precipitate.

From the titration with standard .1M silver nitrate, the percent of potassium chloride and potassium cyanide in the precipitate was determined. It was noted that the precipitate of reaction 1a gave a larger percentage of potassium chloride than the precipitate in reaction 2a. This was due to the fact that there was more potassium cyanide originally in the reaction.

H. Rerun with 5 gram of potassium cyanide and five grams of B-trichloro-N-trimethylborazine. (reaction 1b)

Samples were again weighed out as in step B and C, except only one sample was run. This sample was run exactly as before, except it was only kept reacting for one week. The observations were the same as before. The sample was then set aside, and filtered as it was before.

I. Analysis of the precipitate from reaction 1b.

The analysis was conducted as in steps F and G, and it was noted that the results paralleled the results of reaction 1a.

J. Rerun with twenty five grams of potassium cyanide and five grams of B-trichloro-N-trimethylborazine. (reaction 2b)

The excess sample was run again as in 1b was, and it gave the same observations as 2a.

K. Analysis of the precipitate from reaction 2b.

The analysis was conducted as in steps F and G, and it was noted that these results paralleled the results of the first run (2a).

L. Replacement of potassium cyanide with sodium cyanide.  
(reaction 3)

Sodium cyanide was used instead of potassium cyanide, and was run along the same lines as reaction 2b. That is, twenty five grams of sodium cyanide was reacted with five grams of B-trichloro-N-trimethylborazine in 250 ml of tetrahydrofuran. It was noted that the solvent became much darker after the one week reaction time than it did on the four previous runs with potassium cyanide.

M. Analysis of the reaction 3 precipitate for sodium cyanide and sodium chloride.

The reaction precipitate was filtered, sampled, and analyzed as before, and it was noted that the sodium chloride present was larger than it was with the potassium cyanide. This would tend to indicate a larger amount of cyanoborazine formed.

N. Calculation of the percentage of borazine converted.

From the percentages of cyanide and chloride in the precipitate, and the weights of the starting materials, the percentages of conversion of the B-trichloro-N-trimethylborazine to B-cyano-N-trimethylborazine was calculated. This figure was calculated for both the mono substituted, and the tri substituted borazine.

## RESULTS

Run	Weight Borazine	Weight Cyanide	Percent Chloride	%conversion Tri	% conversion Mono
2a	5.09 g	5.10 KCN	13.1%	1.32%	3.96%
2b	5.03 g	24.43 KCN	4.88%	2.31%	1.11%
3	6.06 g	26.88 NaCN	9.1%	4.35%	13.05%

## DISCUSSION

The reactions with potassium cyanide and the borazine were carried out four times, twice with equimolar amounts, and twice with an excess of potassium cyanide. The resulting percentages of conversion of the chloroborazine to cyanoborazine between the two different amounts of cyanide showed that the excess cyanide about doubled the conversion to cyanoborazine. On replacement of potassium cyanide with sodium cyanide, it was noted that the percentage of conversion was again doubled. Due to this, it could be stated that the more active the alkali metal in the cyanide salt the more forward the reaction would proceed. This would indicate, that if lithium cyanide were used instead of sodium cyanide or potassium cyanide, the percentage of cyanoborazine formed would probably increase.

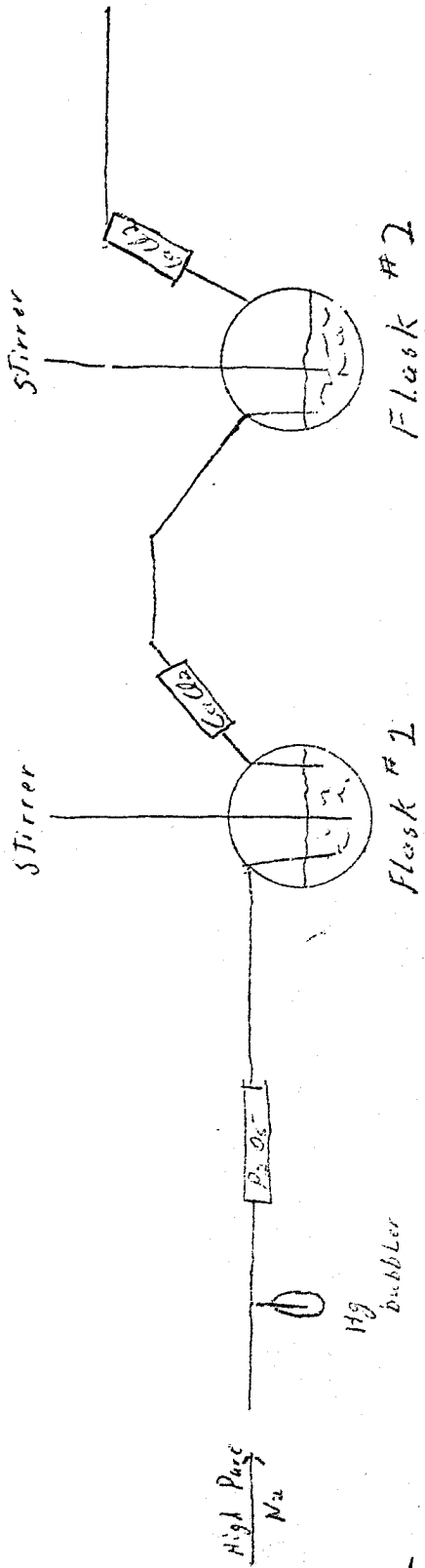
It should be noted that the value of the percent conversion should be given as a range, due to the fact that it was not determined whether the mono, di, or tri cyanoborazine was formed.

It should also be noted here that the analytical method used for the determination of the percentage of potassium chloride, and potassium cyanide in the reaction precipitate is a high point in this research. This method allows one to analyse the products very easily, which eliminated a lot of difficult separations on the two components in the pre-

cipitate. The potassium chromate was added to the precipitate to give an endpoint after the precipitation of the silver chloride.

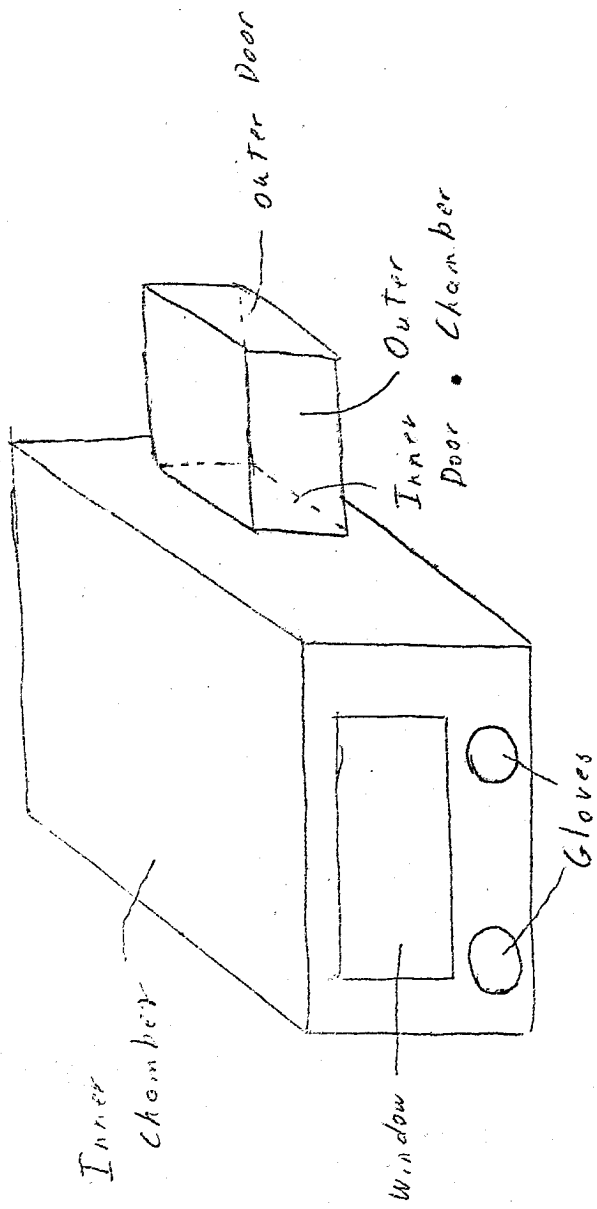
In general it could be said that with the proper cyanide salt, and dry conditions, the cyanoborazine could be prepared with a large enough yield to permit further research to be done on it, with the possibility of forming other substituted borazines with the active cyanide group. By using lithium cyanide, one could possibly increase the yield by a factor of two again, this giving a possible twenty five percent yield if the mono product forms.





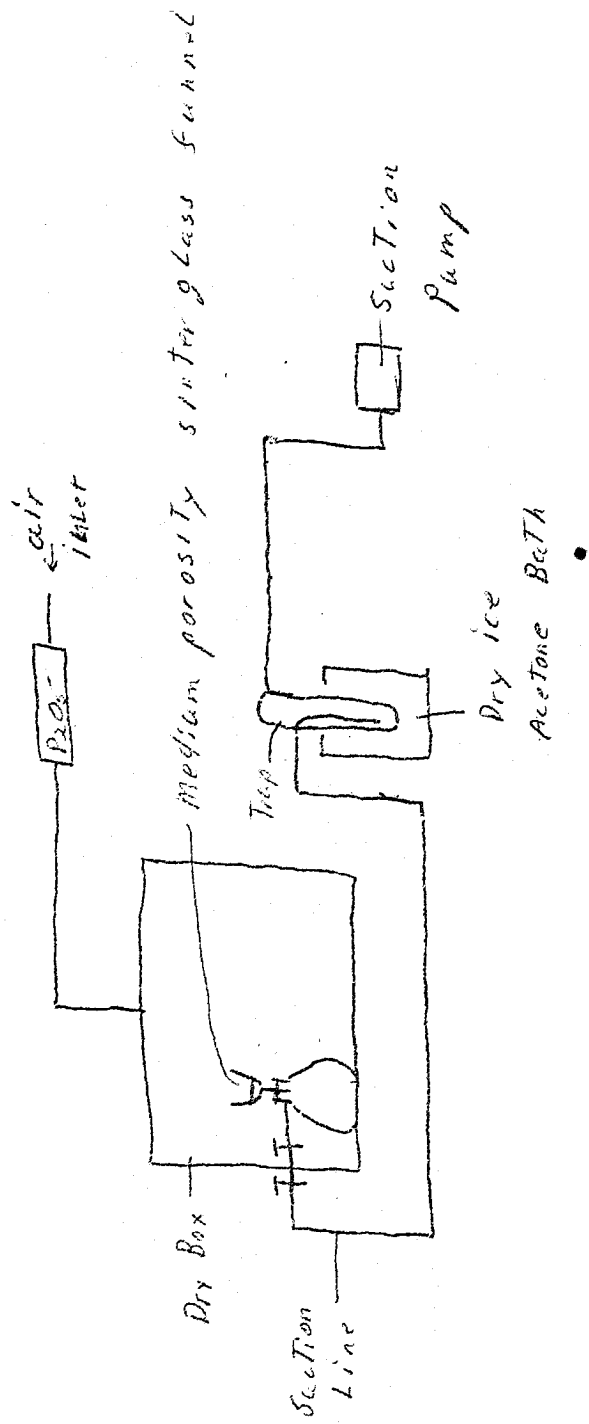
Apparatus for the Reaction of  $B_3Cl_3$ ,  $N_3Mes$  and  $MeCN$

Diagram # 1



Dry Box

Diagram # 2



Filter Apparatus

## ACKNOWLEDGEMENTS

The author would like to express his thanks to Dr. John A. White whose help and guidance during this project proved to be invaluable. I would also like to thank Mr. Robert J Konig for his familiarizing me with the apparatus used in borazine chemistry.

FOOTNOTES

- <sup>1</sup>E. Wiberg and A. Bolz, Ber. 73, 209 (1940)
- <sup>2</sup>E. Wiberg and K. Hertwig, Z. Anorg. Chem., 225, 141 (1947)
- <sup>3</sup>Charles A. Brown and A. W. Laubengayer, J.A.C.S., 77, 3699, (1955)
- <sup>4</sup>G.E. Ryschkewitsch, J. J. Harris and Harry H. Sissler J.A. C.S. 80, 4515, (1958)
- <sup>5</sup>Brennan, Dahl, and Schaeffer, J.A.C.S., 82, 6248, (1960).

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