SYNTHESIS OF METHYL CHLORSILANES

A thesis presented to the Chemistry Department of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

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ABSTRACT

The reaction of methyl magnesium chloride and methyl magnesium iodide with silicochloroform gave a mixture of methyl dichlorsilane, dimethyl chlorsilane, trimethyl silane, and an unidentified high boiling liquid which gave no chlorine on analysis.

The addition of the grignard reagent to silicochloroform in a one to one molar ratio gave a mixture of the methyl derivatives. The addition of grignard to silicochloroform in a two to one molar ratio gave the di and tri methyl derivatives. The reverse addition gave nearly all trimethyl silane.

INTRODUCTION

In 1901, Kipping began his intensive studies of organosilicon compounds, continuing and enlarging upon the work of such great nineteenth century investigators as Friedel, Crafts, and Ladenburg [1]. However, due to the lack of simple inexpensive methods of synthesis, it was not until nearly 1940 that large scale studies of these compounds and their properties were initiated. Even with this accelerated program of research, some reactions of organic reagents with silicon compounds have been neglected or deemed of such little importance that little mention of them has been made in the literature. One such reaction is that of methyl magnesium halide, the well-known and much used grignard reagent, with silicochloroform. It was the purpose of this investigation to study the synthesis of methyl chlorosilanes using this reagent.

This method of synthesis, first used by Kipping [2] and Dilthey [3], has become the classic preparation of organosilicon compounds and may be represented as

$$nRMgX \not- mHSiCl_3 = RHSiCl_2 \not- R_2HSiCl \not- R_3HSi \not- nMgClX$$

where R is any organic radical such as CH_3- or C_2H_5- and X is any member of the halogen family with the exception of fluorine. This reaction has the advantages of being easily carried out at ordinary temperatures and pressures, in a solution of a suitable solvent, without the need of complicated apparatus.

While trimethyl silane [4] and methyl dichlorsilane [5] have both been reported in the literature, at this writing dimethyl chlorsilane has not been isolated as such. Emeleus and Robinson [5] attempted to make this compound using the above reaction and succeeded in isolating methyl dichlorsilane. However, due to the lack of an efficient still, they did not succeed in separating dimethyl chlorsilane from silicochloroform. The present work attempted to separate and identify this compound.

EXPERIMENTAL

Reagents

The n-butyl ether was obtained from the Eastman Company, Rochester, New York. Peroxides were removed by shaking with aqueous ferrous sulfate [6], other impurities (predominantly alcohols and other grignard-destroying compounds) removed by addition of phenyl magnesium bromide and distillation of the ether from the grignard. The purified ether was stored over freshly pressed metallic sodium ribbons.

Part of the silicochloroform was obtained from the General Electric Company, Schenectady, New York. It was fractionated on a 27 theoretical plate Fenske column, using a mixture of dry ice and acetone to condense the vapor, and the fraction boiling from 31.8 to 32°C and analysing 77.4% chlorine (theoretical 78.6%) was used for experimental work. The rest of the silicochloroform was made from copper-silicon powders, pressed into bars, by passing hydrogen chloride gas over the pressed powders at 300°C [7]. This process yielded a mixture of chlorosilanes which was fractionated and the fraction boiling from 31.5 to 32.5°C used for experimental work.

The methyl iodide was made by the dropwise addition of dimethyl sulfate to aqueous potassium iodide with constant removal of the methyl iodide as it was formed [8]. The product boiled from 42.1 to 42.5°C after having been dried over anhydrous calcium chloride for two days.

The methyl chloride was the commercial compressed gas, obtained from the Matheson Company, Rutherford, New Jersey.

Preparation of the grignard reagent.

The apparatus for the preparation of methyl magnesium chloride from methyl chloride consisted of a five liter, four necked flask, fitted with a mercury-seal stirrer, a thermometer, a gas inlet tube that reached to the bottom of the flask, and a mercury valve. A liquid trap and a flow indicator were connected to the gas inlet tube, these in turn being connected to the needle valve on a tank of compressed methyl chloride gas. The mercury valve served a double purpose; to keep moist, carbon dioxide-laden air from entering the reaction system and to increase the internal pressure of the system, thus increasing the solubility of the methyl chloride gas in the solvent. Pressure tubing was used for all glass to glass connections.

Some difficulties were encountered with this apparatus. It was necessary to control the flow of methyl chloride gas with extreme care in order to maintain a constant pressure within the system as fluctuations in the internal pressure caused mercury to be pushed into the reaction flask from the stirrer. Careful control of the temperature of the system was also necessary to minimize the effect of the solvent vapor on the system's internal pressure.

Because of the low boiling points of the products (Table I), a high boiling solvent, di-n-butyl ether, was used. However, because of the seeming insolubility of methyl magnesium chloride in this solvent, it was necessary to use large amounts of solvent and to double the molar amount of magnesium needed. Table II summarizes the results of the grignard preparations.

TABLE I

Compound	Boiling Point, °C	Mol. Wt.	% Cl (calc.)
$HSiCl_3$	32	135.45	78.5
CH_3SiHCl_2	42	115.00	61.7
$(CH_3)_2SiHCl$	34-8	94.57	37.5
$(CH_3)_3SiH$	12	74.13	0

TABLE II

Run No.	Methyl Halide	Vol. Solvent for Grignard	Mols Mg	Mols Grignard
1	CH_3Cl	1000 ml.	2	* - -
2	"	3000 ml.	2	1
3	"	3000 ml.	2	.9
4	CH_3I	1000 ml.	1	1
5	"	1000 ml.	1	1

* Unreacted magnesium not weighed

The preparation of the methyl magnesium chloride was carried out as follows: with the mercury-seal stirrer off, approximately one ml. of methyl iodide was added with a pipette to the butyl ether-magnesium mixture in the flask, the tip of the pipette having been thrust into the magnesium turnings. After sealing the system and starting the stirrer, the temperature of the reaction mixture was raised to 100°C and the flow of methyl chloride started and adjusted to a moderate rate. After the reaction was underway, the flow of methyl chloride was varied to maintain a nearly constant pressure within the system as explained above. After about half of the magnesium had reacted, no further reaction took place. The suspension of grignard was siphoned off and the unreacted magnesium recovered and weighed to determine the amount of grignard formed.

Because of the difficulties inherent in the foregoing procedure, a more convenient method of grignard preparation was sought. Methyl iodide, because of its extreme reactivity with magnesium, was chosen as the methyl halide. The apparatus consisted of a two liter, three-necked flask, fitted with a mercury-seal stirrer, separatory funnel for dropwise addition of methyl iodide, and a reflux condenser, cooled with a brine ice mixture circulated with a centrifugal pump. The system was protected from moisture and carbon dioxide by a calcium chloride-soda lime mixture in a calcium chloride tube at the top of the condenser tube. By using this method, the amount of solvent needed was reduced and the reaction proceeded more rapidly and to a greater degree.

The methyl iodide was added to the ether-magnesium mixture over a period of two hours. Initially, external heat was applied by a steam bath but it became necessary to cool the reaction mixture with an ice bath as the reaction proceeded quite rapidly with the evolution of heat. When the addition was completed, the reaction mixture was heated on a steam bath for one hour after which only a small amount of fine magnesium particles were left in the flask. The methyl magnesium iodide was much more soluable in butyl ether than was the methyl magnesium chloride, the former giving a grey solution and the latter giving a suspension of white particles. The ease of preparing methyl magnesium iodide made this method the desirable one to use.

Reaction of silicochloroform with methyl grignard.

In order to study the effect of the order of addition, the first run was made by adding the silicochloroform to the grignard reagent while the other four were made by adding the grignard reagent to silicochloroform (Table III).

TABLE III

Run No.	Mols Grignard	Mols $HSiCl_3$	Vol. Solvent for $HSiCl_3$	Addition
1	- -	2	200 ml.	$HSiCl_3$ to grignard
2	1	1	100 ml.	Grignard to $HSiCl_3$
3	.9	.9	100 ml.	" " "
4	1	1	100 ml.	" " "
5	1	1	100 ml.	" " "

The grignard reagent was placed in a five liter, four-necked flask, fitted with a mercury-seal stirrer, thermometer, separatory funnel for dropwise addition of silicochloroform, and a reflux condenser connected to a trap cooled with a mixture of acetone and dry ice. After the reaction flask and grignard had been cooled to 5°C in an ice bath, the silicochloroform, dissolved in butyl ether, was added slowly with constant stirring. The reaction mixture was then heated on a steam bath for two hours to insure complete reaction. The low boiling materials were then driven off by heating the reaction mixture in an oil bath. All materials boiling below 142°C were collected in the dry ice trap. These low boiling materials were fractionated through a 48 inch Fenske column having an efficiency of 27 theoretical plates. For a description of this still, see the appendix, page 17. The data of this run are given in Table IV.

TABLE IV - RUN 1

Cut No.	Boiling Point °C	Vol.	Wt.	% Cl Obs.	% Cl Calc.*	Product
1	6.5-11.5	60 ml.	44 g.	2.13	0.0	$(CH_3)_3SiH$
2	11.5-31.6	6 ml.	16 g.			
3	31.6-34	30 ml.	26 g.			$HSiCl_3$
4	34.0-49.3	5 ml.	13 g.			
5	49.3-71	40 ml.	16 g.			
6	71-74	6 ml.	9.4 g.	0	- -	High boiler
7	74-78	160 ml.	101 g.	0	- -	High boiler

*Incomplete because of evaporation of cuts through the caps of storage bottles.

The chlorine analyses were carried out in the following manner: the sample to be analysed was weighed in a cork-stoppered glass vial and cooled in a brine-ice mixture to decrease the volatility of the chlorosilanes. The vial was then unstoppered and the cork, quickly followed by vial and sample, dropped into a glass stoppered Erlenmeyer flask containing an ethyl ether-ice mixture. The contents of the flask were then gently swirled for several seconds and the HCl in the water layer titrated with standard sodium hydroxide using methyl red as the indicator. It was found that the initial end point was not the true one as the complete hydrolysis of the chlorosilanes did not take place immediately. However, with alternate shaking and standing of the ether-water mixture, an end point was reached that did not change upon further standing.

The most interesting of the products was cut 7 (Table IV). This was a clear liquid having no hydrolysable chlorine. It was found to be insoluable in water, sodium hydroxide, and sulfuric acid, while it was soluable in ethyl ether. Active hydrogen analysis [9] gave a value of 0.289% by weight. Several suggestions have been made as to the identity of this compound, the two most logical of these being hexamethyl disiloxane and tetramethyl disiloxane but no conclusions can be drawn until an ultimate quantitative analysis of the compound has been made.

An effort was made to partially identify this compound by means of the molar refraction. The theoretical molar refraction was calculated from the data of Sauer [10] and for tetramethyl disiloxane, it was found to be 40.22. The observed value of the molar refraction was 37.0. The calculations were made as follows, from Sauer's data:

$$r_D\ (SiCH_3) = 7.57$$

$$r_D\ (Si\text{-}O) = 1.75$$

$$r_D\ (Si\text{-}H) = 3.22$$

$$4\ r_D(Si\text{-}CH_3) = 4 \times 7.57 = 30.28$$

$$2\ r_D(Si\text{-}O) = 2 \times 1.75 = 3.50$$

$$2\ r_D(Si\text{-}H) = 2 \times 3.22 = 6.44$$

$$\text{Total} = 40.22$$

For the high boiling compound, considering it as tetramethyl siloxane for a value of the molecular weight

$$n_D^{25^\circ} = 1.3990$$

$$d^{25^\circ} = 0.877$$

$$r = \frac{1}{d}\,\frac{n^2-1}{n^2+2}$$

where r = specific refraction

n = refractive index

d = density

$$r = \frac{1}{0.877} \times \frac{(1.399)^2-1}{(1.399)^2+2} = .0276$$

Molar refraction = Mr = 134 x 0.276 = 37.0

These values are not close enough for positive identification but they do agree fairly well.

The same apparatus and procedure were used for the second run as were used for the first run, with the exception that the order of addition was reversed (Table III). The data of run 2 are given in Table V.

TABLE V - RUN 2

Cut No.	Boiling Point °C	Vol.	Wt.	% Cl Obs.	% Cl Calc.	Product
1	13-15	12 ml.	- -	- -	0.0	$(CH_3)_3SiH$
2	15-29.0	15 ml.	15 g.	- -	- -	
3	29.0-34	10 ml.	12.2 g.	46.0	78.5	$HSiCl_3$
4	34-36	8 ml.	11 g.	- -	- -	
5	36-38	10 ml.	13 g.	33.0	37.5	$(CH_3)_2SiHCl$
6	38-45	5 ml.	6.2 g.	57.4	61.7	CH_3SiHCl_2
7	45-74.8	20 ml.	18 g.	18.2	- -	- - - -

The same apparatus and procedure were also used for run 3 as were used for run 2. However, the reaction mixture stood for an extended period of time from the time of addition until fractionation. When finally fractionated, only a small amount of low boiling material was obtained. After about fifteen ml. of trimethyl silane had been recovered, the boiling point rose rapidly and passed completely through the boiling point range of the desired products to give mostly the high boiling liquid noted before.

The same apparatus and procedure were also used for run 4. Methyl magnesium iodide was used as the grignard reagent instead of methyl magnesium chloride. The data of run 4 are given in Table VI.

TABLE VI - RUN 4

Cut No.	Boiling Point °C	Vol.	Wt.	% Cl Obs.	% Cl Calc.	Product
1	18-19.5	8 ml.	- -	5.2	0.0	$(CH_3)_3SiH$
2	19.5-28.2	18 ml.	16.2 g.			
3	28.2-33.9	12 ml.	14 g.	67.3	78.5	$HSiCl_3$
4	33.9-37	7 ml.	9.8 g.	32.1	37.5	$(CH_3)_2SiHCl$
5	37-38.6	11 ml.	13.7 g.	- -	- -	
6	38.6-46.4	7 ml.	7.1 g.	56.2	61.7	CH_3SiHCl_3
7	46.4-66.2	4 ml.	4.6 g.	16.3	- -	
8	66.2-112	14 ml.	16 g.	- -	- -	

The same apparatus and procedure were used for run 5 as were used for run 4. The molar ratio of grignard reagent to silicochloroform was 2 to 1 instead of 1 to 1 (Table III). The data of run 5 are given in Table VII.

TABLE VII - RUN 5

Cut No.	Boiling Point °C	Vol.	Wt.	% Cl Obs.	% Cl Calc.	Product
1	8-11.7	30 ml.	23 g.	2.73	0.0	$(CH_3)_3SiH$
2	11.7-29.1	7 ml.	9.1 g.	38.3	- -	
3	29.1-30.2	13 ml.	13.8 g.	62.0	78.5	$HSiCl_3$
4	30.2-42	10 ml.	14.9 g.	32.5	37.5	$(CH_3)_2SiHCl$
5	42-89.6	13 ml.	42 g.	9.33	- -	

DISCUSSION OF RESULTS

TABLE VIII

	Product	Mol Percent	% Grignard Acc'ted for	% $HSiCl_3$ Acc'ted for
Run 1:	$(CH_3)_3SiH$	59.4		
	$HSiCl_3$	19.3	89.1	39.35
Run 2:	$(CH_3)_3SiH$	10.8		
	$HSiCl_3$	7.38		
	CH_3SiHCl_2	4.14		
	$(CH_3)_2SiHCl$	13.0	62.54	35.32
Run 4:	$(CH_3)_3SiH$	22.5		
	$HSiCl_3$	10.3		
	CH_3SiHCl_2	6.16		
	$(CH_3)_2SiHCl$	10.4	94.46	49.36
Run 5:	$(CH_3)_3SiH$	31.0		
	$HSiCl_3$	10.2	103.2*	41.2

* Probably part $HSiCl_3$ calculated as $(CH_3)_3SiH$.

Table VIII contains the calculated molar percent of products, taking into account only those cuts identified by boiling points and chlorine analyses. In every case, recovery of products based on silicochloroform is not 100%. However, in all cases except run 2, nearly all of the grignard may be accounted for. Because the intermediate cuts were of doubtful composition, no effort was made to calculate their effect on the total of recovered products.

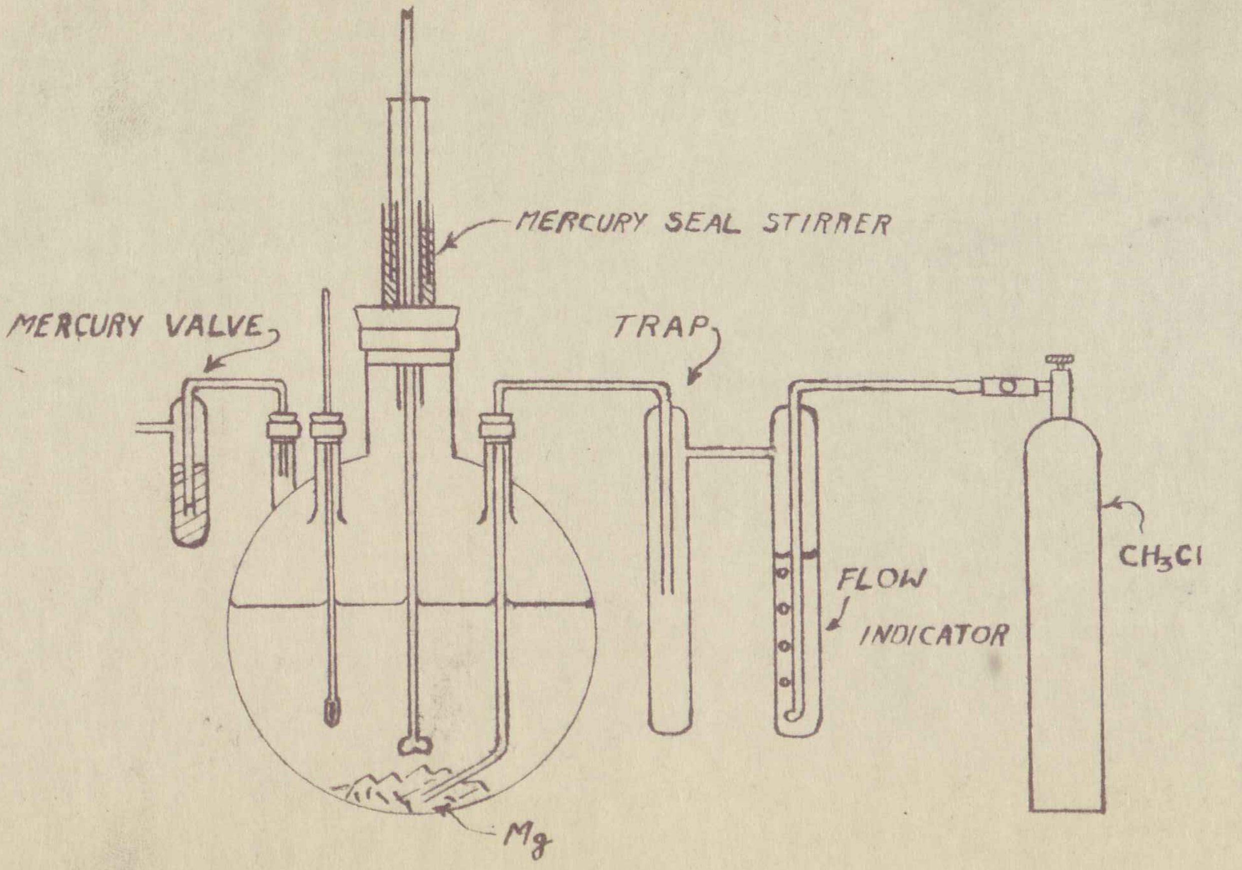
By comparing runs 1, 2, and 4, it is apparent that the addition of silicochloroform to the grignard reagent favors the formation of trimethyl silane. This is to be expected as the initial concentration of grignard is high for this order of addition and should give polysubstitution.

By comparing runs 2 and 4, it is apparent that the reverse order of addition (i.e., the grignard to the silicochloroform), although still giving predominantly trimethyl silane, affords a method of preparing the mono- and disubstituted products. While the chlorine analyses were low in all cases, there was good agreement between the two runs as to the formation of the mono- and disubstituted products. A definite trend was noticed in the chlorine analyses in that they were initially low, rose to a maximum for the silicochloroform cut, then dropped off for the dimethyl chlorsilane cut, and rose again for the methyl dichlorsilane. This indicated the presence of the mono- and disubstituted products. Some loss of chlorine was noted in the method of analysis when the glass vial was unstoppered. A strong odor of HCl was noticed immediately. Perhaps this difficulty could be remedied by using a solvent (butyl ether) to decrease the vapor pressure of the samples and thus make the analyses more exact.

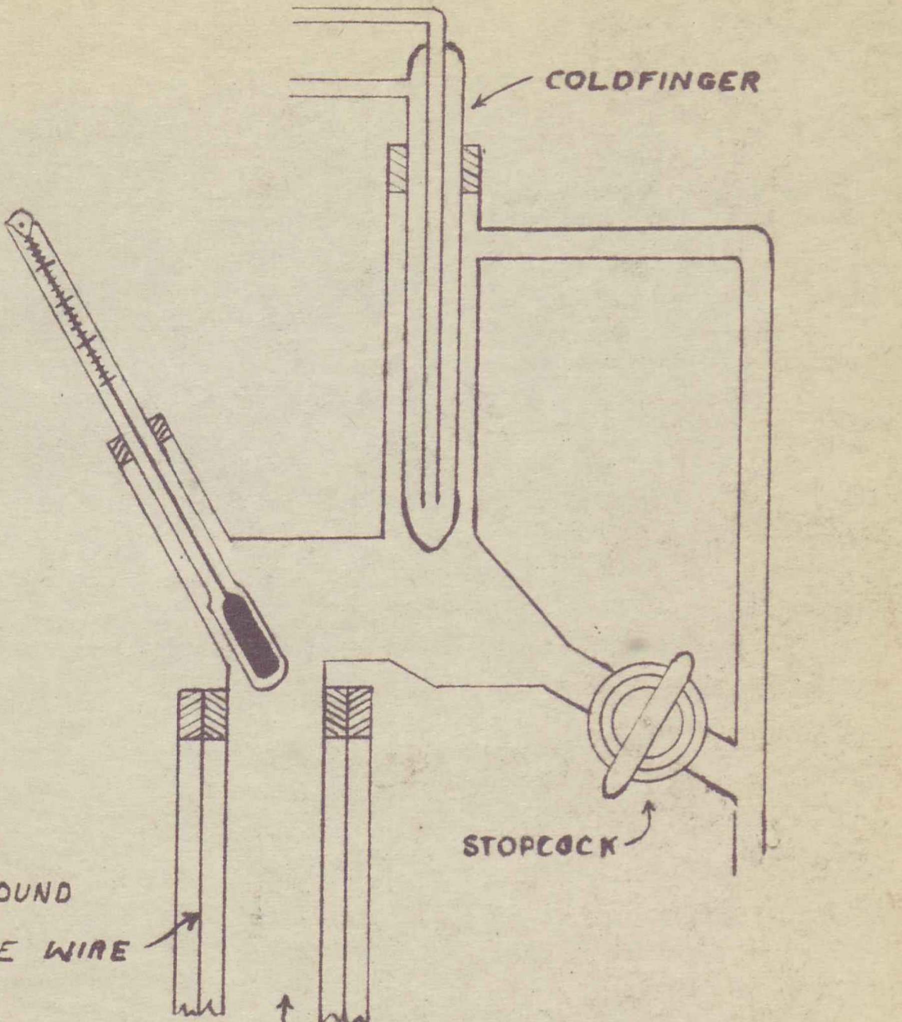
An explanation for the low recovery of silicochloroform could be the adsorption of this material on the magnesium halide formed in the reaction. This seems even more likely when one considers the reaction noted when water was added to the ether-magnesium halide mixture after stripping off the low boiling materials. This reaction was violently exothermic and was noted in all runs.

SUMMARY

The reaction of methyl grignard with silicochloroform was studied. Trimethyl silane was prepared by the addition of silicochloroform to methyl grignard. The mono- and disubstituted methyl chlorosilanes were prepared by reversing this order of addition. An unidentified high boiling liquid was obtained in all runs.

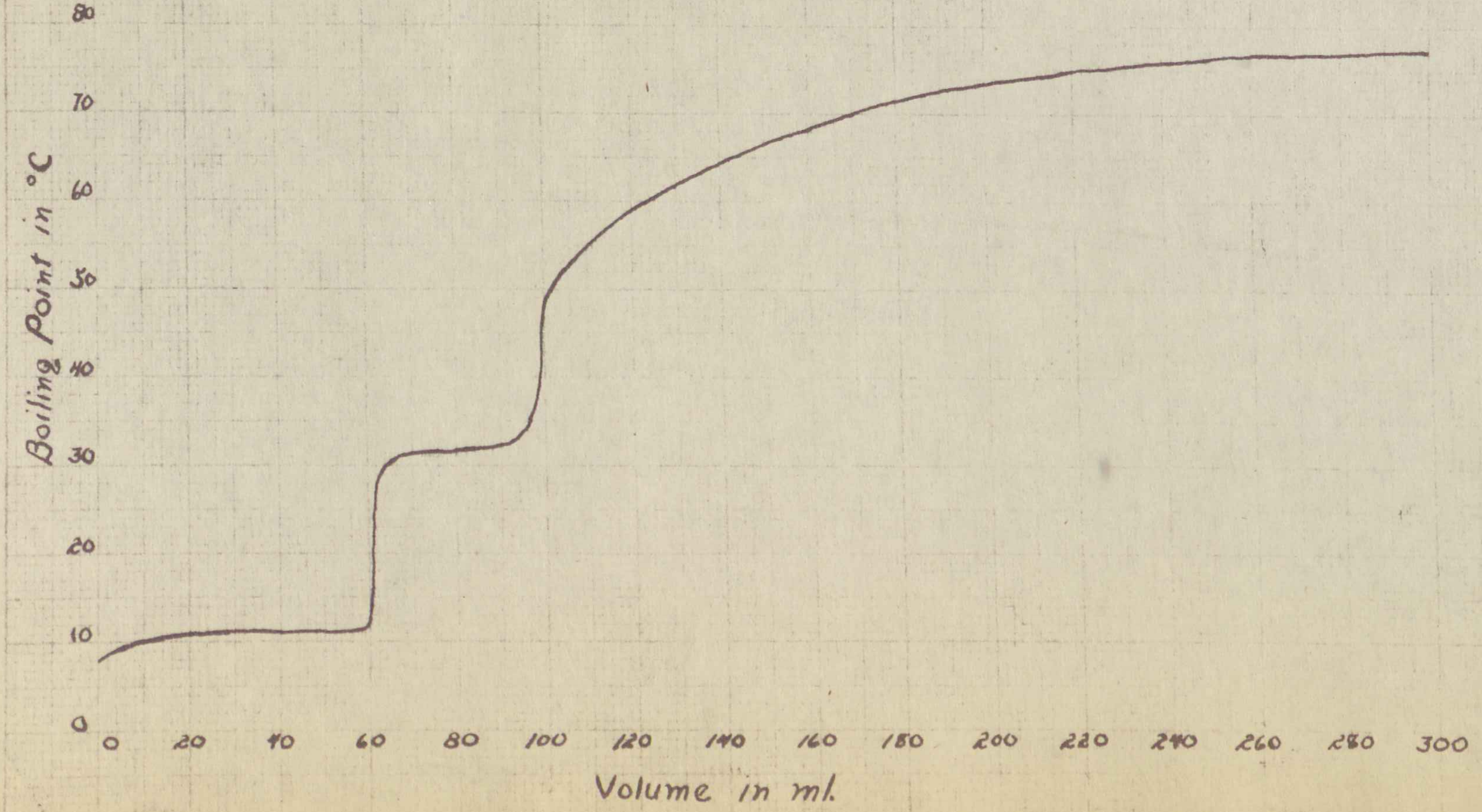


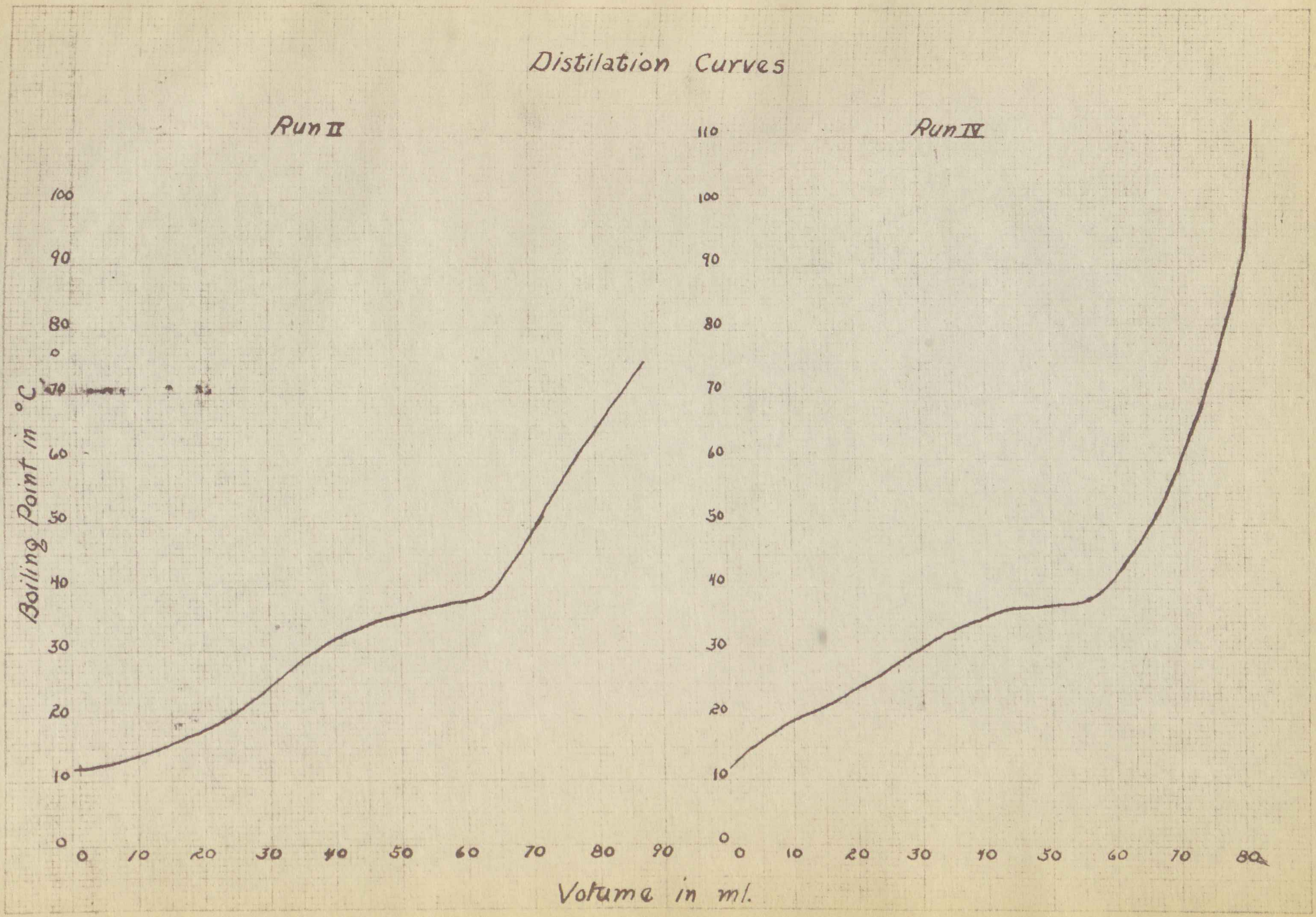
APPARATUS FOR MAKING CH_3MgCl



FRACTIONATING
COLUMN

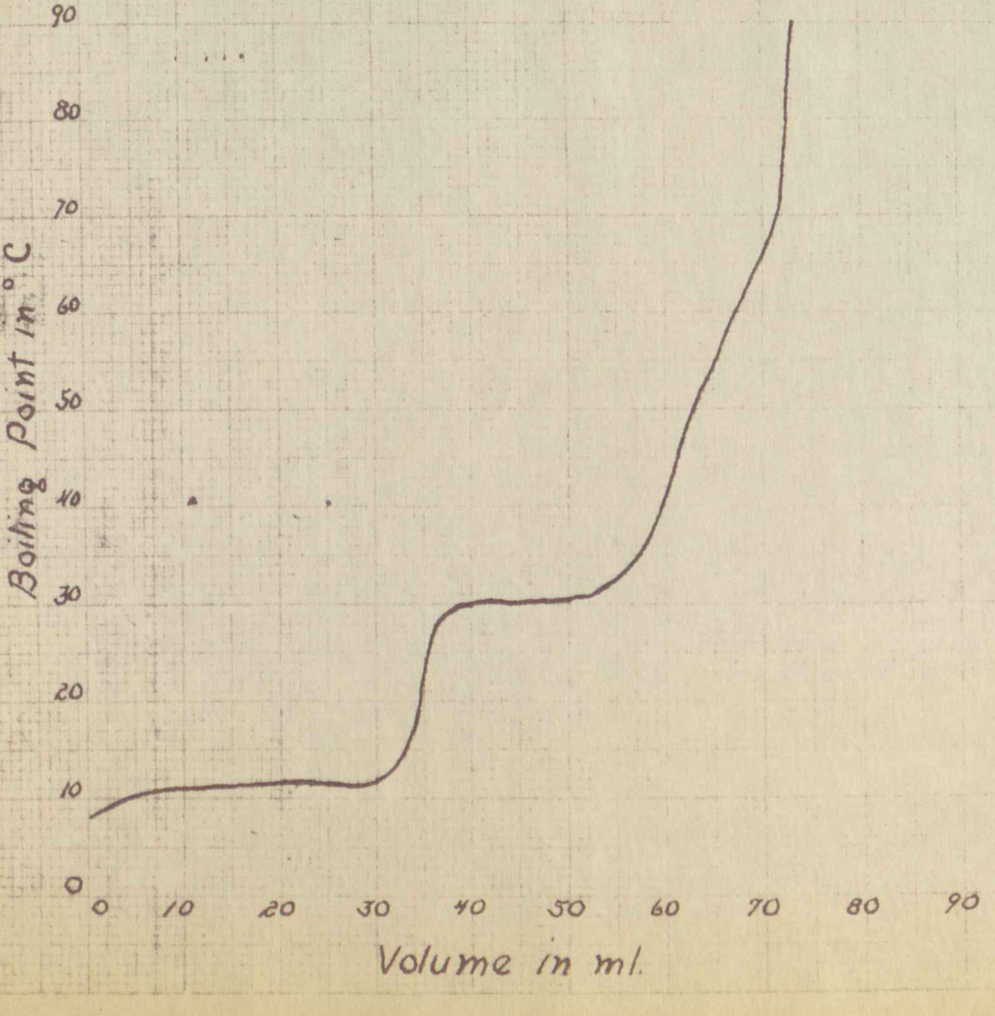
Distilation Curve
Run 1





Distilation Curves

Distilation Curve
Run V



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