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Reaction of Boron Chloride with Methoxyamine Hydrochloride

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REACTION OF BORON
CHLORIDE WITH
METHOXYAMINE
HYDROCHLORIDE

ROBERT J. KONIG

JUNE 1966

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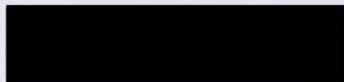
ROBERT J. KONIG

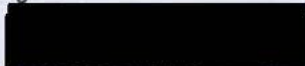
JUNE, 1966


THESIS

SUMBITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR CREDIT IN THE ROCHESTER INSTITUTE
OF TECHNOLOGY COURSE IN CHEMICAL RESEARCH PROJECTS

APPROVED


Project Advisor


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ABSTRACT

Boron chloride and methoxyamine hydrochloride were reacted in refluxing chlorobenzene. The reaction product was then identified as possibly being N-trimethoxy-B-trichloroborazine. The identification was made by comparing the Infra-red spectrum of the reaction product with the spectra of N-trimethyl-B-trichloroborazine, methoxyamine hydrochloride and, the addition compound $\text{MeNH}_2\text{-BCl}_3$.

In 1955 Brown and Leabengayer devised a new method for the preparation of B-trichloroborazine. A mixture of chlorobenzene and $\text{Me}_3\text{N}\cdot\text{HCl}$ was refluxed in the presence of BCl_3 vapor. The apparatus consisted of a one liter three necked flask, fitted with a stirrer, water cooled reflux condenser leading to a dry ice acetone reflux head and an inlet tube extending to the bottom of the flask. To the inlet tube were attached a tube of BCl_3 , and a tube of dry nitrogen.

Three years later Fynskewitz, Sigler and Harris used a slight modification of the above method to prepare N-trimethyl-B-trichloroborazine. A slight excess of BCl_3 was added, and the reaction time was extended until no more HCl was being produced. This reaction produced an almost quantitative yield of pure product, and may be

INTRODUCTION

The preparation of substituted borazines had been given very little attention until around 1940. In 1940, Wiberg and Bolz were the first to prepare B-trichloroborazine¹ by the thermal decomposition of the addition compound of borazine and HCl ($B_3N_3H_6 \cdot 3HCl$). Several years later Wiberg and Hertwig prepared N-trimethyl-B-trichloroborazine by the reaction of BCl_3 with methylamine hydrochloride, at 250° C.²

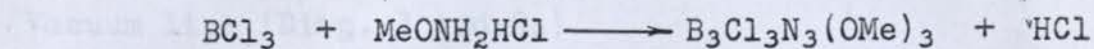
In 1955 Brown and Laubengayer devised a new method for the preparation of B-trichloroborazine.³ A mixture of chlorobenzene and NH_4Cl was refluxed in the presence of BCl_3 vapor. The apparatus consisted of a one liter three necked flask, fitted with a stirrer, water cooled reflux condenser leading to a dry ice acetone reflux head and, an inlet tube extending to the bottom of the flask. To the inlet tube were attached a tube of BCl_3 , and a tank of dry nitrogen.

Three years later Ryschkewitz, Sisler and Harris used a slight modification of the above method to prepare N-trimethyl-B-trichloroborazine.⁴ A slight excess of BCl_3 was added, and the reaction time was extended until no more HCl was being produced. This reaction produced an almost quantitative yield of pure product, and may be

written as,



The present reaction is based on a slight modification of the method described above, and may be written as,



MATERIALS AND APPARATUS

Chlorobenzene (dried)
Methoxyamine Hydrochloride
Lecture cylinder of boron chloride
Vacuum line (Diag. 3 and 3a)
Dry Box (Diag. 2e)
Modified graduated cylinder (Diag. 2c)

The apparatus depicted by diagram 1 was then assembled. The following is a systematic account of the events leading up to the initiation of the reaction.

A. Assembly of apparatus

All the following glassware was cleaned by rinsing with distilled water, then with chromic acid, distilled water, and acetone. The assembly will be described with reference to diagram 1, the description leading from left to right.

A tank of H₂ Pure nitrogen was connected to a mercury bubbler (Diag. 2a) with rubber tubing. The bubbler in turn was connected to a column of P₂O₅ (Diag. 2b) with glass beads; the P₂O₅ tube being connected to the center assembly (Diag. 2c) with a ground glass joint. The center assembly consisted of a T-joint, one arm of which (Diag. 2d) contained a stopcock followed by a

EXPERIMENTAL

The solubility of methoxyamine hydrochloride in toluene and chlorobenzene was determined. This was done in order that it could be seen whether starting material could be separated from product on the basis of solubility alone. Methoxyamine hydrochloride was found to be insoluble in both solvents.

The apparatus depicted by diagram 1 was then assembled. The following is a systematic account of the events leading up to the initiation of the reaction.

A. Assembly of apparatus

All the following glassware was cleaned by rinsing with chromic acid, distilled water, and acetone. The assembly will be described with reference to diagram 1, the description leading from left to right.

A tank of Hi Pure nitrogen was connected to a mercury bubbler (Diag. 2a.) with rubber tubing. The bubbler in turn was connected to a column of P_2O_5 , (mixed with glass beads) the P_2O_5 tube being connected to the center assembly (Diag. 2d.) with a ground glass joint. The center assembly consisted of a T-joint, one arm of which (stem of T) contained a stopcock followed by a

ground glass joint, and the remaining arms having only ground glass joints. The T-joint was positioned with the stopcock facing down (to fit the modified graduated cylinder). A second T-joint (containing three ground glass joints), was attached horizontally to the remaining arm of the center assembly. A 250 ml., one necked boiling flask was attached vertically to this T-joint, to act as a safety flask. The remaining arm of this T-joint was attached to the BCl_3 induction tube (Diag. 2b.), which fit into a 1000 ml., three necked boiling flask. The upper neck of the flask contained a stirrer, and the remaining neck led to a reflux condenser (water cooled). A calcium chloride drying tube was attached to the top of the condenser with ground glass fittings. The drying tube was then connected to a three necked, 250 ml. boiling flask, containing NaOH (to trap any BCl_3 which did not react). This was then followed by a second NaOH trap and an H_2O bubbler. The H_2O bubbler was used to determine the nitrogen flow.

A 100 ml. graduated cylinder was modified by attaching a stopcock and ground glass joint to the top (Diag. 2c.). The modified graduated cylinder was used as a BCl_3 container.

B. Transfer of BCl_3 from lecture bottle to graduated cylinder.

14 ml. of BCl_3 was transferred from a lecture bottle to

the modified graduated cylinder using the assembly shown in figure 3. Both the lecture bottle and modified graduated cylinder were connected to the vacuum line using ground glass joints. The graduated cylinder and cold finger trap were both surrounded by dry-ice acetone baths. Stopcocks 1,2,3 and 6 were then opened, and the line was evacuated. Stopcock 1 was then closed, and stopcocks 4 and 5 opened. BCl_3 was allowed into the vacuum line,, from which it condensed into the graduated cylinder. The dry-ice acetone bath was periodically removed from the cylinder to determine the amount of BCl_3 transferred.. After about fifteen minutes the required amount had been transferred, and stopcock 4 was closed. The system was left in this state for fifteen minutes in order that the maximum amount of BCl_3 , still in the line, could be condensed into the storage cylinder. Stopcock 5 was then closed, and the storage cylinder was removed from the line, still surrounded by the dry-ice acetone bath.

C. Measuring of starting materials

All solids were measured as rapidly and accurately as possible, in order to reduce the possibility of moisture attacking them. The chlorobenzene was filtered through a CaCl_2 filter, to minimize its possible water content.

After the foregoing preparations had been completed, the apparatus was readied by connecting the BCl_3 container to the center assembly, passing dry nitrogen through the apparatus to remove moisture, and heating the reaction flask (with vigorous stirring).

When the reaction mixture reached reflux temperature, the BCl_3 stopcock was opened, allowing the BCl_3 to be slowly carried into the reaction flask by the flow of nitrogen. The vapor pressure of BCl_3 is 400 mm at $-3.6^\circ\text{C}.$, and 760 mm at $+12.7^\circ\text{C}.$ The dry-ice acetone was replaced with an ice water bath when the BCl_3 container was opened to the apparatus.

The flow of BCl_3 was regulated by raising or lowering the ice bath until a flow rate of one milliliter per fifteen minutes was achieved and maintained. After about four hours the BCl_3 was removed, the reaction flask cooled, and the apparatus left assembled.

The following day the dry nitrogen was attached to the line leading into the H_2O bubbler. Pressure was exerted, thereby forcing the liquid reaction mixture from the boiling flask into the safety flask by way of the BCl_3 induction tube. The safety flask was then removed, and immediately stoppered. The reaction train was also resealed to exclude moisture.

The separation of crystalline product from solution

was now initiated. The safety flask containing reaction product was first taken into the dry box (Diag. 2e.). The inner chamber of the dry box had previously been scourged of moisture by the presence of an open dish of P_2O_5 . The safety flask, and a second dish containing P_2O_5 , were placed in the outer chamber, and left for two hours. This was done in order that no moisture would enter the inner chamber of the dry box through the outer chamber. The inner chamber was then opened, and the safety flask was taken in. The clear liquid was then transferred to a one necked, 250 ml. boiling flask, leaving some yellow colored powdery product in the safety flask. The crystals were then scraped from the bottom of the flask, blotted on a wad of filter paper, and washed with hexane. The yield from this process was about 0.5 gms.

The boiling flask to which liquid had been transferred was then stoppered, and taken out of the dry box. This liquid was then vacuum distilled using the vacuum line as shown in diagram 3a.

The apparatus was assembled in a manner which permitted continuous use of the vacuum pump, with no chance of any substance entering the pump. The only path between solvent and pump proceeded through two dry-ice acetone cold fingers. The two cold fingers ensured the condensation of any gas

approaching the pump.

The solvent was distilled to a black residue. The residue was then washed with hexane. A small amount of yellow crystal product was seen to enter the hexane. The hexane was then vacuum distilled, as above. As a result of this distillation the crystals were lost, probably due to sublimation at low pressure.

The remainder of the solvent, which had not been distilled, was taken into the dry box and filtered through No. 1 filter paper, into a bottle. Very little product was found on the filter paper. (less than 0.1 gms.) The solvent was transferred from the bottle to a boiling flask, and the bottle was left in the dry box. After two days a white powder product was found in the bottom of the bottle. This product came from the slow evaporation of the small amount of liquid left in the bottle. Approximately 0.05 gms. of product were obtained in this way, this product being used for an infra-red spectrum. The spectrum obtained in this way was the best defined of all from the this reaction.

Qualitative tests to determine the presence of boron and chlorine were carried out on the reaction product. A positive test for boron was made by dissolving a small amount of product in dilute hydrochloric acid, titrating to a phenolphthalein end point with a dilute solution of sodium hydroxide, and adding mannitol. Upon the addition of mannitol

the phenolphthalein color dissapeared, indicating the presence of boron. A positive test for chlorine was then made by dissolving a small amount of product in dilute nitric acid, adding some silver nitrate solution, and observing the precipitation of white crystals. The white crystals were found to be soluble in ammonium hydroxide, indicating the presence of chlorine.

A determination of the amount of boron chloride which passed through the reaction was made. This was done by testing the solution in the two sodium hydroxide traps for boron in the manner described above.

RESULTS

The Infra-Red spectra of the reaction product of BCl_3 and methoxyamine hydrochloride, N-trimethyl-B-trichloro-borazine, methoxyamine hydrochloride and, the addition compound $\text{MeNH}_2\text{-BCl}_3$. All figures are in μ .

Reaction Product	$\text{B}_3\text{Cl}_3\text{N}_3\text{Me}_3$	MeONH_2HCl	$\text{MeNH}_2\text{-BCl}_3$
	2.95s		
✓ [*] 3.15sb	3.20sb	3.3-4.0 (H-Bonding)	3.10s 3.80vw
4.45vw		4.60vw 5.30s	
[*] 6.20sh	6.20w	6.3-7.2	6.40s
^{**} 7.10sb	7.10mb		6.90m 7.05w 7.50s
	8.10m	7.90m	
^{††} 8.40m		8.50s (Methoxy group) ⁵	
^{**††} 9.20wb	9.20m		9.10m
[†] 9.80wb	9.80m	9.9s	
[†] 10.90w	10.90mb		10.10s
11.40w		11.50s	
12.50s			11.80s
^{†††} 15.40w	14.30vw		13.50mb 15.20s (BCl mode)

- ^{*} In agreement with $\text{B}_3\text{Cl}_3\text{N}_3\text{Me}_3$
^{††} In agreement with MeONH_2HCl
^{†††} In agreement with adduct $\text{MeNH}_2\text{-BCl}_3$
^{*} Wavelength assigned to CH_3N ⁶
^{**} NH in plane bending wavelength⁷

DISCUSSION

The reaction of methoxyamine hydrochloride with boron chloride was carried out three times. The first reaction was carried out in toluene, while the last two reactions were carried out in chlorobenzene. The solvent was changed to chlorobenzene because of the great amount of black residue formed in the toluene. In all of the cases very little reaction product was obtained. This was attributed to the fact that the product was very easily sublimed. It is suggested that a further reaction be performed in hexane as a solvent. Upon completion of the reaction, the product should be separated using vacuum techniques. The vacuum used should be no greater than that needed to evaporate the hexane. If the pressure is not made too great there is a possibility that the reaction product will not sublime, thus giving a substantially better yield than that obtained in the past.

All the infra-red spectra reported were made from potassium bromide pellets. Additional spectra were obtained using a Nujol mol. In all cases the spectra made with Nujol were poorly defined. A satisfactory explanation for this error has not been arrived at.

The reaction product from the second reaction gave

infra-red spectra which were of very poor quality when compared with the spectra of the first and third products. The reason for this deviation has not been ascertained.

The first and third reaction products gave spectra which were identical in peak position and intensity. The spectrum, shown on page 17, was made on the third reaction product.

The evidence supporting the hypothesis that the reaction product is N-trimethoxy-B-trichloroborazine will now be discussed.

The reaction product was characterized using spectra obtained by Philipp Schuessler⁸. Mr. Schuessler prepared both an adduct and a borazine, which are the methyl analogs of the possible reaction products. These spectra may be found on page 18 of this report.

When the infra-red spectra of B-trichloro-N-trimethylborazine and the reaction product were compared, the positions of six spectral peaks were found to be in agreement. These six points occurred at 3.15 μ , 6.20 μ , 7.10 μ , 9.20 μ , 9.80 μ and 10.90 μ .

The points listed above are the strongest evidence obtained to support the hypothesis that the reaction product is in actuality the Borazine.

Other evidence to suggest the presence of the borazole included the presence of the wavelength generally assigned to the methoxy group (8.40)⁵. This evidence may also suggest the

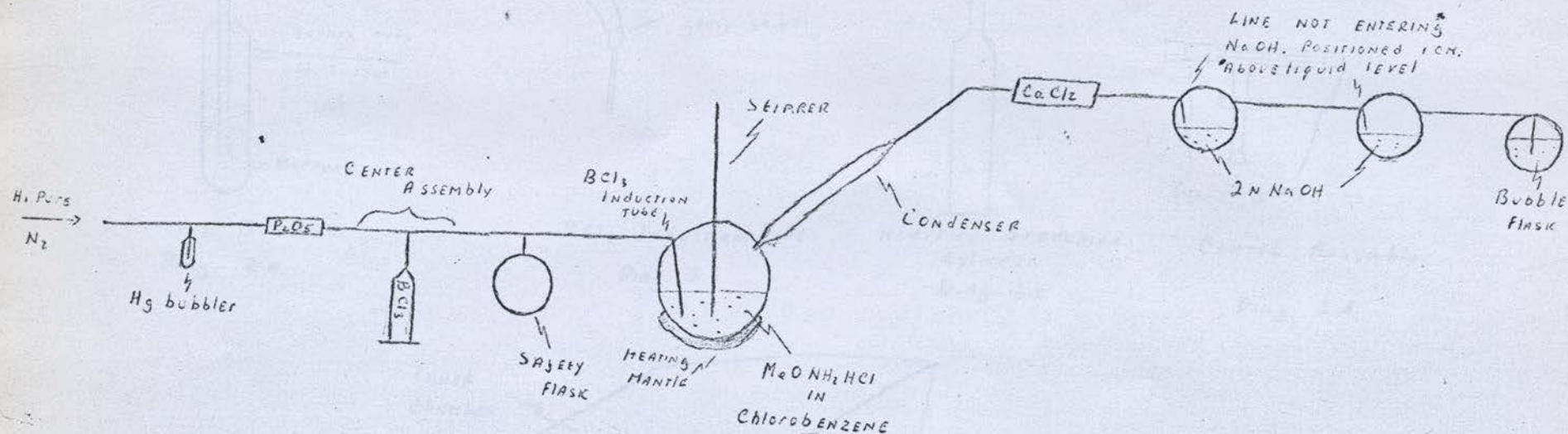
adduct $\text{MeONH}_2\text{-BCl}_3$.

The following evidence supported the presence of the adduct, which made it impossible to state that the reaction product was definitely the borazine desired.

The spectrum of the reaction product showed agreement with the adduct at 15.40μ . This is not a clear cut agreement due to the differing nature of the two peaks. The reaction product showed a very small peak, while the adduct exhibited a large peak at this wavelength. The spectrum of the reaction product also had a peak corresponding to NH in plane bending $(9.24)^7$, which is characteristic of the adduct, and not characteristic of the borazine.

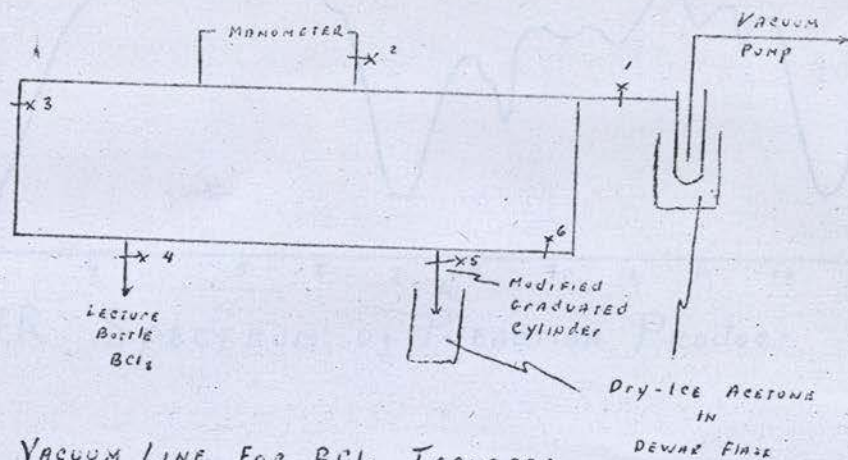
The qualitative tests for boron and chlorine did not shed any new light on the characterization of the product as borazine or adduct.

The general trend of the information above indicates the presence of a borazine product, but the evidence supporting the presence of adduct discount the definite characterization of the product as N-trimethoxy-B-trichloroborazine.

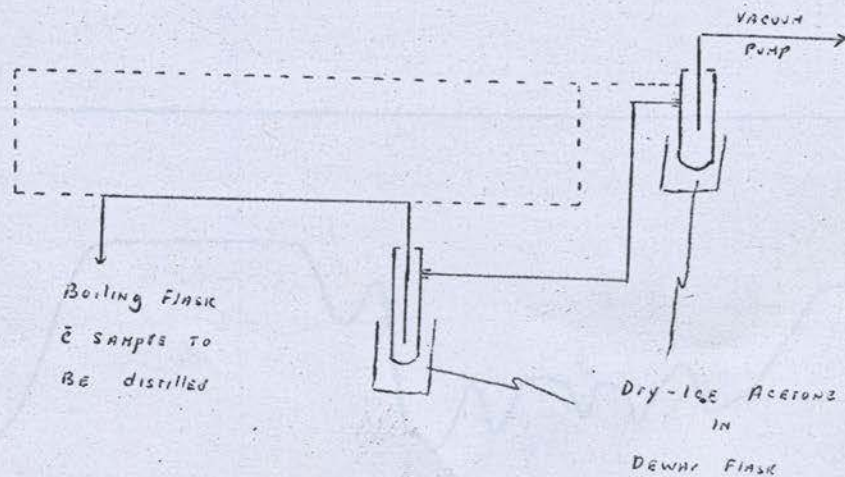


Apparatus For the Reaction of Boron Chloride With Methoxyamine Hydrochloride

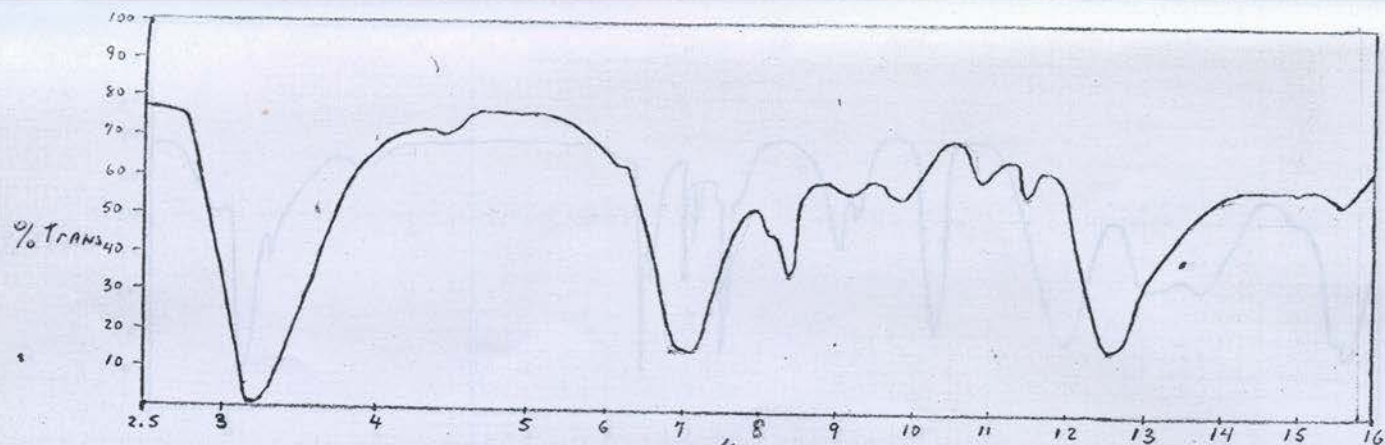
Diagram 1.



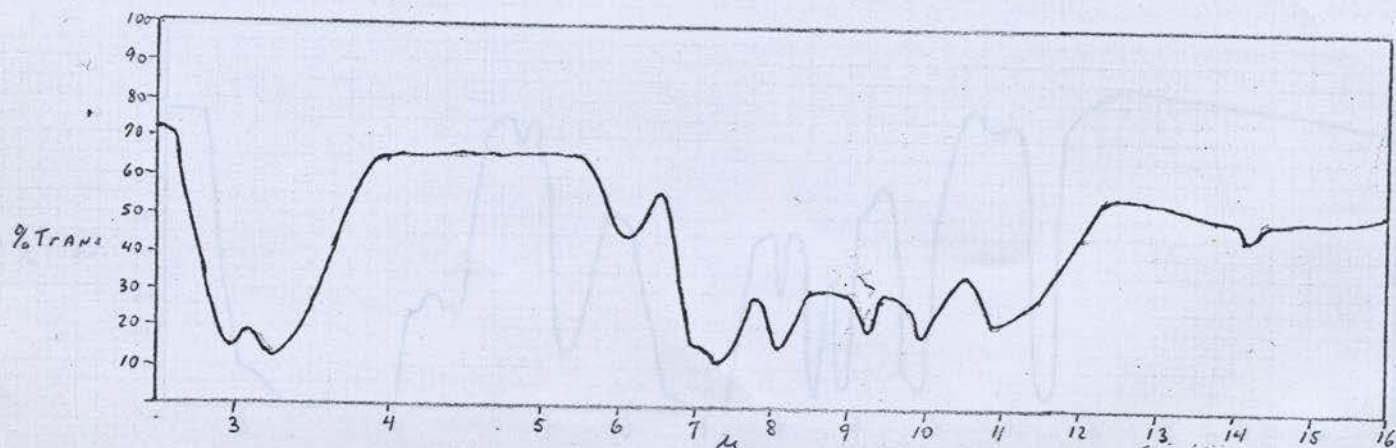
VACUUM LINE FOR BCl_3 TRANSFER
 Diag. 3



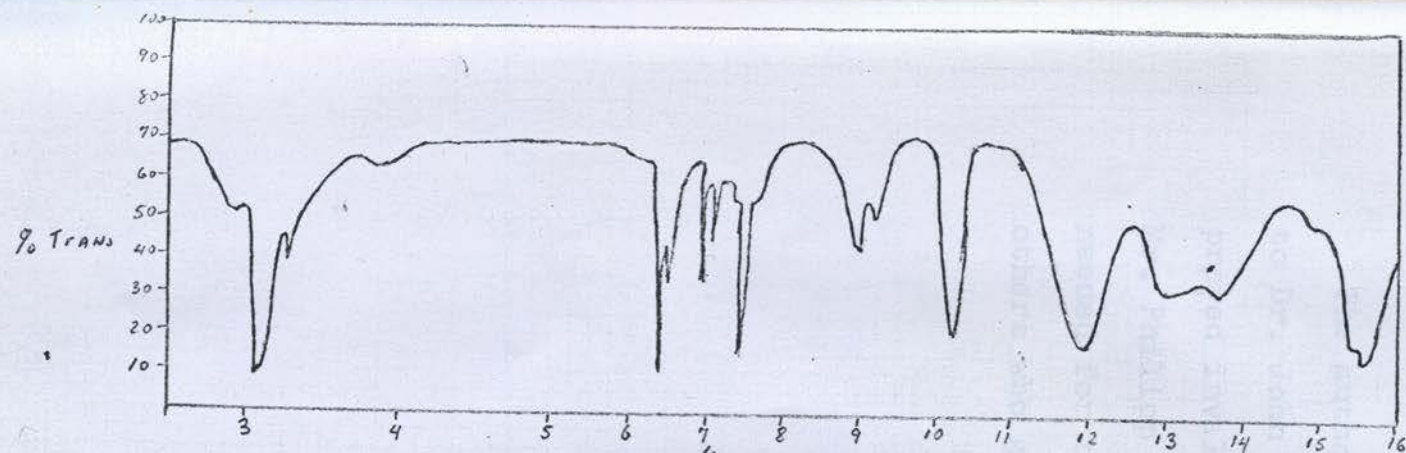
VACUUM LINE FOR DISTILLATION
 Diag. 3a



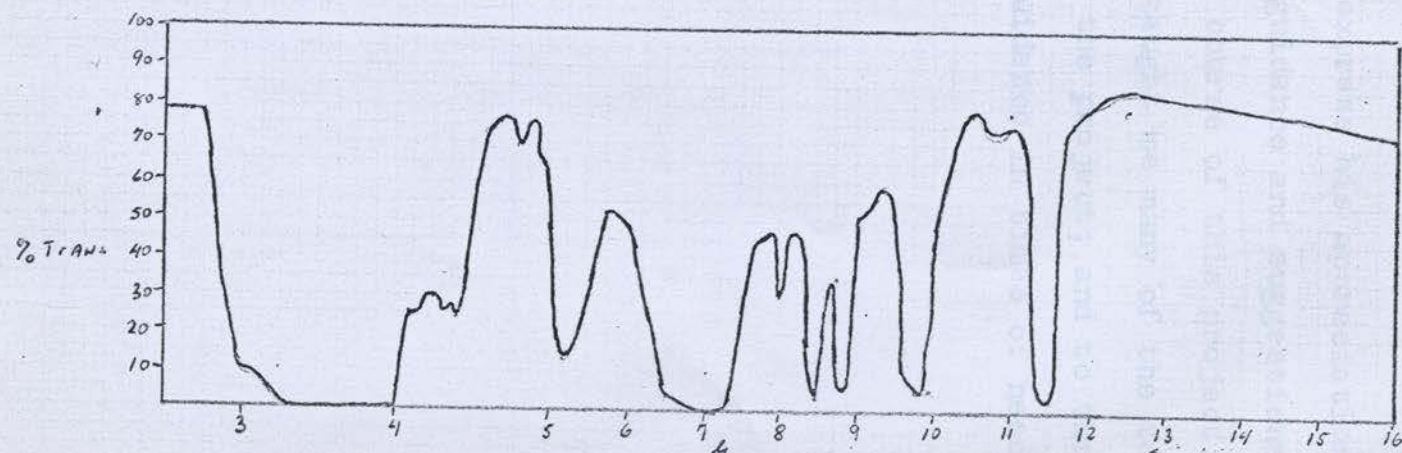
I.R. SPECTRUM of REACTION PRODUCT



I.R. SPECTRUM of $B_3Cl_3N_3ME_3$



I.R. SPECTRUM of $\text{MeNH}_2\text{-BCl}_3$



I.R. SPECTRUM of $\text{MeONH}_2\text{.HCl}$

ACKNOWLEDGEMENTS

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FOOTNOTES

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- ² E. Wiberg and K. Hertwig, Z. Anorg. Chem., 225, 141 (1947)
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- ⁸ Schuessler, Philipp W.H., The Synthesis of B-Trichloro-N-Trimethyl Borazine and its Reaction with Chromium Hexacarbonyl, Rochester Institute of Technology, Rochester, New York, 1966, p. 23
- ⁹ Ibid. p. 22

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