

6-1946

Degree of substitution in Ethylchlorosilanes

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DEGREE OF SUBSTITUTION IN ETHYLCHLOROSILANES

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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.

Written by Charles Guare

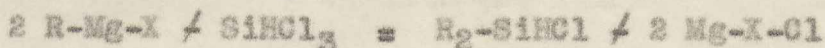
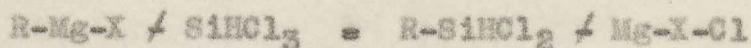
Approved by Howard E. Sheffer

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ABSTRACT

When an organo-magnesium halide is reacted with an excess of trichlorosilane, a mixture of products results according to the equations



wherein R = an alkyl or aryl group

X = a halogen, usually Br or Cl.

If phenyl magnesium bromide is used, a mixture of high boiling products results, the highest boiling point of which is approximately 250°C at 14 mm. pressure.

If ethyl magnesium bromide is used, it may be shown that, making certain assumptions and under the conditions of the experiment, if the ethyl magnesium bromide is added to the trichlorosilane, monosubstitution is promoted, whereas if the trichlorosilane is added to the ethyl magnesium bromide, polysubstitution is promoted.

Sept. 14, 1949

thesis

INTRODUCTION

An organo-silicon compound is a compound which has the carbon atom of an organic radical attached directly to a silicon atom. Although this type of compound has been known for about the past ninety years, their investigation on a sizeable scale did not begin until rather recently. Even the literature of the early part of this decade revealed meager information on organo-silicon compounds, and so, in January of 1948, a problem was offered in the synthesis of the phenyl derivatives of trichlorosilane by means of a reaction between phenyl magnesium bromide and trichlorosilane.

However, work was not long in progress when a paper ¹ appeared describing the synthesis and identification of those particular compounds; therefore, an alternate problem was proposed. The object of this alternative was to study the effect produced upon the amount of polysubstitution by varying the order in which ethyl magnesium bromide and trichlorosilane are added to each other.

In the past years, experience and theory ² showed that a reaction similar to this of SiCl_4 with two moles of methyl grignard should yield predominantly disubstitution product, $(\text{CH}_3)_2\text{SiCl}_2$. But it was thought that conditions could be set up to control the amount of substitution in some degree. If, at any time, there is a large number of trichlorosilane molecules competing for the ethyl groups on a small number of ethyl magnesium bromide molecules present, monosubstitution

should be promoted and $C_2H_5SiHCl_2$ should be produced in the majority; but, if the situation is reversed and there are more than enough ethyl groups to satisfy the demands of each trichlorosilane molecule, polysubstitution should be promoted and $(C_2H_5)_2SiHCl$ and $(C_2H_5)_3SiH$ should be formed.

DESCRIPTION OF APPARATUS AND PROCEDURE

There were two possibilities for getting the necessary trichlorosilane -- buying it or making it. Some was purchased from the General Electric Company in Schenectady through its educational sales division, but this proved rather expensive and it was made more cheaply. A satisfactory method ³ was the passing of HCl gas over a mixture of silicon and copper powders, pressed into small, porous bars which were broken into convenient sized pieces and held at a temperature of 300 plus or minus twenty degrees centigrade. The products were collected in a trap cooled in a dry ice-acetone bath and then fractionated. That fraction boiling between 31.5°C and 32.5°C, about three-fourths of the yield, was collected and used for the reaction.

Both the phenyl and the ethyl magnesium bromides were prepared in the apparatus shown in Figure 1, that is, a three-necked flask having a motor driven stirring rod with a mercury seal in the center neck and a reflux condenser and separatory funnel in the other necks. Here and elsewhere in the experiment all openings to the air were protected by calcium chloride tubes.

Since both the phenyl and ethyl magnesium bromides and the trichlorosilane are destroyed by moisture, complete dryness of all apparatus and materials was necessary. Calcium chloride dried ether well enough for starting an alkyl or aryl magnesium bromide manufacture, but it did not remove all the water and so was unsatisfactory. Both ethyl magnesium bromide and sodium metal produced complete dryness in ether, but they also produced solid products and it was necessary to distill the ether to remove the solids. The method finally adopted was distillation of ether dried with sodium immediately before use. It was necessary to refrain from distilling to dryness because of danger from peroxides which were difficult to remove or prevent from forming.

Some ether which had been purified by distillation and also some ethyl magnesium bromide solution were stored under calcium chloride tubes. After several days, however, it was found by adding SiHCl_3 to the ether that the ether was no longer dry; also, the $\text{C}_2\text{H}_5\text{MgBr}$ had been partly destroyed, so although calcium chloride provided a satisfactory protection against moisture for short periods of time, it was unsatisfactory for long periods.

The phenyl magnesium bromide was made by adding one-half of a mole (79.5 g.) $\text{C}_6\text{H}_5\text{Br}$ from the separatory funnel to one-half of a mole of magnesium turnings (12.2 g.) in 450 ml. of dry n-butyl ether. The ethyl magnesium bromide was made by adding the correct amount of $\text{C}_2\text{H}_5\text{Br}$ to the correct amount of

magnesium turnings which was determined by the size of the run to be made. Stirring was not necessary because the ether boiled so vigorously during addition of the C_2H_5Br . In some cases the solution was refluxed in an attempt to get a complete reaction.

The trichlorosilane-phenyl or ethyl magnesium bromide reactions were carried out in the same apparatus. The phenyl derivatives were produced by adding dropwise with stirring the phenyl magnesium bromide to 0.6 moles (82.3 g.) $SiHCl_3$ in 100 ml. of dry n-butyl ether. The reaction flask was kept in an ice water bath. The liquid, solvent and products, was removed from the solid formed in the reaction by boiling. The unreacted $SiHCl_3$ and the solvent were removed on a fractionating column, and the products were separated by a conventional vacuum distillation.

The ethyl derivatives were made in two ways. In the first two ethyl runs, the ethyl magnesium bromide solutions were added to trichlorosilane in ethyl ether. In the second two runs, the trichlorosilane in ethyl ether was added to the ethyl magnesium bromide solutions. In all runs, addition was dropwise and with stirring. As before, the reaction flask was kept in an ice water bath.

In the first ethyl run, the liquid was removed by boiling and then fractionated. In the second run siphoning was tried, and in the two remaining runs decantation was used. The last three runs each had 100 ml. of n-butyl ether added before

fractionating so that all of the products, which boil higher than the unreacted SiHCl_3 or the solvent but lower than n-butyl ether, could be removed without distilling to dryness.

Several liquids were pumped through the condenser jacket by a centrifugal pump in an effort to find a good cooling agent. For the manufacture of the phenyl magnesium bromide, ice water condensed all vapors, but in all other cases where ice water was used, it was unsatisfactory. The best cooling agent tried was acetone cooled in a dry ice-acetone bath. This refluxed all vapors whereas SiHCl_3 , ether and possibly some $\text{C}_2\text{H}_5\text{Br}$ passed the ice water condenser.

For the fractionation of the second ethyl run, an insulated column two feet by one-half inch and packed with stainless steel helices $3/32$ of an inch in diameter was used. Heat was provided to the pot by means of an electric heating mantle and to the column by means of resistance wire wound about a tube enclosing the column. Rate and type of stripping were controlled by means of a stopcock, see Figure 2.

The ether and unreacted SiHCl_3 of the third ethyl run were removed up to a temperature of 38°C by means of a stripping still made from a Vigreux column packed with the same helices. The remainder of this run and all other runs were fractionated on a column which differed from the previous one in that it was four feet long, uninsulated and had about thirty plates to the former's ten.

Analyses were made for active chlorine by hydrolyzing samples and titrating the HCl formed with sodium hydroxide using methyl red as an indicator. The hydrolysis was carried out in an ice water-ether mixture.

Cuts eight, nine and ten of the phenyl run were analyzed for active hydrogen by hydrolyzing the chlorosilane off in alkaline solution and measuring the volume of escaping hydrogen ⁴.

DISCUSSION

A summary of the experimental data is shown in Table 1. It is noted that Phenyl-1 has no analytical data extant other than the boiling ranges. Since the chlorine analysis titrations were very small, since the hydrogen analyzed very low, and since the boiling ranges were rather broad, it is felt that no specific conclusions may be drawn other than that some extremely high-boiling materials were formed -- probably the phenyl derivatives of trichlorosilane. Cuts nine and ten were taken at 14 mm. pressure.

The table also shows that Ethyl-1 yielded nothing boiling higher than 51.0°C. Tetralin (tetrahydronaphthalene) was added to this run as a chaser to facilitate removal of products from solids in the reaction flask by boiling. Apparently the tetralin reacted with the silanes to destroy any high boiling materials including itself -- see Table 2.

TABLE 1

<u>Time in Minutes</u>	<u>Temperature in Degrees Centigrade</u>		<u>Weight in Grams</u>					
<u>Run</u>	<u>Amount of Reactants</u>	<u>Order of Addition</u>	<u>Time for Addition</u>	<u>Reflux Time</u>	<u>Cut No.</u>	<u>Boiling Range</u>	<u>Weight of Cut</u>	<u>Weight Active Chlorine</u>
Phenyl-1	.5 moles C_6H_5Cl	C_6H_5Cl added to $SiHCl_3$	30	None	1	60-102	--	
					2	87-98	--	
	3				102-138	67.2		
	4				139-145	116.4		
	5				110-138	95.1		
	6				138-145	133.4		
	7				140-143	78.3		
	8				90.5-200	7.8		
	9				223-243	4.6		
	10				250	--		
Ethyl-1	2 moles each	C_2H_5Cl added to $SiHCl_3$	270	None	1	34.5-51.0	620.6	
Ethyl-2	1.5 moles each	C_2H_5Cl added to $SiHCl_3$	80	30	1	33.5-35.9	456.1	30.9
					2	39.8-72.0	39.9	--
					3	72.0-77.0	18.9	7.2
					4	77.0-98.5	10.5	2.6
					5	98.5-101.5	.8	.1
					6	101.5-113	.4	.1
					7	113-140	--	--
Ethyl-3	2 moles C_2H_5Cl	$SiHCl_3$ added to C_2H_5Cl	55	150	1	32.4-35.0	--	105
					2	35.0-75.0	20.3	--
					3	75.0-77.0	6.7	1.5
	4	77.0-98.0			8.8	1.3		
	5	98.0-103			2.2	.3		
	6	106			3.5	.4		
Ethyl-4	1 mole each	$SiHCl_3$ added to C_2H_5Cl	60	30	1	31.4-34.1	--	--
					2	34.1-73.5	--	--
					3	73.5-97.0	--	--
					4	97.0-102.5	4.3	.16
					5	102.5-107	--	--
					6	107-110	2.5	--

TABLE 2

Compound	Formula	Boiling Range	Weight % Active Cl
Trichlorosilane	SiHCl_3	31.8°C	78.54
Ethyl Ether	$\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$	34.6°C	---
Ethylchlorosilane	$\text{C}_2\text{H}_5\text{SiHCl}_2$	$75.5\text{-}76.5^\circ\text{C}$	54.96
Diethylchlorosilane	$(\text{C}_2\text{H}_5)_2\text{SiHCl}$	$99\text{-}100^\circ\text{C}$	29.15
Triethylsilane	$(\text{C}_2\text{H}_5)_3\text{SiH}$	107°C	---
n-Butyl Ether	$\text{C}_4\text{H}_9\text{-O-C}_4\text{H}_9$	141°C	---
Tetralin	$\text{C}_{10}\text{H}_{12}$	206°C	---

Run Ethyl-2 was the first to produce material in the expected boiling ranges as shown by Tables 1 and 2. The actual weights of active chlorine found in cuts three, five, and six both of Ethyl 2 and 3 are compared with the weights of active chlorine which should be present if those cuts were pure mono-, di- and trisubstituted products, respectively. It is seen that the chlorine analyzed low in those cuts. There are three possible explanations for this: first, the cut may be contaminated with ether containing some SiHCl_3 ; second, the cut may be contaminated with $(\text{C}_2\text{H}_5)_2\text{SiHCl}$ and $(\text{C}_2\text{H}_5)_3\text{SiH}$; third, both the first and second possibilities may be correct. Now, considering that the column used had ten theoretical plates and that the temperature of the material was at least at 74°C , it is assumed that very close to all of the ether and remaining trichlorosilane had been removed by the time cut three was reached. This leaves possibility number two as the explanation.

At this point, two more assumptions are made, the first being that since $(C_2H_5)_2SiHCl$ and $(C_2H_5)_3SiH$ boil only $7^\circ C$ apart, they are present in equal amounts as contaminants, and the second being that no $C_2H_5SiHCl_2$ is present in cuts five and six.

Then it may be shown that for cut three of Ethyl-2, if of the 18.9 grams total which yield 7.2 grams of active chlorine

10.9 g. are $C_2H_5SiHCl_2$ yielding $10.9 \times .55 = 6.0$ g. Cl

4.0 g. are $(C_2H_5)_2SiHCl$ " $4.0 \times .29 = 1.2$ g. Cl

4.0 g. are $(C_2H_5)_3SiH$ " $4.0 \times 0 = 0.0$ g. Cl

the net result is 18.9 grams yielding 7.2 grams of active chlorine. By similar reasoning, Table 4 for Ethyl-2 and Table 5 for Ethyl-3 are constructed.

TABLE 3

Run	Cut	Weight of Cut	% Cl if Pure	Wt. Cl if Pure	Wt. Cl Found
Ethyl-2	3	18.9 g.	55	10.4	7.2
	4	10.5	--	--	2.6
	5	.8	29	.2	.1
	6	.4	--	--	.1
Ethyl-3	3	6.7	55	3.7	1.5
	4	6.8	--	--	1.3
	5	2.2	29	.64	.3 (calc.)
	6	3.5	--	--	.4

TABLE 4

Ethyl-2

Cut Number	3	4	5	6	Total Wt.	# of Moles	Relative # Moles
Wt. $C_2H_5SiHCl_2$	10.9	2.7	--	--	13.6	.16	2.3
Wt. $(C_2H_5)_2SiHCl$	4.0	3.9	.4	.2	8.5	.07	1.0
Wt. $(C_2H_5)_3SiH$	4.0	3.9	.4	.2	8.5	.07	1.0

TABLE 5

Ethyl-3

Cut Number	3	4	5	6	Total Wt.	# of Moles	Relative # Moles
Wt. $C_2H_5SiHCl_2$	1.4	.1	--	--	1.5	.01	1.0
Wt. $(C_2H_5)_2SiHCl$	2.65	4.4	1.1	1.5	9.6	.08	8.0
Wt. $(C_2H_5)_3SiH$	2.65	4.4	1.1	2.0	10.1	.09	9.0

In run Ethyl-2, the ethyl magnesium bromide was added slowly to the trichlorosilane in an effort to satisfy the requirements of the theory for monosubstitution to prevail; namely, a small number of ethyl magnesium bromide molecules for a large number of trichlorosilane molecules. The last column of Table 4 shows that monosubstitution prevailed if the assumptions are correct.

In run Ethyl-3, the order of addition was reversed so that polysubstitution would be promoted according to theory.

The last column of Table 5 shows that polysubstitution did take place in the largest degree:

In each case, the second cut was omitted. This may have changed the results, but it is not believed that any changes would be on a large enough scale to invalidate the present results.

The data in Table 1 on Ethyl-4 show only one analysis-- that for cut four, but this showed cut four to be principally $(C_2H_5)_3SiH$ according to the line of reasoning followed in the other analyses. It is probably true that any higher boiling cuts would be $(C_2H_5)_3SiH$ to an even greater extent. Also, the boiling ranges indicate very little $C_2H_5SiHCl_2$. Roughly, then, Ethyl-4 produced mostly polysubstituted products so that Ethyl runs 3 and 4 are in agreement as to order of addition and type of substitution.

Even if the previous assumptions are incorrect, a consideration of the data in Table 1 on runs Ethyl-2, 3 and 4 leads to the same conclusion. That is in Ethyl-2, of cuts three, five and six -- which have the boiling ranges of the three products -- most material was collected in cut three which strongly indicates a preponderance of the monosubstituted product; but, in Ethyl-3, most of the material in those cuts was collected in cuts five and six which strongly indicates mostly polysubstitution. Again, in Ethyl-4, polysubstitution prevailed. In this run, no cut is shown having

a boiling range of 75.0-77.0°C which indicates that such a small amount of monosubstituted product was formed it could not be isolated.

This evidence alone shows that amount of substitution depends upon order of addition.

SUMMARY

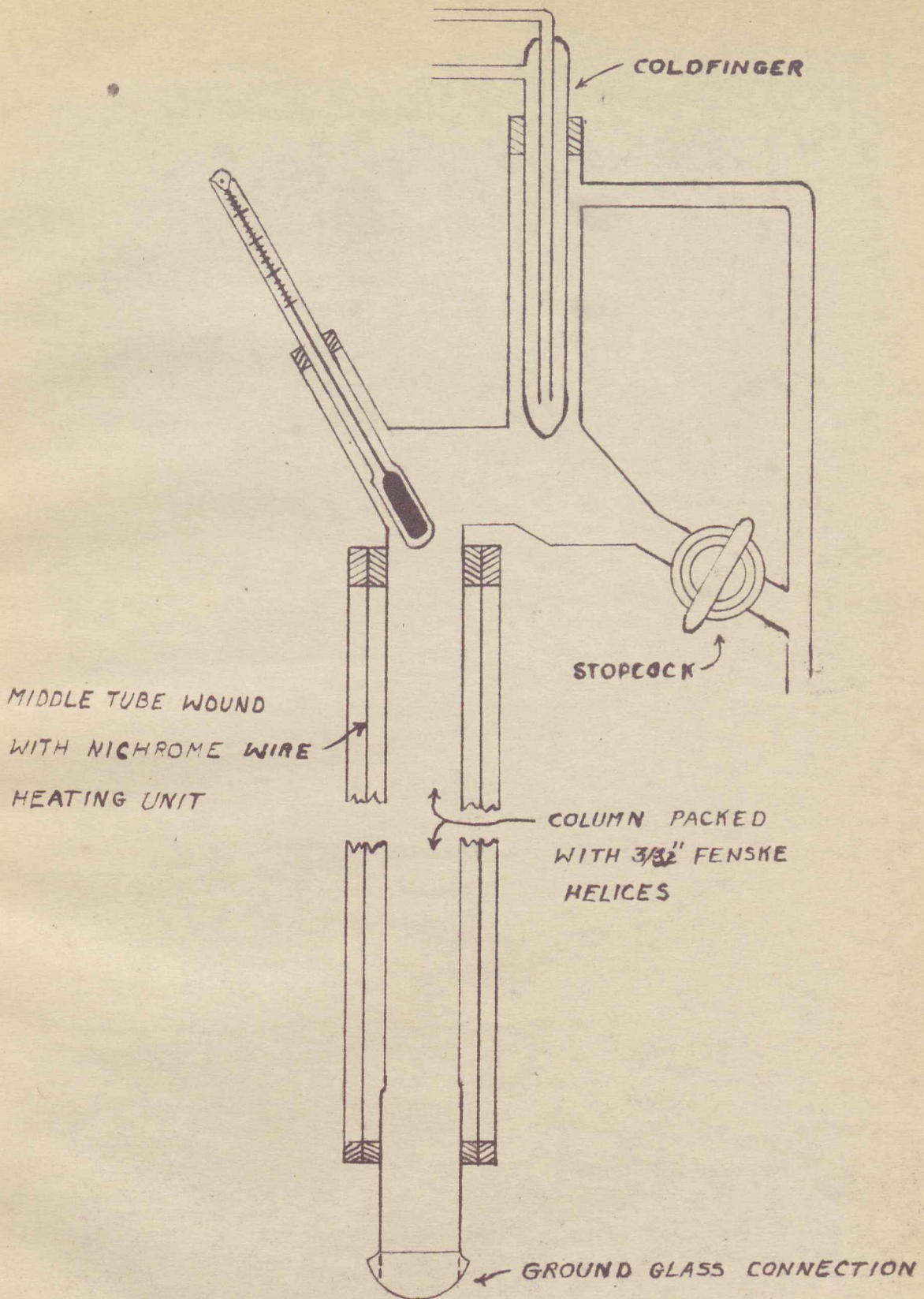
When phenyl magnesium bromide was reacted with an excess of trichlorosilane, some high boiling products were formed.

When ethyl magnesium bromide and trichlorosilane were varied in order of addition to each other, the data showed, on the basis of certain assumptions, that the degree of ethylation depended markedly on the order of addition.

REFERENCES

- | | | | | |
|---|----------------------|-------------------|----------------|--------|
| 1 | Emeleus and Robinson | J. Chem.Soc. | 1592 | (1948) |
| 2 | Fuoss | J. Am. Chem. Soc. | <u>65</u> 2406 | (1943) |
| 3 | Booth and Stillwell | J. Am. Chem. Soc. | <u>56</u> 1529 | (1934) |
| 4 | Price | J. Am. Chem. Soc. | <u>69</u> 2600 | (1947) |

APPENDIX



FRACTIONATING
COLUMN

REFLUX CONDENSER
STIRRING MOTOR
SEPARATORY FUNNEL
MERCURY SEAL
MERCURY
RUBBER STOPPERS
STIRRING ROD
REACTION FLASK

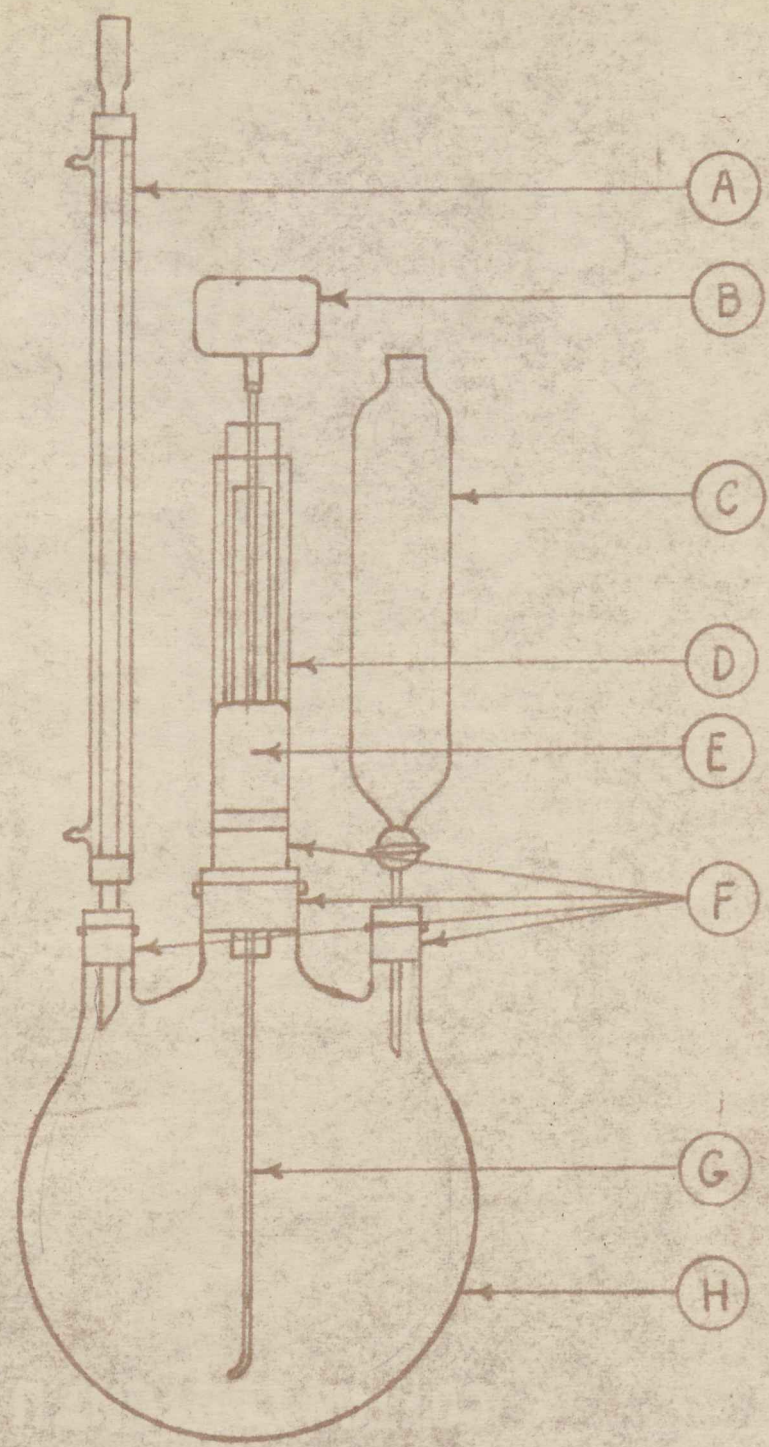


FIGURE 1

SILICON-ETHYL 2
DISTILLATION CURVE

NOTE - 600 ML. B.P. 31.5-34.0
OF CUT 1 OMITTED

140

130

120

110

100

90

80

70

60

50

40

30

TEMPERATURE
IN °C

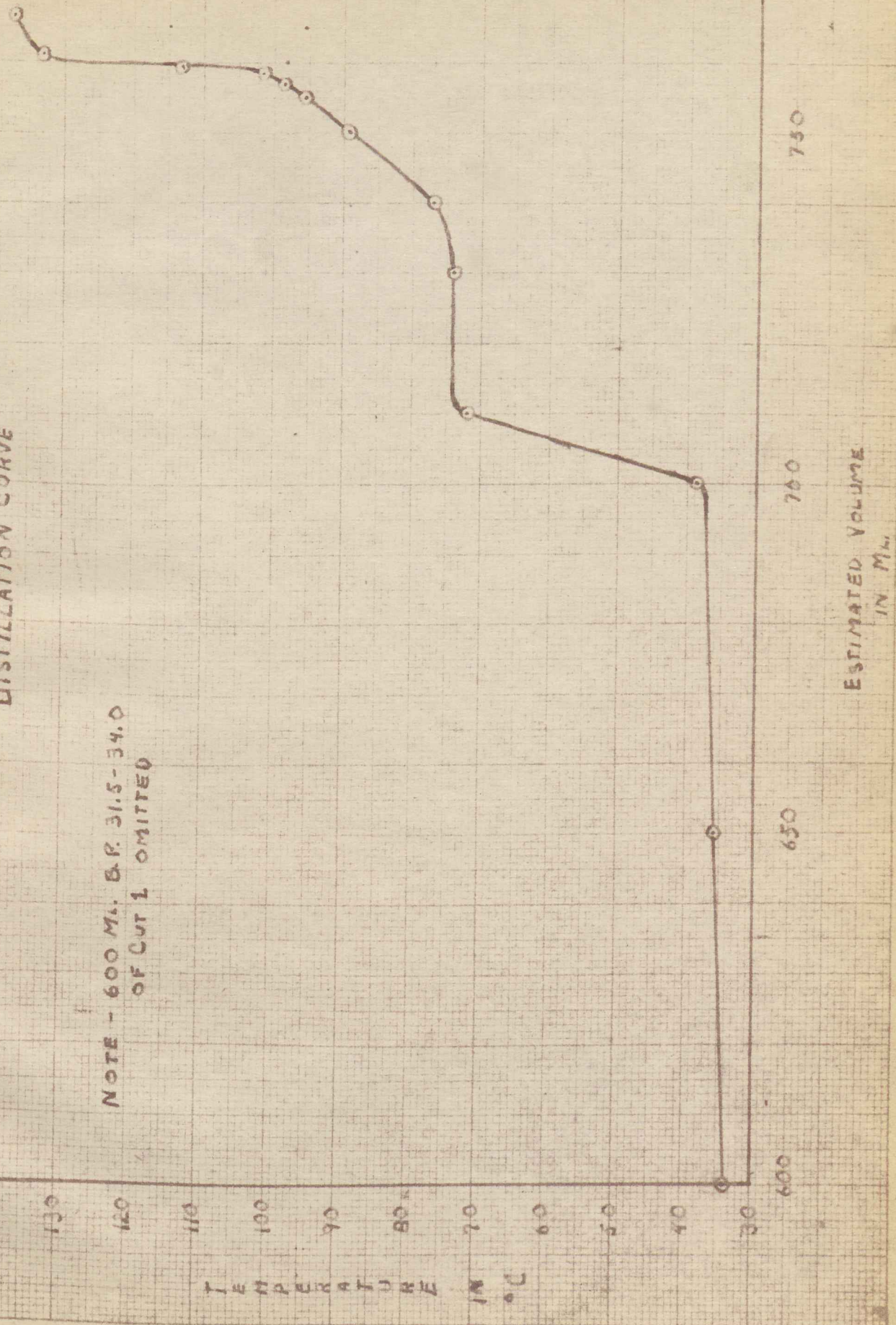
600

650

700

750

ESTIMATED VOLUME
IN ML



SILICON-ETHYL 3
DISTILLATION CURVE

NOTE - CUT 1, B.P. 32.5 - 35.0
VOL. 670 ML. IS
OMITTED.



SILICON-ETHYL 4
DISTILLATION CURVE

