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Methylchlorosilanes

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"METHYLCHLOROSILANES"

by

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Approved by *Howard E. Sheffer*

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INTRODUCTION

Although some work had been done in the field of organo-silicon chemistry as early as 1863 by Friedel, Crafts, and Ladenburg (1), not much progress had been made up to the turn of the century. In 1901, Kipping of England began his extensive research which lasted over a period of 43 years. His papers are still important reference sources for workers in the field.

There are two main classes of reactions by means of which carbon-silicon bonds may be established. The first consists of the reactions of silicon halides with metal-organic reagents such as Grignards at moderate temperatures. The second class of reactions take place at high temperatures and involves the direct reaction of the alkyl or aryl halides in the vapor phase with silicon metal activated by finely divided copper (2). Inasmuch as there are fewer complications with the Grignard reaction, this method is the one most widely used.

On studying the Grignard method of synthesis, it is apparent that poly-substitution always tends to take place, since there is always the initial mono-substituted product present to take part further in the reaction. A typical such reaction may be represented as

$$nRMgX + mHSiCl_3 = RHSiCl_2 + R_2HSiCl + R_3HSi + nMgXCl$$
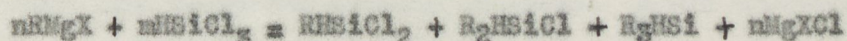
where R is any organic radical such as CH_3- or C_2H_5- and X is any halogen with the exception of fluorine. In order to get the maximum yields of the lower substitution products it is necessary to vary the molar proportions of the Grignard reagent to the silicochloroform and also the order of addition. Thus, triethylsilane (3)(4) has been prepared by adding an ether solution of silico-chloroform to ethyl magnesium bromide. The diethylmonochlorsilane has been prepared by Pizzotti (5) who added the silicochloroform to the ethyl Grignard reagent. Emeleus and Robinson (6) prepared both the monoethyl and diethyl

chlorosilane by adding 1.25 moles of ethylmagnesium bromide to 1 mole of
silicochloroform. Another new way of making alkyl chlorosilanes with hydrogen
on the silicon nucleus is by the reaction of triethylsilane with diethyldichloro-
silane (5). Lessor(7) prepared the analagous methyl substituted silanes by the
addition of methyl Grignard to silicochloroform in 2:1 and 1:1 molar ratios. A
variation has been described by Rust and MacKenzie (8) who prepared substituted
chlorosilanes by adding the alkyl or aryl halide to a mixture of the silicon
halide and magnesium turnings in ether, thus eliminating a step in the conven-
tional Grignard synthesis.

The primary objective of this investigation was to prepare and improve
the separation of the mono- and di- methyl substituted chlorosilanes by
fractional distillation.

EXPERIMENTAL

Purification of n-Butyl Ether

The n-butyl ether as procured from the Eastman Company was a practical
grade and therefore had to be purified. The peroxides were removed by washing
the ether thoroughly with an aqueous solution of ferrous sulfate. The ether
was then dried over anhydrous calcium chloride. After treating with phenyl-
magnesium bromide to remove any Grignard destroying compounds (such as n-butyl
alcohol), the ether was decanted off the solids formed and refluxed over magnesium
turnings, thus removing any excess phenyl bromide which may have been in the
Grignard. (In the future it is recommended to use an excess of magnesium to
make certain there is no free phenyl bromide.) The ether was then distilled
through a Vigreaux column and the fraction boiling at 140-141 C was collected
and stored over fresh sodium ribbon. By running a sodium fusion and testing
for halogens (9), the absence of any halogen containing compounds was confirmed.

Preparation and Purification of Silicochloroform

The silicochloroform was prepared by a method similar to that used by Booth and Stillwell (10), who passed hydrogen chloride over copper-silicon alloy. In this case, however, a mechanical mixture of copper and silicon was used; i.e., copper and silicon powder mixed and pressed into bars. The bars were broken up and placed in a pyrex glass tube, 36 mm. x 60 cm., which was inserted into a horizontal crook furnace. A hydrogen chloride tank was connected to a flow meter which in turn was attached to the inlet side of the reaction tube. The outlet was

TABLE I

Run Number	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6	SC-7	SC-8
Time, Hours	13	7	14	10	14	$11\frac{1}{2}$	$14\frac{1}{4}$	$16\frac{1}{2}$
Temperature, C	300	320	305	310	310	305	305	290
Reactants: 84% Si-16% Cu	--	--	--	--	--	--	--	--
Feed: HCl	--	--	--	--	--	--	--	--
Initial Wgt. of Si-Cu in Gms.	317	287	327	332	312	304	300	354
Flow Meter Readings	29	30	25	32	30	28	33	30(Hg flow meter)
Final Wgt. of Si-Cu	219	236	215	253	198	207	192	199
Mole % Product Recovered in Distillation	91.9	111.4*	--	--	--	--	86.2	52.9
Conversion, Mole %								
H_2SiCl_2	2.9	2.2	--	--	--	--	2.3	--
H_2SiCl_2-$HSiCl_3$	5.4	14.4	--	--	--	--	--	--
$HSiCl_3$	72.4	73.6	--	--	--	--	74.4	48.1
$HSiCl_3$-$SiCl_4$	4.3	12.2	--	--	--	--	1.5	--
$SiCl_4$	3.2	3.2	--	--	--	--	4.0	4.8
Residue as $SiCl_4$	3.7	5.8	--	--	--	--	3.9	--

* Due to erroneous weighing.

then led through a liquid trap to a dry ice and acetone trap where the mixture

of products was condensed and collected. A summary of these runs is given in

Table I. The chlorosilane mixture was fractionated in a four foot fractionating

column packed with 5/32" Fenske helices. Acetone, cooled in dry ice and acetone,

was circulated through the cold finger in the head. The cuts of typical fraction-

ations, together with their boiling points and hydrogen and chlorine analysis,

are given in Table II. The fraction boiling from 30.0 to 33.5 C was used for

experimental work.

TABLE II

	Product	Boiling Point C	% Chlorine Obs.	Calc.	% Hydrogen Obs.	Calc.
Run 1	H_2SiCl_2	18-19	--	70.20	0.850	2.02
	H_2SiCl_2-$HSiCl_3$	27-30	72.5	--	--	--
	$HSiCl_3$	31-33.5	76.8	78.54	0.737	0.744
	$HSiCl_3$-$SiCl_4$	53.3-56.7	81.7	--	--	--
	$SiCl_4$	55.7-56.7	82.6	83.46	--	0.00
Run 2	$HSiCl_3$	30-32	79.2	78.54	--	0.744
Run 7	$HSiCl_3$	30.1-31.6	77.4	78.54	--	0.744
	$SiCl_4$	55.4-56.5	81.8	83.46	--	0.00
Run 8	$HSiCl_3$	31.0-32.5	76.3	78.54	--	0.744
	$SiCl_4$	56-57	84.2	83.46	--	0.00

Preparation of the Grignard Reagent:

The apparatus used in the preparation of the Grignard reagent was a two

liter round bottom flask with a Y adapter fitted in the neck. Into the arms

of the adapter were fitted a 125 ml. dropping funnel and a brine-ice cooled

reflux condenser. The system was protected from moisture and carbon dioxide by a drying tube, filled with a calcium chloride-lime mixture, placed at the top of the reflux condenser.

Inasmuch as the products are low boiling (Table III), a high boiling solvent, n-butyl ether, was used. The methyl iodide was added slowly to the ether-magnesium mixture over a period of three hours. As the reaction progressed, the mixture of ether and Grignard turned from a rusty red to light yellow colloid and finally, when the reaction was completed, the mixture was a gray solution. When the addition was completed, the reaction mixture was refluxed for one hour. The ether solution was decanted off the unreacted magnesium, which was weighed afterwards to determine the yield of methyl magnesium iodide. A summary of these runs is given in Table IV.

TABLE III

Compound	Boiling Point, C	Mol. Wt.	% Cl (calc.)
$HSiCl_3$	31.8	135.45	78.54
CH_3SiHCl_2	41.0	115.00	61.65
$(CH_3)_2SiHCl$	36-38	94.58	37.48
$(CH_3)_3SiH$	9-11	74.16	0.00

TABLE IV

Run No.	Mols of CH_3I	Mols of Mg	Vol. Solvent for Grignard	Mols Grignard
1	1	1	1000 ml.	0.82
2	2	2	2000 ml.	1.72

Reaction of Silicochloroform with Methyl Grignard:

The addition reaction was carried in a three liter, three necked Grignard
flask, equipped with a brine-ice reflux condenser, a mercury seal stirrer, and
a one liter separatory funnel. A dry ice-acetone trap was attached to the out-
let of the reflux condenser to insure against losses. The silicochloroform
dissolved in butyl ether was placed in the reaction flask and the mixture was
cooled with a brine-ice bath. When the temperature had dropped to 5 C, the
Grignard reagent was added slowly through the separatory funnel with constant
stirring. This reaction was carried out the day after the Grignard was prepared
because further delay would result in serious decomposition due to the action
of the air (11):

$$2RMgX + O_2 = 2ROMgX$$
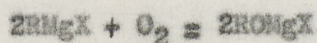
When the addition was completed, the mixture of products was heated on an oil
bath at 90-100 C for one hour. The products boiling below 142 C (boiling point
of n-butyl ether) were stripped off through a Vigreaux column and condensed and
collected in a dry ice and acetone trap. A small amount of ether was allowed
to come over to act as a chaser.

TABLE V

Run No.	Mols Grignard	Mols HSiCl$_3$	Volume of n-Butyl Ether for HSiCl$_3$	Addition
1	0.82	1	100 ml.	Grignard to HSiCl$_3$
2	1.72	2	200 ml.	Grignard to HSiCl$_3$

Analysis:

The products were analyzed for chlorine as follows: a sample was weighed
out in a cork stoppered vial. After cooling in an ice bath, the vial was

unstoppered and the cork and vial dropped into a glass stoppered Erlenmeyer flask containing an ethyl ether-cracked ice mixture. It was necessary to replace the glass stopper as rapidly as possible so as to minimize the loss of hydrogen chloride. The stoppered flask was shaken vigorously for several seconds in order to complete the hydrolysis. The hydrochloric acid in the water layer was then titrated with standard sodium hydroxide, using methyl red as the indicator. Since hydrolysis was not always complete at the initial endpoint, it was necessary to shake the mixture thoroughly until a permanent end point was reached.
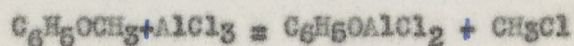
Fractionation:

TABLE VI

Cut No.	Boiling Point $^{\circ}$C	Vol.	Weight	% Chlorine Obs.	Calc.	Product
1	10-17	35 ml.	27.9 g.)	2.29	0.00	$(CH_3)_3SiH$
2	20-30	15 ml.	18.0 g.)			
3	31.8-35.6	32 ml.	39.1 g.	23.5	78.54	$HSiCl_3$
4	35.6-36.2	6 ml.	10.2 g.	25.4	---	$HSiCl_3-(CH_3)_2SiHCl$
5	36.2-38.8	15 ml.	22.9 g.	27.8	37.48	$(CH_3)_2SiHCl$
6	38.8-41.6	5 ml.	5.5 g.	45.2	61.65	CH_3SiHCl_2
7	41.6-47.8	2 ml.	2.0 g.	38.1	---	CH_3SiHCl_2- ?
8	53.0-75.0	15 ml.	15.5 g.	10.5	---	---
9	75.0-77.0	50 ml.	45.7 g.	1.14	---	?

The reaction products from Runs 1 and 2 were combined and fractionated using butyl ether as a chaser. Dry ice-acetone was used as the condensing medium. The preceding table summarizes the distillation. Plateaus were obtained at 10, 33, 36, and 77 C. These represent trimethyl silane, silicochloroform, dimethyl-chlorosilane, and butyl chloride (vide infra), respectively.

The same high boiler which Lessor (7) reported was also found in this distillation (Table VI). However, contrary to Lessor's report, this liquid did have a small percentage of hydrolyzable chlorine, 1.14%. This may have been due to a poor separation. It was thought that the presence of the high boiling liquid might have had something to do with the disappearance of a large unaccountable portion of silicochloroform (Table VII). Recalling the following reaction of aluminum chloride with an ether (12)

$$C_6H_5OCH_3 + AlCl_3 = C_6H_5OAlCl_2 + CH_3Cl$$

it was thought that silicochloroform might have a similar action on butyl ether:

$$C_4H_9OC_4H_9 + HSiCl_3 = C_4H_9OSiCl_2 + C_4H_9Cl \text{ (Boiling Point = 78 C)}.$$

The boiling point of the high boiling fraction was 75-77 C (uncorrected) which compared favorably with the boiling point of n-butyl chloride given above. The most convenient means of confirming the identity of the compound was to analyze for chlorine. First, the fraction was shown to contain very little active chlorine. Then an analysis for inactive chlorine was carried out as follows (13): a small sample was weighed out in a pyrex pressure tube (2.5 cm., inside diameter; 3 mm., wall thickness; 30 cm., length) sealed at one end. After 8 ml. of concentrated nitric acid and 2.4 gm. of silver nitrate was added, the tube was sealed and heated in a vertical furnace at 300 C for five hours. The tube was allowed to cool and then opened and the precipitate of AgCl removed. The sample was found to contain 27.6% chlorine. The percentage of chlorine in butyl chloride was calculated to be 38.4%. Although the results did not check very well, it was evident that some inactive chlorine was present in the compound. A more efficient analysis may give a better check.

As a further means of identification, the refractive index was measured. Before taking the measurement, however, the component of the fraction containing the hydrolyzable chlorine was removed by washing a portion of the fraction with water. On contact with water, a white gelatinous material was formed which

remained above the water layer. The water was removed and the remainder of the fraction was separated from the gelatinous material by vacuum filtration. This unhydrolyzable portion of the fraction was then dried over calcium chloride. The reading was taken and is given below together with the refractive index of n-butyl chloride:

$$n^{20} = 1.4086 \text{ Observed}$$

$$n^{20} = 1.4015 \text{ Table value for n-butyl chloride}$$

The above evidence strongly indicates that n-butyl chloride is the high boiling fraction.

DISCUSSION OF EXPERIMENTAL RESULTS

TABLE VII

Compound	Weight of Cut*	% Chlorine Obs.	% Chlorine Calc.	Wgt. Pure Material	Moles	Silicon Balance	Methyl Balance
$SiHCl_3$	---	78.5	78.54	406.50 g.	3	---	---
CH_3MgI	---	---	---	---	2.54	---	---
$SiHCl_3$	44.2 g.	23.5	78.54	13.2 g.	0.098	0.098	---
CH_3SiHCl_2	6.5 g.	45.2	61.65	4.8 g.	0.042	0.042	0.042
$(CH_3)_2SiHCl$	28.0 g.	27.8	37.48	20.8 g.	0.22	0.22	0.44
$(CH_3)_3SiH$	45.9 g.	2.29	0.00	45.9 g.	0.62	0.62	1.86
						0.98	2.342

*The mid-cuts have been taken into account.

By using the ratio of the actual percentage of chlorine to the calculated percentage as a correction factor, the number of moles of pure products are calculated in Table VII. It is seen from the methyl balance that almost all of the Grignard reagent is accounted for, while 2.02 moles or almost 2/3 of the original amount of silicochloroform is unaccounted for. As has already been

suggested this may be due to a reaction between silicochloroform and n-butyl ether, and the residues of the distillation show the presence of hydrolyzable chlorine.

The low chlorine analyses could be accounted for only by the presence of a compound containing unhydrolyzable halogen. It should be noted that, although a four foot column was used, the presence of any compound whose boiling point is near the boiling range of the products (Table III), could easily complicate an already rather difficult separation. At first it was thought to be due to the formation of an azeotrop with trimethylsilane (boiling point 9° C). This would account for the low chlorine analysis for the silicochloroform cut but that it interfered with the separation of the mono- and dimethyl products is very improbable. Another possibility, however, was that the methyl iodide (boiling point 42.4° C), was interfering with the separation. An iodine analysis (9) of one of the cuts (Cut 5, Table II), was strongly positive, indicating the presence of the only possible iodine containing compound, methyl iodide. The presence of methyl iodide is easily accounted for by noting (Table IV) that there was a total of 0.5 moles which had not reacted with magnesium in the Grignard preparations.

The boiling points of methyl- and chloro- substituted silanes have been arranged in Table VIII in such a way as to show the regular increase in boiling caused by the substitution of a chlorine atom or a methyl group for hydrogen in chlorosilanes.

TABLE VIII

SiH_4	SiH_3Cl	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
b.p. -112°C	b.p. -10°C	b.p. 12°C	b.p. 32°C	b.p. 57°C

CH_3SiH_3	CH_3SiH_2Cl	CH_3SiHCl_2	CH_3SiCl_3
b.p. -57°C	b.p. 13°C*	b.p. 41°C	b.p. 66°C

$(CH_3)_2SiH_2$	$(CH_3)_2SiHCl$	$(CH_3)_2SiCl_2$
b.p. -20°C	b.p. 36°C*	b.p. 70°C

$(CH_3)_3SiH$	$(CH_3)_3SiCl$
b.p. 9°C	b.p. 58°C

$(CH_3)_4Si$
b.p. 26°C

*Approximate values

It can thus be seen that:

1. The replacement of a hydrogen atom by a chlorine atom raises the boiling point of a chlorosilane by an average of 22°C except for monochlorsilane in which the chlorine atom raises the boiling point 102°C.

2. The replacement of a hydrogen atom by a methyl radical raises the boiling point of a dichlorsilane by an average of 29°C.

3. The replacement of a hydrogen atom by a methyl radical raises the boiling point of a monochlorsilane by an average of 23°C. The fractionation graph contains a plateau at 35.5°C which agrees with the estimated value of the boiling point of dimethylchlorsilane.

The rate equations for the consecutive competitive reactions of a trifunctional system have been worked out (13). By making certain assumptions, the maximum possible yields of the individual products can be calculated. The assumptions are namely that the reaction rate of the trifunctional molecule is three times the rate for the monofunctional molecule and the rate for the

difunctional molecule is twice the rate for the monofunctional molecule. The maximum possible yield for methyldichlorsilane has been worked out in the appendix (pg. 16). If the silicochloroform reacts with the butyl ether as has been postulated, it would be expected that the yield would deviate from this theoretical value. If the silicochloroform had not reacted with the solvent and had been available to react with the Grignard reagent, then according to the rate equation the yield of monomethyldichlorsilane should have been 44% for the 1:1 ratio of reactants. From the analyses, the ratio of Grignard to silico-chloroform that reacted, was 1:2.4. This latter ratio would be expected to yield approximately equal proportions of dimethylchlorosilane and trimethylsilane. However, trimethylsilane predominated in the reaction product. This would indicate that the reaction rates of the three consecutive reactions were not only dependent on the number of chlorines present on silicon.

This investigation, while not successful in separating the methylchlor-silanes, has indicated certain definite lines to follow for further research. Firstly, methyl chloride should be used rather than methyl iodide in the preparation of the Grignard reagent. Although this Grignard preparation (7) is more difficult, there is no possibility of the excess methyl chloride inter-fering in the fractionation since it is a gas. Secondly, because silicochloro-form reacts with the solvent, a ratio of silicochloroform to Grignard of three to one is recommended in further attempts to prepare monomethyldichlorosilane. Finally, a more complete analysis of the purified high boiling fraction should be carried out to positively identify it as n-butyl chloride.

SUMMARY

This investigation attempted to prepare and separate the pure monomethyl-
and dimethyl- chlorosilanes. Although not successful in this respect the
results did show that:

1. There is as much as 74 mole percent conversion to silicochloroform
when hydrogen chloride is passed over compressed silicon-copper powder.

2. The excess methyl iodide from the Grignard preparation was
interfering with the fractionation.

3. The high boiling fraction which Lessor reported seems to be
n-butyl chloride, thus substantiating the postulate that the butyl ether solvent
is split by the silicochloroform.

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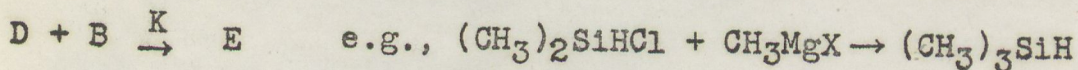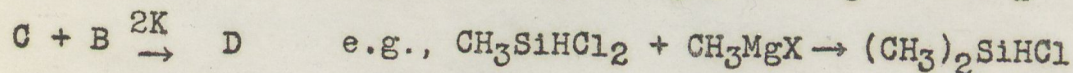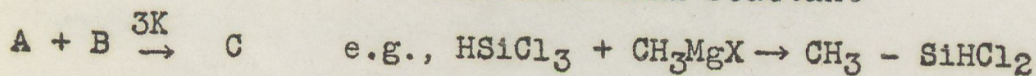   <u>25 B</u>, 415-419 (1947).

APPENDIX

RATE EQUATIONS FOR CONSECUTIVE COMPETITIVE REACTIONS

Let: A = trifunctional compound

C = difunctional   "

D = monofunctional   "

B = monofunctional reactant

$A + B \xrightarrow{3K} C$ e.g., $HSiCl_3 + CH_3MgX \rightarrow CH_3 - SiHCl_2$

$C + B \xrightarrow{2K} D$ e.g., $CH_3SiHCl_2 + CH_3MgX \rightarrow (CH_3)_2SiHCl$

$D + B \xrightarrow{K} E$ e.g., $(CH_3)_2SiHCl + CH_3MgX \rightarrow (CH_3)_3SiH$

Initial Conditions:

$$C_o \neq 0$$

$$D_o = 0$$

$$E_o = 0$$

$$B + C + 2D + 3E = B_o$$

$$A + C + D + E = A_o$$

------O------

$$\frac{dC}{dt} = 3K\,[B]\,[A] - 2K\,[C]\,[B] = K\,[B]\,(3\,[A] - 2\,[C])$$

$$\frac{dA}{dt} = -3K\,[A]\,[B]$$

$$\frac{dB}{dt} = -3K\,[A]\,[B] - 2K\,[C]\,[B] - K\,[D]\,[B]$$

$$= -K\,[B]\,(3\,[A] + 2\,[C] + [D])$$

$$\frac{dD}{dt} = 2K\,[C]\,[B] - K\,[D]\,[B]$$

$$= K\,[B]\,(2\,[C] - [D])$$

$$\frac{dE}{dt} = K\,[D]\,[B]$$

$$\frac{dC}{dA} = \frac{2C - 3A}{3A}$$

Let $A = y$ $C = X$

$A_o = y_o$ $C_o = 0 = X_o$

$$\frac{dx}{dy} = \frac{2x - 3y}{3y}$$

$$3y\,dx = (2x - 3y)dy$$

Let $y = vx$ $v = \frac{y}{x}$; $v_o = \infty$

$$dy = v\,dx + x\,dv$$

$$3v\,dx = (2 - 3v)v\,dx + (2 - 3v)x\,dv$$

$$(3v + 3v^2 - 2v)\,\frac{dx}{x} = (2 - 3v)dv$$

$$\frac{dx}{x} = \frac{2 - 3v}{v(3v + 1)}\,dv$$

$$\frac{dx}{x} = \frac{2\,dv}{v(3v + 1)} - \frac{3\,dv}{3v + 1}$$

$$\ln x = 2\ln \frac{v}{3v + 1} - \ln(3v + 1) + k$$

$$\frac{\ln k'x(3v + 1)^3}{v^2} = 0$$

$$\frac{k'x(3v + 1)^3}{v^2} = 1$$

$$k'x(3v + 1)^3 = v^2$$

$$k'x \left(\frac{3y}{x} + 1\right)^3 = \frac{y^2}{x^2}$$

$$k'(3y + x)^3 = y^2$$

At: $t = 0$, $x_o = 0$

$$y_o = A_o$$

$$k'(3A_o)^3 = A_o{}^2$$

$$27k'A_o{}^3 = A_o{}^2$$

$$k' = \frac{1}{27A_o}$$

Therefore:

$$\frac{(3A + C)^3}{27A_o} = A^2$$

but, at $C_{max. A}$:

$$\frac{dC}{dA} = \frac{2C - 3A}{3A} = 0$$

$$2C - 3A = 0$$

$$C = \frac{3}{2}A$$

Therefore:

$$\frac{(3A + \frac{3}{2}A)^3}{27A_o} = A^2$$

$$\frac{\left(\frac{9}{2}\right)^3 A^3}{27A_o} = A^2$$

$$\frac{81 A}{24 A_o} = 1$$

$$A = \frac{8}{27} A_o \quad \text{or } 29.5\% \text{ A still unreacted}$$

or,

$$C_M = \frac{4}{9} A_o \quad \text{or } 44\% \text{ maximum yield of C}$$

Distillation of Runs 1 & 2

Boiling Point °C

Weight in gms.