A STUDY OF THE GASEOUS BY-PRODUCTS FORMED

BY THE REACTION OF ZINC ETHYL AND

TERTIARY BUTYL CHLORIDE

By

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ACKNOWLEDGEMENT

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INTRODUCTION

The reaction of zinc alkyls with alkyl halides has been used in the preparation of highly branched aliphatic hydrocarbons. The reaction had been written for many years in the literature as $ZnR_2 + 2R'X \longrightarrow 2RR' + ZnX_2$, however only once was a yield reported over 50% and that one was of 51%. It was suspected that only one of the alkyl groups of the zinc alkyl was available in this reaction and that the reaction proceeded

$$ZnR_2 + R'X \longrightarrow RR' + RZnX.^{+}$$
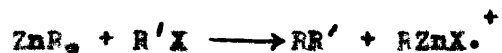
It was the purpose of this work to study the reaction of zinc alkyls with alkyl halides in an effort to discover the true course of the reaction. Zinc ethyl and tertiary butyl chloride were chosen as the two most easily obtainable compounds with which to work.

+ We had reason to believe that RZnX was never formed.

HISTORY

In his attempts to prepare free radicals in the 1840's Frankland had been trying to remove the cyanide group from alkyl cyanides by the action of potassium. In 1849 he shifted his attack to the halides of the alkyl radicals and used zinc instead of potassium. By the reaction of ethyl iodide on zinc, he made zinc ethyl[14] instead of obtaining any free radical. Shortly after that, zinc methyl[15] and other zinc alkyls[3,4,20] were prepared.

The preparation of zinc alkyls has been modified considerably through the years since Frankland first made zinc ethyl. Gladstone and Tribe[21] used a zinc-copper couple instead of pure zinc in the preparation of zinc ethyl. Later[22] they used a mixture of zinc and copper oxide to make their couple in a hydrogen atmosphere. Many other metals were tried, but copper was found to be the best activator. Lachman[30] used essentially the same method as Gladstone and Tribe with the contribution that the optimum ratio of zinc dust to copper oxide was established as 100 to 12. Job and Reich[28] attempted to use the cheaper alkyl bromide in place of the alkyl iodide but were met with either no yield and gaseous products or the necessity of using a catalyst and a long reaction time. Noller[32] found that equimolar mixtures of the bromide and iodide could be used in the preparation without any impairment of yield provided the zinc alkyl was distilled from the reaction mixture under vacuum.

Frankland and Duppa[16,17] made the first use of the new compound in 1863 by reacting zinc ethyl with diethyl oxalate to give ethyl diethylglycollate.

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + Zn(C_2H_5)_2 \longrightarrow \begin{matrix} C_2H_5 \\ | \quad / OZnC_2H_5 \\ C - OC_2H_5 \\ | \\ COOC_2H_5 \end{matrix}$$

$$\begin{matrix} C_2H_5 \\ | \quad / OZnC_2H_5 \\ C - OC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + Zn(C_2H_5)_2 \longrightarrow \begin{matrix} C_2H_5 \\ | \quad OZnC_2H_5 \\ C \\ | \quad C_2H_5 \\ COOC_2H_5 \end{matrix} + Zn \begin{matrix} C_2H_5 \\ OC_2H_5 \end{matrix}$$

$$\begin{matrix} C_2H_5 \\ | \quad OZnC_2H_5 \\ C \\ | \quad C_2H_5 \\ COOC_2H_5 \end{matrix} + 2H_2O \longrightarrow (C_2H_5)_2C(OH)COOC_2H_5$$
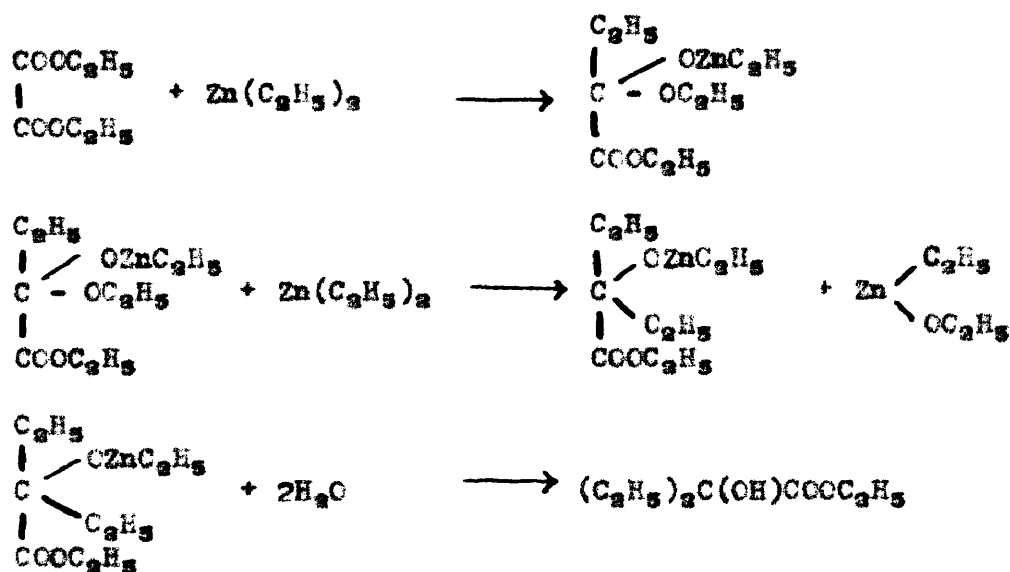
There soon followed many other researches involving zinc alkyls. Freund[18] reacted zinc ethyl with acid chlorides to give ketones and later Butlerow[2] found that the acid chloride would react with two moles of the zinc alkyl to give the tertiary alcohol.

$$CH_3COCl + Zn(C_2H_5)_2 \longrightarrow CH_3C \begin{matrix} OZnC_2H_5 \\ C_2H_5 \\ Cl \end{matrix}$$

$$CH_3C \begin{matrix} OZnC_2H_5 \\ C_2H_5 \\ Cl \end{matrix} + H_2O \longrightarrow CH_3COC_2H_5 + Zn \begin{matrix} OH \\ Cl \end{matrix} + C_2H_6$$

or

$$CH_3C \begin{matrix} OZnC_2H_5 \\ C_2H_5 \\ Cl \end{matrix} + Zn(C_2H_5)_2 \longrightarrow CH_3C \begin{matrix} OZnC_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} + C_2H_5ZnCl$$

$$CH_3C \begin{matrix} OZnC_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} + 2H_2O \longrightarrow CH_3C(OH)(C_2H_5)_2 + Zn(OH)_2 + C_2H_6$$
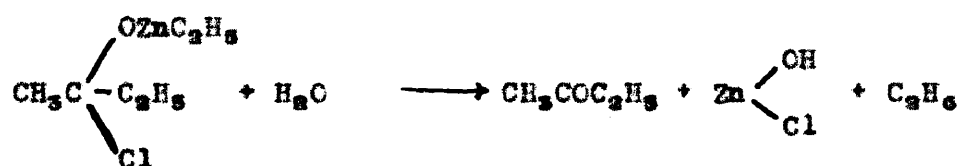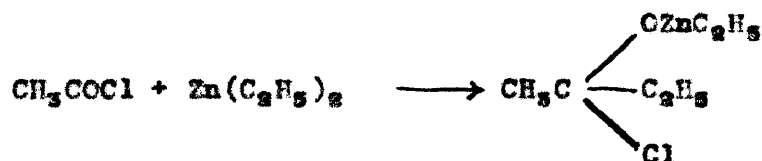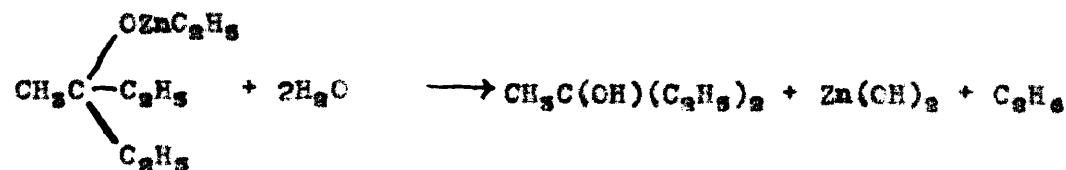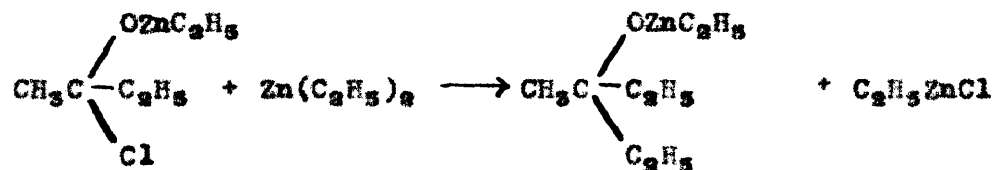
Wagner, Saytzeff, and Kannonikoff[41,42] studied the very similar reactions

of esters with zinc ethyl. Once again one mole of zinc ethyl may be added and hydrolysis gives the ketone or, if a second mole is added, the alcohol is formed on hydrolysis.

Wagner[40] studied the reaction on aldehydes and prepared a number of secondary alcohols. With acetaldehyde and zinc ethyl he obtained the following reaction:

$$CH_3CHO + Zn(C_2H_5)_2 \longrightarrow CH_3CH \begin{smallmatrix} OZnC_2H_5 \\ C_2H_5 \end{smallmatrix}$$

$$CH_3CH \begin{smallmatrix} OZnC_2H_5 \\ C_2H_5 \end{smallmatrix} + 2H_2O \longrightarrow CH_3CHOHC_2H_5 + Zn(OH)_2 + C_2H_6$$

Later formaldehyde was used in this same reaction, giving however the primary alcohol.

$$HCHO + Zn(C_2H_5)_2 \longrightarrow HCH \begin{smallmatrix} OZnC_2H_5 \\ C_2H_5 \end{smallmatrix}$$

$$HCH \begin{smallmatrix} OZnC_2H_5 \\ C_2H_5 \end{smallmatrix} + 2H_2O \longrightarrow n\text{-}C_3H_7OH + Zn(OH)_2 + C_2H_6$$

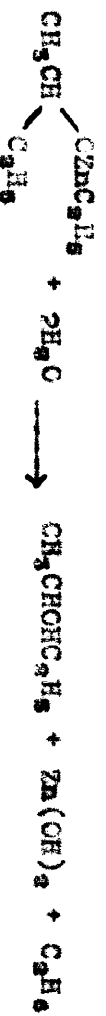Saytzeff[25] applied a similar reaction to ketones and made tertiary alcohols. Using acetone he prepared tertiary amyl alcohol.

$$(CH_3)_2CO + Zn(C_2H_5)_2 \longrightarrow (CH_3)_2C \begin{smallmatrix} OZnC_2H_5 \\ C_2H_5 \end{smallmatrix}$$

$$(CH_3)_2C \begin{smallmatrix} OZnC_2H_5 \\ C_2H_5 \end{smallmatrix} + 2H_2O \longrightarrow (CH_3)_3C(OH)C_2H_5 + Zn(OH)_2 + C_2H_6$$

Thus during the latter half of the nineteenth century, the zinc alkyls were used in syntheses of all sorts where today we commonly use the Grignard reagent. Upon the discovery of the Grignard reagent in 1899, zinc alkyls became much less important since the Grignard reagent is so much easier to handle and gives better yields. The

reactions of the zinc alkyls and of the Grignard reagent are almost exactly parallel. The ease of reaction with ketones is sufficiently different for the two so that we still use zinc alkyl in converting an acid halide or an ester to the ketone. The Grignard reagent is so much more active that extreme care is necessary to stop the reaction at the ketone stage otherwise the tertiary alcohol is formed. Fortunately zinc alkyls do not react with carbon dioxide as does the Grignard reagent, so carbon dioxide may be employed as the inert atmosphere which must be used.

Zinc alkyls react with many other compounds in addition to those mentioned in the foregoing paragraphs.[36] Any compound containing an active hydrogen will react with zinc alkyl to give the corresponding paraffin.

$$Zn(C_2H_5)_2 + C_4H_9CH \longrightarrow C_4H_{10} + Zn \underset{OC_2H_5}{\overset{C_2H_5}{<}}$$

$$Zn \underset{OC_2H_5}{\overset{C_2H_5}{<}} + C_4H_9CH \longrightarrow C_4H_{10} + Zn(OC_2H_5)_2$$
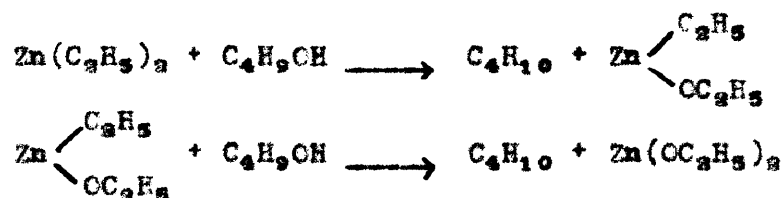
Zinc alkyls, as do any of the metal alkyls, react with the halogens to give the alkyl halides and the metal halides.

$$Zn(C_2H_5)_2 + 2Br_2 \longrightarrow 2C_2H_5Br + ZnBr_2$$

With the chlorides of heavy metals and those of non-metals, zinc alkyls react to form the alkylated products of the metals or non-metals.

$$3Zn(CH_3)_2 + 2PCl_3 \longrightarrow 2(CH_3)_3P + 3ZnCl_2$$

$$3Zn(C_2H_5)_2 + 2SbCl_3 \longrightarrow 2(C_2H_5)_3Sb + 3ZnCl_2$$

Sometimes these reactions give unsuspected end-products by reason of secondary reactions. For example:

$$2Zn(C_2H_5)_2 + 2SnCl_2 \longrightarrow (C_2H_5)_4Sn + 2ZnCl_2 + Sn$$

The metal alkyls of the metals more active than zinc may be made by the direct combination of that metal with zinc alkyl.

$$Zn(C_2H_5)_2 + 2Na \longrightarrow 2C_2H_5Na + Zn$$

Zinc alkyl adds sulfur dioxide to form the zinc salt of the corresponding sulfinic acid.

$$Zn(C_2H_5)_2 + 2SO_2 \longrightarrow (C_2H_5SO_2)_2Zn$$

Nitric oxide adds to zinc ethyl to give a crystalline compound which reacts further with carbon dioxide and water to give the zinc salt of the so-called ethyl dinitro acid $(C_2H_5 \cdot N_2O_2H)$.

Halogenated compounds including the simple alkyl halides and the more complex halogen substituted molecules will replace the halogen with the alkyl of the zinc alkyl. More will be given shortly concerning the reaction on simple alkyl halides. Some of the more peculiar reactions with halogenated compounds follow.

$$2CH_2 = CHBr + Zn(C_2H_5)_2 \longrightarrow 2CH_2 = CHCH_2CH_3 + ZnBr_2$$

$$2(CH_3)_2C(Br)NO_2 + Zn(CH_3)_2 \longrightarrow 2(CH_3)_3CNO_2 + ZnBr_2$$

The chief application at present of the zinc alkyls is in the replacement of the halogen of an alkyl halide by the alkyl of the zinc alkyl. This method is the only known method for approaching many of the highly branched hydrocarbons in reasonable yield. Friedel and Ladenburg[19] first used this type reaction when they combined zinc ethyl with dichlorodimethyl methane. The highly branched heptane, $C_2H_5C(CH_3)_2C_2H_5$ (3,3-dimethylpentane), resulted in poor yield along with large quantities of various unsaturated hydrocarbons. Goriainow[24] used tertiary butyl iodide with zinc ethyl to prepare the 2,2-dimethyl-butane. He developed a purification scheme for the hydrocarbon which is essentially the same as the present method. After addition of

water to remove all the zinc ethyl, the product was distilled, treated with bromine and finally distilled again, this time from sodium.

Recent work on this type reaction has been slight. Whitmore[44] and Howard[26] have used the reaction in the synthesis of 2,2,4,4-tetramethyl pentane. The most comprehensive work regarding the synthesis of hydrocarbons by use of zinc alkyls is the work of Noller.[32,33] In general, his method for the preparation of the zinc ethyl and its reaction with tertiary butyl chloride has been followed in this work.

EXPERIMENTAL

Apparatus:

The apparatus used for the study of the reaction of zinc
ethyl on tertiary butyl chloride is shown diagramatically on Plate I.
Two pictures of the apparatus are also shown on Plates II and III.
Some ideas for this apparatus were gleaned from the work of McCleary
and Degering[31] on the gaseous products formed during zinc alkyl
formation and from the work of Goldman[23] on the handling of gases in
connection with some dehydrogenation studies made in this Laboratory.
This apparatus as described is the final form used after a number of
modifications were made from time to time during the course of the
research. A is a four liter liquid air type Dewar flask equipped
with a pressure escape valve which is charged with dry ice. This
furnishes a supply of carbon dioxide lasting for three weeks. B and
C are drying tubes filled with Drierite, anhydrous calcium sulfate,
and Anhydrone, magnesium perchlorate monohydrate, respectively. Stop-
cock a is used to control the flow of carbon dioxide through the
system. D is an ordinary micro Dumas combustion tube which is packed
with 15cms. of copper (wire-form) and 10 cms. of copper oxide (wire-
form). This tube is placed in furnace E which maintains a constant
temperature of $650°$ C. The tube is so placed that 5 cms. of the
copper oxide is outside of the furnace and the remainder of the
packing is inside. The purpose of this train is to insure dry, pure
carbon dioxide. The copper insures that no oxygen passes through and
the copper oxide is necessary to insure that some of the carbon dioxide
which may have been reduced to carbon monoxide will reform carbon
dioxide. F is a bubble counter filled with dibutyl phthalate. Stopcock
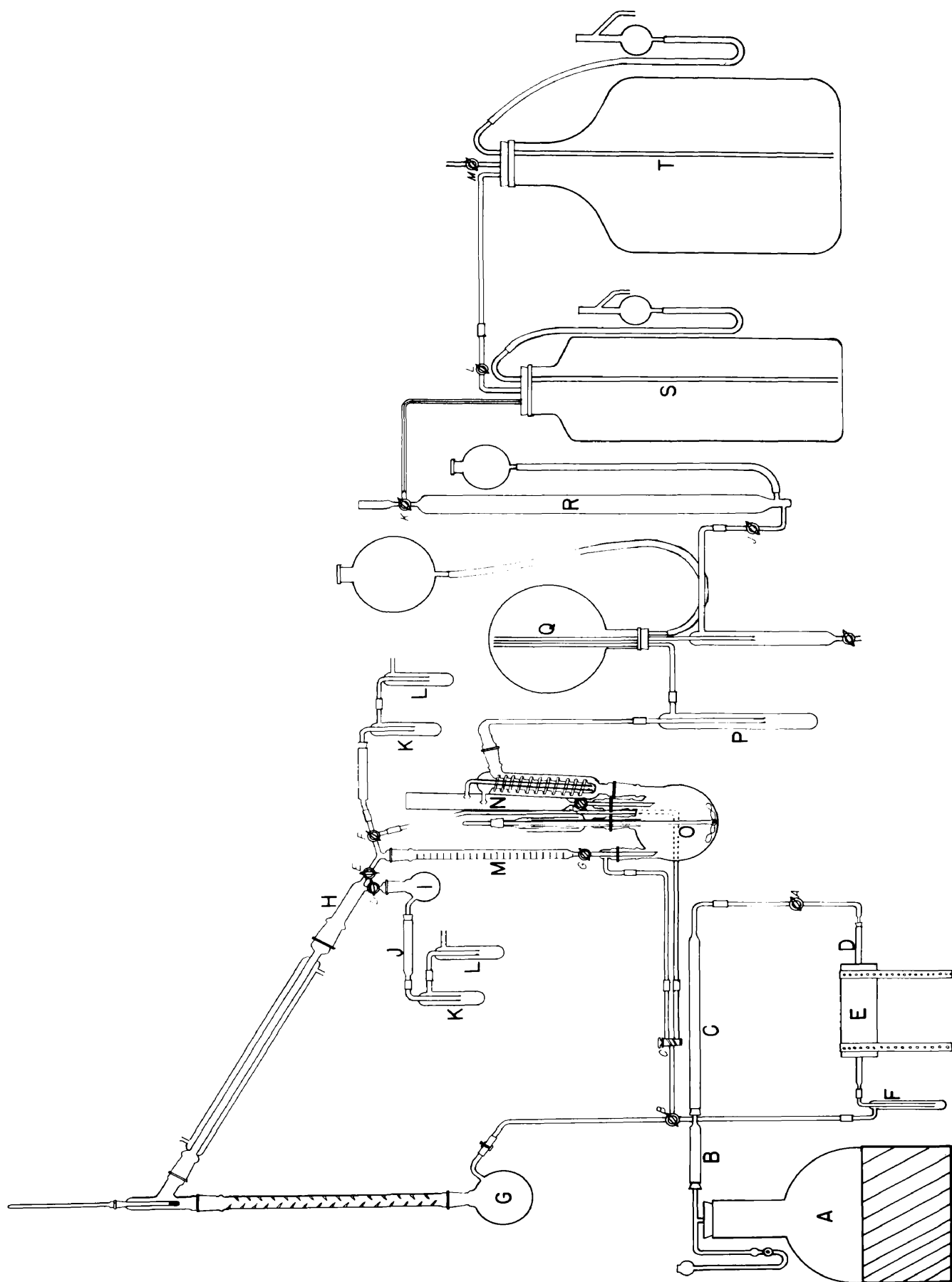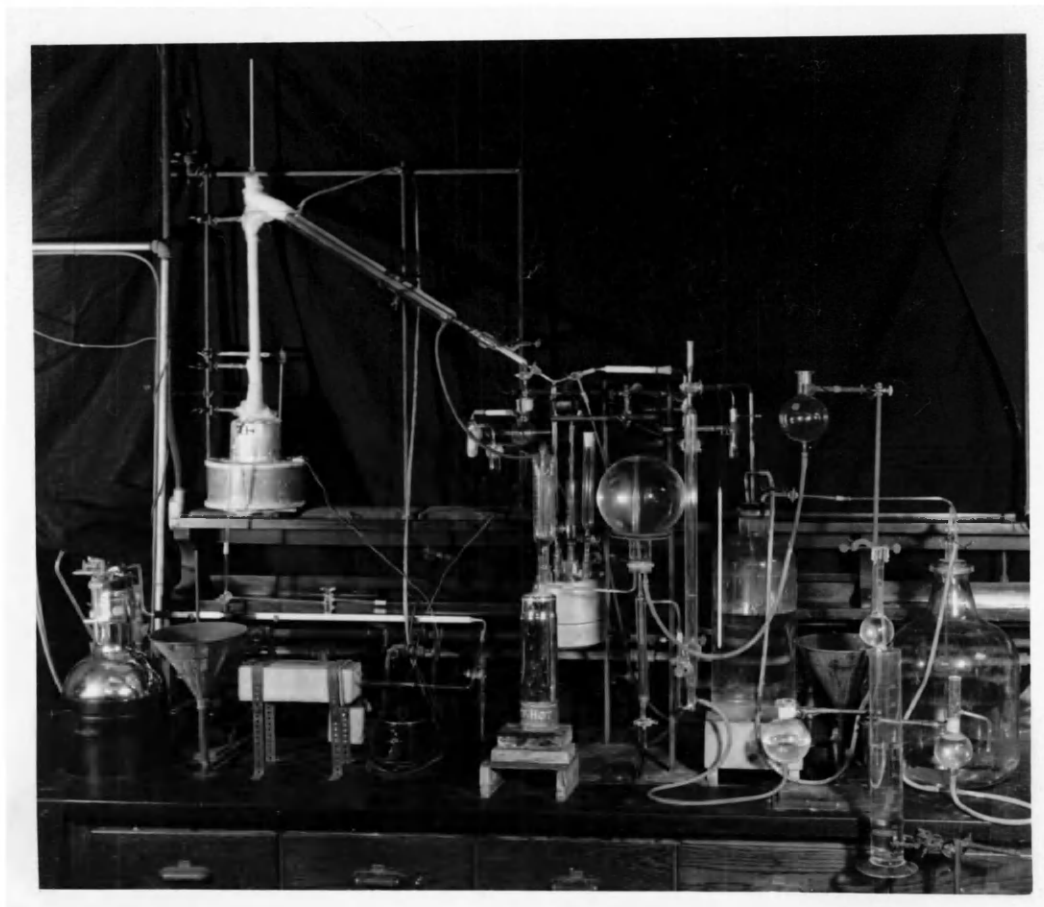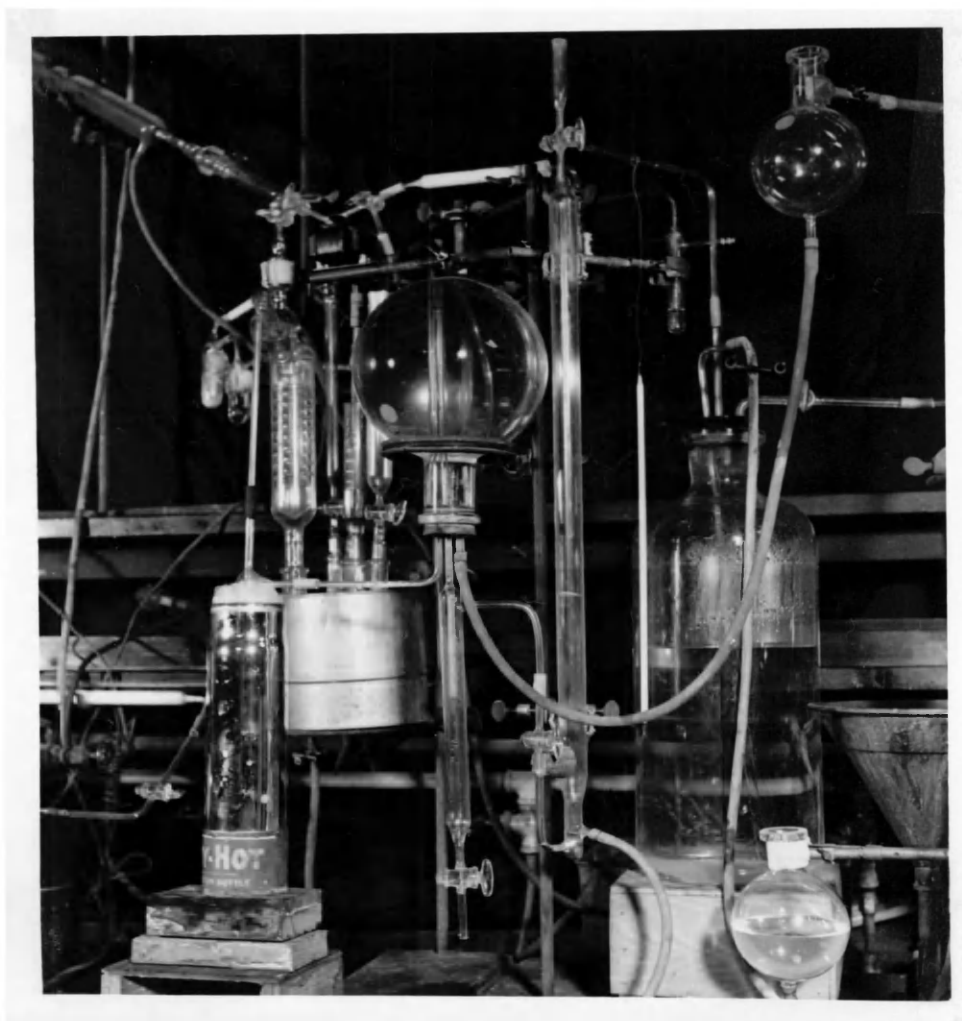
PLATE I

Full View of Apparatus Used for Study of
Reaction of Zinc Ethyl and Tertiary Butyl Chloride

PLATE   II

PLATE III

View of Reaction Flask of Apparatus Used for Study of
Reaction of Zinc Ethyl and Tertiary Butyl Chloride

PLATE   III

b is used to direct the carbon dioxide either directly into the distilling flask or into the reaction flask. Stopcock c is used to control whether the carbon dioxide goes directly into the reaction flask or whether it fills the space above the surface of the zinc ethyl in the measuring burette M so that zinc ethyl can be introduced into the reaction flask. G is a 500 ml. sidearm round bottom flask with a standard taper joint fitted with a 50 cm. Vigreux column and a distilling head to accomodate a thermometer with a standard taper joint. The ordinary Liebig's condenser leads to an adapter H which is equipped with two stopcocks, d and e. At the beginning of a distillation d is opened and e closed so that the forerun may pass into flask I which is of 125 ml. capacity. J is a small drying tube equipped with Drierite and K is a dry "safety-valve" trap with L being a similar trap filled with 6 N hydrochloric acid. Stopcock e leads to the measuring burette M and has the attached stopcook f which is connected to either a source of carbon dioxide or an escape train, or to both. The measuring burette M is of 12 mm. tubing marked to 0.2 ml. with a diamond pencil and has a capacity of 25 ml. It leads into the one liter reaction flask O through stopcock g. Flask O is a four-necked flask equipped with a mercury sealed stirrer assembly using the Hirschberg type stirrer and a Friedrich's condenser in addition to the measuring burette and the dropping funnel N. N is of 100 ml. capacity and has an especially long drip-tip so that the liquid being introduced drops directly upon the liquids in the flask. The trap F at various times during the course of the research was put into either wet-ice or dry ice filled Dewar flasks. P is a reservoir constructed of a three liter flask equipped with a levelling bulb of

one liter capacity and a trap equipped with a stopcock. R is an
absorption tower constructed of 50 cm. of 23 mm. tubing, fitted with
a stopcock j to allow continuous collection of gas in the reservoir
while transferring the gas collected in the tower into the gasometers
S and T through stopcock k. A 50 percent potassium hydroxide solu-
tion is used in this absorber and its levelling bulb to remove all
carbon dioxide from the evolved gas. The gas is collected in the
gasometer bottles S and T. S is of ten liter capacity and T is of
twenty liter capacity. They are so connected that gas may be collected
in them either in parallel or in series so to speak. Both S and T
are equipped with levelling bulbs with sidearms, so that as the gas
collects displacing the magnesium sulfate solution, this solution
can be collected and measured in a graduate. S, S, and T have as
their containing fluid a saturated solution of magnesium sulfate
since the gases to be collected are inappreciably soluble in this
solution but are appreciably soluble in water alone.

The apparatus used in the gas analyses was a Burrell
Universal Gas Analyzer of the Build-Up Model.[+] The particular model
used has three absorption pipettes; one with a helical coil, the
other two of the Francis Auto Bubbler type. A copper oxide tube is
available for hydrogen analysis and a slow burning combustion pipette
is used for combustibles. The gas burette was of 100 ml. capacity and
is equipped with a comparison burette both immersed in the same bath.
The pipette with the helical coil is filled with 30 percent potassium

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[+] This apparatus was used through the kindness of Dr. D. T.
Bonney of the Chemical Engineering Department of the University of
Maryland.

hydroxide solution for carbon dioxide absorption. One of the Francis Auto Bubbler pipettes is filled with a solution recommended by Tropsch and Dittrich.[38,39] This solution is made up by mixing 15 volumes of 0.6 percent silver sulfate in concentrated sulfuric acid with one volume of saturated nickel sulfate in sulfuric acid. This solution is used to absorb unsaturated hydrocarbons and has the decided advantages over fuming sulfuric acid which is commonly used in that it dissolves only very small amounts of the saturated hydrocarbons and also in that it is unnecessary to pass through the potassium hydroxide pipette to remove sulfur trioxide. The other Francis Auto Bubbler pipette contains a solution developed by Fieser[13] for oxygen absorption. This solution consists of 16 grams of 36.7 percent sodium hyposulfite, 13.3 grams of sodium hydroxide, and 4 grams of 95 percent sodium anthraquinone-β-sulfonate all in 100 ml. of water.

The apparatus used in the low temperature, low pressure distillation was a simplified model after the method of Booth.[1] The simplified model used in this work is shown diagramatically on Plate IV. Two pictures of the apparatus are shown on Plates V and VI. The apparatus is equipped with two distillation columns, B, which are connected into the manifold, A. The manifold has three collecting ampoules, E, attached; a detachable ampoule, C, for introducing sample; an ampoule, D, containing activated Columbia carbon; and a freezing point tube, F.

The columns, B, are constructed identically. They are made of 110 cms. of 11 mm. O. D. pyrex tubing into which is fitted a 85 cm. length of 7 mm. O. D. pyrex tubing wound with No. 22 Chromel wire in
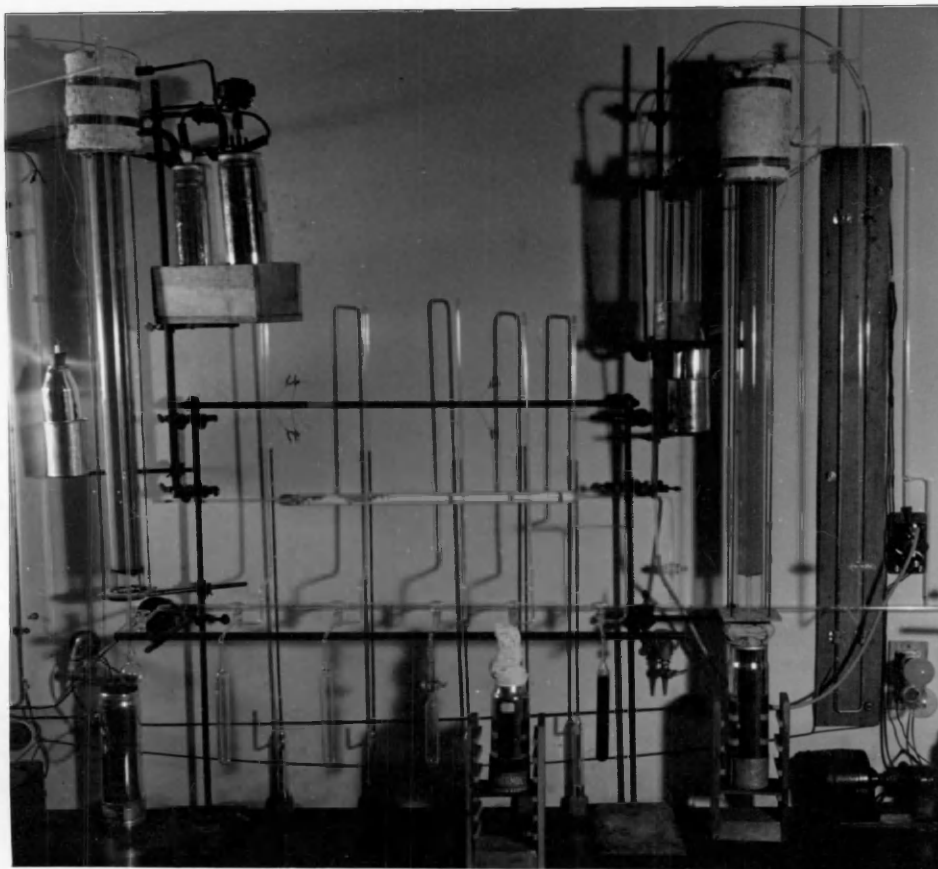
PLATE IV
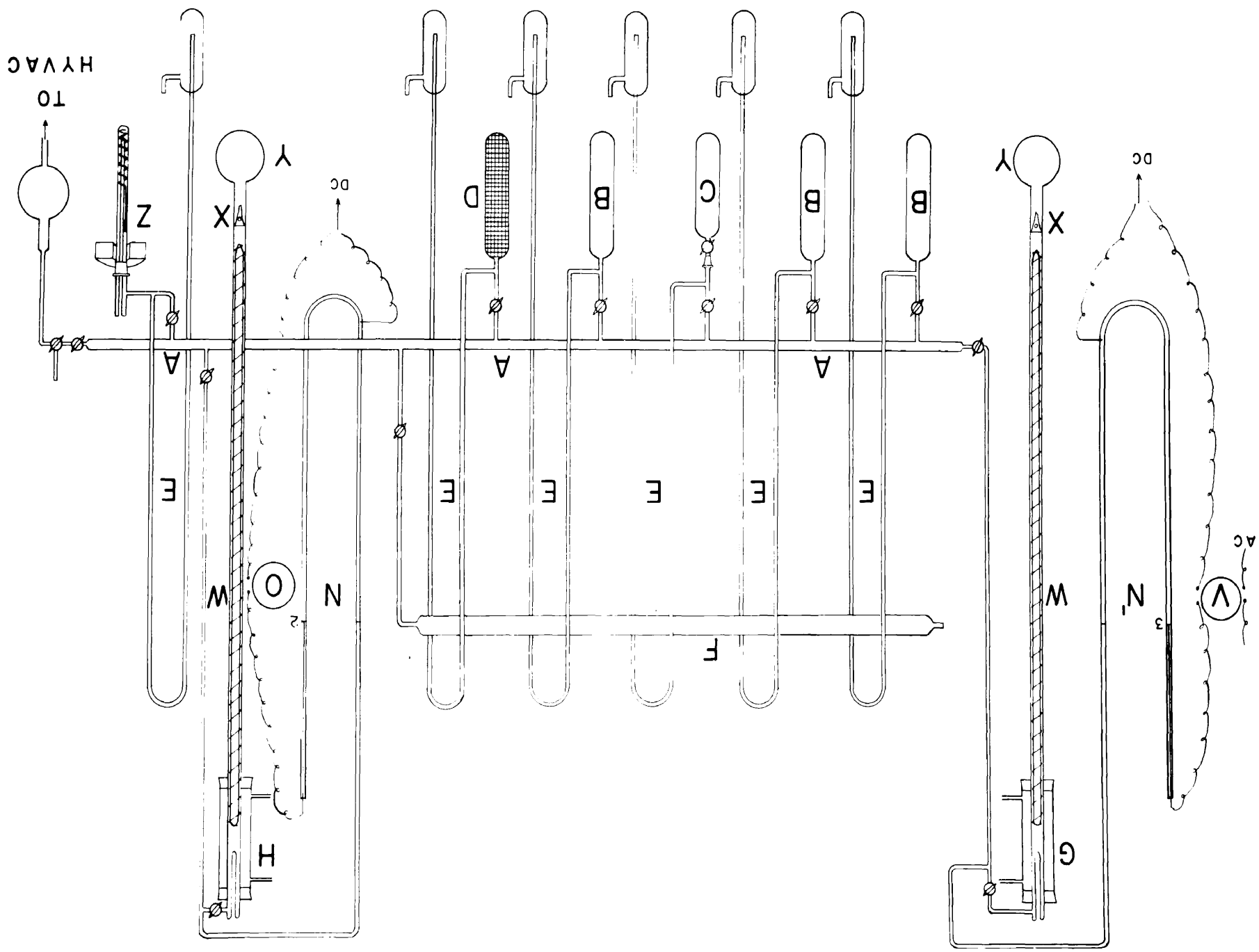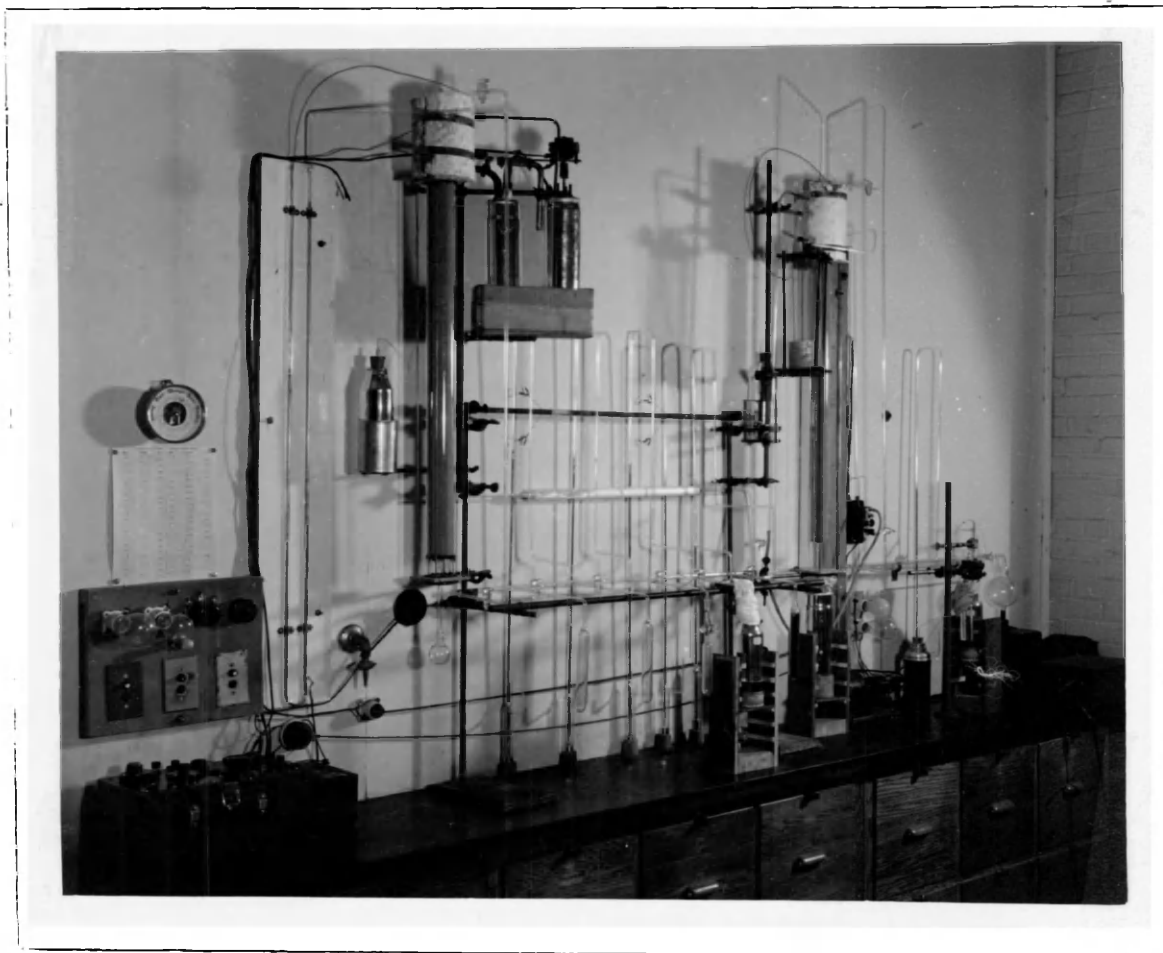
Full View of Low Temperature, Low Pressure
Distillation Apparatus

PLATE   V

Center View of Low Temperature, Low Pressure
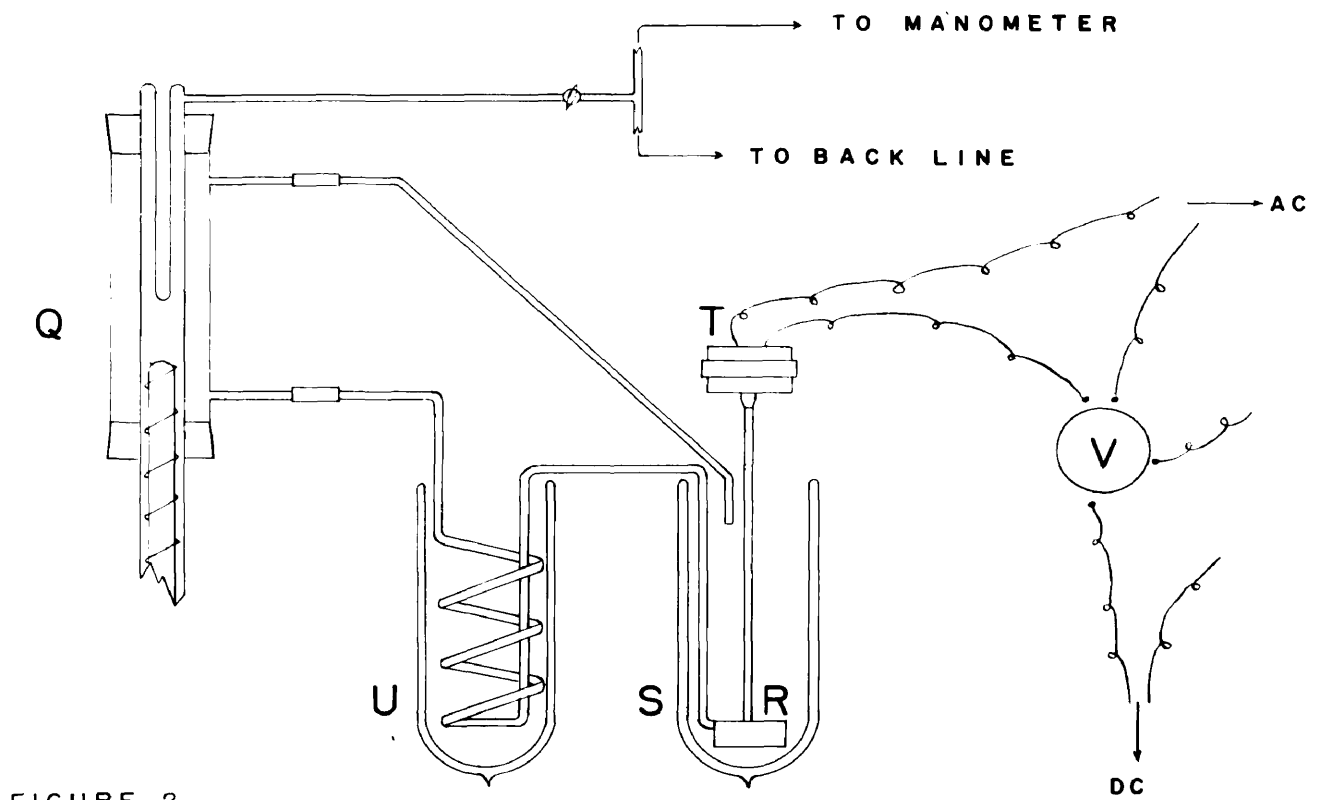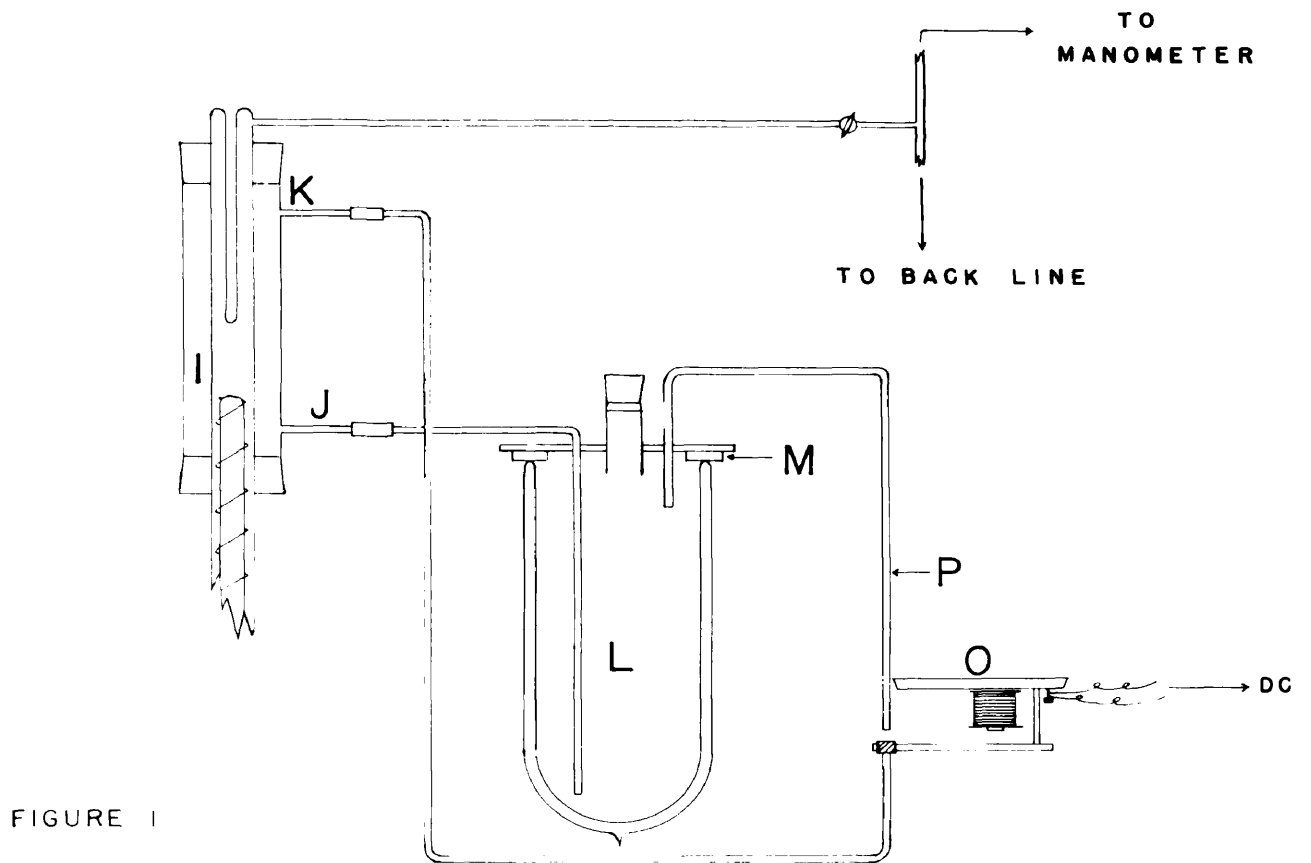
Distillation Apparatus

PLATE VI

the manner of Dufton.[11] The top of the column is fitted with a thermocouple well made from 10 cms. of 4 mm. O. D. pyrex tubing. The bottom of the column is fitted with a dropper, X, incorporated in the column and a stillpot, Y, of 50 ml. capacity. The details of the heads of the columns, G and H, will be described in further detail later. The column is surrounded by a 64 mm. O. D. pyrex tubing jacket which is packed with 20 mesh cork for insulation.

The column is fitted in its take-off side arm with a stopcock known as the "suicide stopcock" and then an open end manometer, N and N', is connected before the manifold. These manometers are made of 7 mm. O. D. pyrex tubing and are about 100 cms. length in each arm. They have a platinum contact point through the glass at the bend and the D. C. circuit is completed by copper wire in the open arm of the manometer. As the pressure varies the mercury level in the manometer varies and contact is made or broken with the adjustable copper wire.

The manifold, A, is made of 12 mm. O. D. pyrex tubing; all other tubing of the apparatus is 7 mm. O. D. pyrex tubing. The ampoules, B, are made of 15 cm. lengths of 24 mm. O. D. pyrex tubing. Ampoule, C, is only 10 cms. long and is fitted with a stopcock and a 10/30 standard taper ground glass joint. The ampoule, D, is identical with the ampoules, B, except that it contains activated carbon. It is by this means that a very high vacuum can be obtained since the activated carbon at liquid air temperature adsorbs enormous quantities of air and other gases. E is a drying tube made from 30 cms. of 24 mm. O. D. pyrex tubing and is filled with phosphorus pentoxide. This tube is used to admit dry air into the apparatus. The freezing point tube, Z, is made of 10 mm. O. D. pyrex tubing. From top to bottom the tube is

23 cms. long and the tube is divided by a 14/35 standard taper

ground glass joint 4 cms. from the top. A thermocouple well of

4 mm. O. D. pyrex tubing goes the entire length of the tube. Around

this well is a glass helix to the top of which is attached a tube

containing a bit of iron. This constitutes the stirrer. It is

activated by a solenoid made of several turns of fine copper wire

wound on a spool. The strength of the field is controlled by a

lamp bank in series with the solenoid. The freezing point tube,

as well as each of the ampoules, is fitted with a safety manometer,

S. These manometers are of 7 mm. O. D. with a 15 cm. by 24 mm. O. D.

trap at the bottom. This trap serves as a safety factor so that if

for any reason the gas vaporizes with consequent rapid expansion,

there is a way out without breaking the apparatus.

The detailed diagrams of the two cooling heads are given

in Plate VII. The liquid air head, H, is enlarged on figure 1. I

is a brass tube of 3 cms. diameter which is 24 cms. long and assembled

on the column with paraffined corks. This tube is covered with heavy

magnesia pipe covering for insulation. J is the inlet tube and K

is the exit tube. L is a clear quart Dewar flask fitted with a cork

containing an escape tube, P; the tube, J, which introduces the liquid

air into the head; and a large tube for introducing the charge of

liquid air. In order to make the Dewar air-tight, a sponge rubber

gasket, M, is held firm to the top of the flask by inserting the

Dewar in a frame made of two pieces of fiber board pulled together

by threaded brass rods. The telegraph sounder key, C, is activated

by the manometer and it controls the injection of the liquid air.

The sounder key is connected through the manometer so that when the

TO MANOMETER

TO BACK LINE

K

I

J

M

P

L

O

DC

FIGURE I

TO MANOMETER

TO BACK LINE

Q

T

AC

V

U

S

R

DC

FIGURE 2

PLATE VII

pressure increases to cause contact at point 2 in the manometer, the sounder key is activated. Usual evaporation of the liquid air is accomodated by the escape tube, F, which leads to the sounder key. When the sounder key is activated the escape tube is cut off and the pressure built up in the Dewar causes liquid air to inject into the head. The exit tube, K, is also connected to the sounder key however from the other side. This tube is only open when the key is activated and liquid air is injecting. This method allows a closer control over the injection than if tube, K, is open to the atmosphere.

The dry ice head, G, is enlarged on figure 2. A is a brass tube of 3 cms. diameter which is 19 cms. long and assembled on the column with rubber stoppers. This head is insulated in the same way as that of the liquid air column. The cooling agent is actually ethyl alcohol which circulates in an all-copper system from and to the wide mouth quart Dewar flask, S. The circulation is brought about by the centrifugal pump, R, from which the alcohol passes through the coil in the Dewar flask, U. After passing through the head the alcohol returns to the Dewar, S, for recirculation. The coil in the Dewar, S, is surrounded by a slurry of pulverized dry ice and alcohol. The pump is activated by the induction motor, I, which is operated by the relay, V. This relay is connected through the manometer so that when the pressure increases to make the mercury contact point 3 in the manometer, the relay is activated and the motor is started.

The temperatures are read by use of copper-constantan thermocouples. The one in the dry ice head is a three-junction

couple, whereas those in the liquid air head and the freezing point
tube are two junction couples. Only two junctions are necessary
since the temperatures read on these columns are for the most part
quite low. The potential developed by the thermocouples is read on
a Rubicon potentiometer.

Reagents:

Ethyl Bromide

Ethyl bromide, practical grade, as purchased from Dow Chemical
Company was purified after the method of Kamm and Marvel.[29] The
method consists of washing the bromide with concentrated sulfuric acid,
sodium carbonate, sodium bicarbonate, and water, drying the product
over Drierite, and finally distilling the purified bromide from
phosphorus pentoxide.

Ethyl Iodide

Ethyl iodide was made* according to the method patterned
after the preparation of methyl iodide by Weinland and Schmid.[43]
The more recent directions of Hartman[25] were followed. The method
essentially is to allow diethyl sulfate to react with a water solution
of potassium iodide in which a slurry of powdered calcium carbonate
is suspended by efficient stirring. The purification was in the
same fashion as was used for the ethyl bromide with the single exception
that distillation was from phosphorous pentoxide and solid potassium
iodide. The latter is added to prevent any iodine from volatilizing
with the product.

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* This preparation was run in large scale by Mr. L. Goldman
of this Laboratory.

Zinc-Copper Couple[+]

Zinc shot and copper pellets in a weight ratio of 97:3 are melted together into an alloy in a refractory crucible in a resistance furnace. At first a layer of molten zinc is allowed to cover the bottom of the crucible, then some copper pellets are sprinkled on the surface and allowed to heat. After a few minutes a thicker layer of zinc is placed over the copper and allowed to melt without stirring. The mixture is stirred and the process repeated until all of the metal is added. The molten metal is cast into a tall, thin, cylindrical mold so that lathe turning will be easy. Alloy shavings are turned on a lathe and then the shavings are washed with petroleum ether and dried in the oven.

Zinc Ethyl

Three-hundred and ninety grams of the zinc-copper alloy turnings is placed in a two liter flask equipped with a mercury sealed stirrer and a Dimroth condenser set at reflux. The flask is swept with carbon dioxide before the mercury is added to the seal. The apparatus is so arranged that the only escape for the gas is through the seal. The flask and alloy are heated for ten minutes and then allowed to cool, all the while carbon dioxide passing through. When cool, mercury is added to the seal and the carbon dioxide stream is diverted across the top of the reflux condenser. Thirty-nine ml. (0.5 mole) of ethyl bromide and 20 ml. (0.25 mole) of ethyl iodide are added as quickly as possible. The mixture then is heated with an oil bath with stirring. In about one-half an hour

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[+]The author wishes to thank Mr. A. C. Whiton for this material.

the reaction begins to fume and the fuming is allowed to continue
for fifteen minutes, after which 172 ml. (2 1/4 moles) of ethyl
bromide is added as rapidly as possible. Heating is continued until
reflux stops. The mixture is then cooled after pulling the stirrer
above the surface of the unreacted alloy. The product is distilled
under water pump vacuum (20-30 mm. pressure) keeping the oil bath
temperature at 80° C. until the end of the distillation when it is
taken to 170° C. A hydrochloric acid trap must be between the
apparatus and the aspirator for otherwise the aspirator rapidly is
clogged with zinc oxide. The vacuum is released by admitting dry
carbon dioxide to the system.

Tertiary Butyl Chloride

The method followed was that of Norris and Olmsted.[34] The
direct reaction of tertiary butyl alcohol with hydrochloric acid
produces tertiary butyl chloride which is satisfactory for use after
several sodium bicarbonate and water washings and a single distil-
lation from potassium hydroxide.

Dibutyl Ether

Dibutyl ether from class preparations was washed several
times with potassium hydroxide solution and then distilled from solid
potassium hydroxide.

Diamyl Ether

The diamyl ether used was also a class preparation and was
purified in the same manner as the dibutyl ether.

Toluene

Commercial toluene was purified by azeotropic distillation
and then sodium ribbon was added and allowed to stand overnight.

Finally the toluene was distilled from the sodium.

Experiments:

Experiment One

The purpose of these first few experiments was to determine
if the apparatus would allow a quantitative study of the reaction.
Zinc ethyl should react with any compound containing an active hydrogen
and give the corresponding paraffin. First hydrochloric acid was
chosen to supply the active hydrogen.

Several modifications of the apparatus shown in Plate I
were not present in the original apparatus used in this experiment.
These changes will be described first.

Flask G was fitted with a gas inlet tube instead of a
simple sidearm as shown. The tube from stopcock b to burette M
just below stopcock g was non-existent. The measuring burette M
was of 100 ml. capacity being constructed of 24 mm. O. D. pyrex
tubing. In lieu of the gas inlet pictured below stopcock g on the
measuring burette, a gas by-pass tube was attached from the top to
bottom of the measuring burette for otherwise it would have been
impossible to sweep the reaction flask O at the conclusion of the
reaction. The trap, F, was non existent.

The apparatus was assembled as described using Lubriseal
to lubricate all ground glass joints. The parts of the apparatus
were kept in a drying oven until assemblage and after assemblage
available parts were flamed while a fast stream of carbon dioxide
was passing through. Sweeping with carbon dioxide was allowed to
continue overnight and before the addition of any zinc ethyl to the
apparatus, microbubbles were tested for in the absorber R.

About 75 ml. of zinc ethyl was added to the distilling
flask C and 45.5 ml. was distilled into the measuring burette K
after first taking off the forerun into flask I. By the time this
distillation had been completed the gas inlet tube which extended
below the liquid surface in the distilling flask had become clogged.
This necessitated supplying the carbon dioxide by means of the by-
pass from stopcock b to stopcock f. Ten and five-tenths ml. (0.1
mole) of zinc ethyl was allowed to pass stopcock g into the reaction
flask C. Stirring was begun and 2 N hydrochloric acid in the dropping
funnel H was allowed to drop into the reaction flask. The water had
sufficient surface tension so that it did not drop from the stopcock
h down through the dropping tube but instead filled that tube gradually.
Then when the tube was full and the first drop fell off the entire
tube-full followed it. The rate of evolution of the gas was too rapid
and much of the gas blew through the mercury seal stirrer.

The quantitative aspects of this particular experiment were
thus doomed to failure but the reaction was continued to become familiar
with the apparatus. Extremely slow addition of the acid made it
possible to control the reaction so that all the rest of the gas could
be collected. A check on the amount of zinc ethyl added and the
volume of gas evolved indicates promise of giving reasonable results
provided a control for the evolution of the gas can be worked out.

The next experiment was an attempt to control gas evolution
by diluting the active hydrogen in the liquid which is added from the
dropping funnel. The distilling flask also was changed to one with
an ordinary sidearm as shown in Plate I.

Experiment Two

It was decided to use a solution of absolute ethyl alcohol in dry benzene to attain the necessary dilution of the active hydrogen. The apparatus was assembled and swept with carbon dioxide as before.

About 25 ml. of zinc ethyl was placed in the distilling flask and 12.5 ml. was distilled into the measuring burette. Ten and five-tenths ml. (0.1 mole) of zinc ethyl was added to the reaction flask and stirring was begun. Then a solution of 20 ml. of absolute ethyl alcohol in 400 ml. of benzene was added dropwise over a period of five hours. During this time the flask remained at room temperature. It was noted that after about one-third of this solution had been added the evolution of gas ceased. By means of a water bath the reaction flask was heated slowly to 100° C. with the consequent evolution of further gas. Then the apparatus was swept with carbon dioxide for one hour. By this time the volume of gas calculated to standard conditions was 5258 ml. This value is 17 percent higher than that anticipated for pure ethane evolution.

It was supposed that this fact indicated formation of some ethylene and hydrogen thus boosting the volume of gas beyond that expected. Unfortunately the gas evolved in this experiment was discarded before it was decided that ethylene might be a product. The only way to verify the presence of ethylene is to run a gas analysis on the product. The next experiment was used to make gas for analysis.

Experiment Three

For this experiment, the method used in experiment two was followed closely. The alcohol was dissolved in only 200 ml. of benzene for this experiment. At the conclusion of the run it was

noticed that microbubbles were never obtained and that a layer appeared on the potassium hydroxide solution in the absorber. This liquid was obviously benzene judging from its odor. In the calculation of the gas volume to standard conditions, the vapor pressure of benzene is taken into account, the corrected volume of gas at standard conditions is 4550 ml. which represents 6.107 grams of ethane. This value is just 1.55 percent below the theoretically expected value.

Gas analysis of the gaseous products was first carried out with a small Fisher portable analyzer which used no mercury, had no slow combustion tube, and no copper oxide tube. The results of a single run are shown below.

Percent carbon dioxide   1.3

Percent unsaturates   7.2

Percent oxygen   2.8

It was decided that if satisfactory results were to be obtained a more accurate gas analysis outfit was necessary. Recourse was taken to the Burrell apparatus described on page 19. First a run was made using fuming sulfuric acid to absorb the unsaturates with the results which follow.

Percent carbon dioxide   0.1

Percent unsaturates   9.9

Percent oxygen   1.9

Percent ethane   83.0

Since it was suspected that the ethane was dissolving in the fuming sulfuric acid, the reagent for unsaturates described on page 14 was used for another run which gave the results which follow.

Percent carbon dioxide	0.2
Percent unsaturates	7.8
Percent oxygen	0.7
Percent ethane	87.4

These high values for the unsaturates were difficult to explain until it was realized that the benzene vapor which had increased the volume of the gas was acting in these analyses as unsaturates. Therefore this gas was passed through a large dry ice-alcohol trap several times to remove the benzene. The resultant gas gave the analysis which follows.

Percent carbon dioxide	0.1
Percent unsaturates	1.8
Percent oxygen	.7
Percent ethane	97.5

Thus it was concluded that gas analysis was unnecessary since the gas evolved is pure ethane. The slight inconsistency in the analysis probably represents solution of ethane in the reagent.

Experiment Four

In view of the fact that it was desirable to study the reaction at all temperatures, it was decided to use some active hydrogen donor other than ethyl alcohol which required 100° C. for completion. Thus a solution of excess dry hydrogen chloride in dry diamyl ether replaced the alcohol-benzene solution.

The apparatus was prepared as before but the zinc ethyl was measured into the flask and the flask swept overnight. As a result some of the zinc ethyl evaporated and low results should be obtained. The hydrogen chloride-amyl ether solution was added over

five hours with the flask kept surrounded by ice. Sweeping, then elevation of the temperature to 100° C., and further sweeping showed that the reaction was complete at the lower temperature. The volume of gas collected at standard conditions, allowing for the vapor pressure correction for saturated magnesium sulfate solution was 4656 ml. The result is 3.6 percent below theoretical which is as suspected.

Experiment Five

Experiment four was repeated but for two slight modifications. The hydrogen chloride in the amyl ether was replaced by sulfuric acid in amyl ether, since it was so much easier to add sulfuric acid to amyl ether directly than bubble hydrogen chloride through amyl ether over a period of time. The addition of the sulfuric acid to the amyl ether must however be carried out slowly at a decreased temperature otherwise polymerization takes place. The other modification was an operational one involving the addition of the zinc ethyl to the reaction flask just prior to the beginning of a run.

To the 10.5 ml. of zinc ethyl 10.7 ml. of concentrated sulfuric acid in 200 ml. of amyl ether was added dropwise over a period of three and one-half hours. Reaction temperature was kept low by keeping the flask in an ice bath. Five hours sweeping gave 4712 ml. of gas corrected to standard conditions. This represents an error of 5.2 percent above the theoretical value.

Just prior to this run a small amount of amyl alcohol had been added to the saturated magnesium sulfate solution to prevent mold formation. Since there was a possibility that the vapor pressure of the added amyl alcohol might be appreciable enough to cause this

error in gas volume, it was decided that the next experiment should
use saturated magnesium sulfate solution containing no amyl alcohol.

Experiment Six

Air was bubbled through the saturated magnesium sulfate
solution overnight and the solution was returned to the reservoir
and the gasometer. Experiment five was then repeated with the time
of addition being seven hours and the time of sweeping being five and
one-half hours. Four thousand six hundred and eighty-one ml. of gas
corrected to standard conditions was collected representing a high
result of 4.5 percent.

It was concluded from this result and the similar ones
preceding that the error may be caused by an error in the design of
the apparatus. It had been noted that microbubbles were never quite
obtained at the end of the sweeping. A possible reason was that the
zinc ethyl remaining in the measuring burette was probably continuously
volatilizing and getting into the gas stream passing the by-pass
described in experiment one. If this happened, a small quantity of
ethane would be continually formed in the reaction flask and thus
sweeping would never be complete. This was corrected by modifying
the construction of the measuring burette as shown in Plate I.

Experiment Seven

Using the modified apparatus as described under experiment
six and with one other modification, the preceding experiment was
repeated. The one other modification was the use of dibutyl ether
to replace diamyl ether. This was necessitated by the depletion of
the supply of the diamyl ether. The addition time was five hours and
the sweeping time five and one-half hours. The volume of gas resulting

corrected to standard conditions, was 4722 ml., a value 5.6 percent high. A layer of butyl ether collected over the potassium hydroxide solution, which is fair indication of the reason for the high results.

For the next experiment, in order to keep back the dibutyl ether, the trap L was introduced into the system. This trap was kept in a dry ice-alcohol medium during the run. Another possible source of error would be the measuring burette. As constructed originally one ml. is represented by only one-eighth of an inch vertically on the column. It would be beyond the possible limits of accuracy to measure better than 0.5 ml. which entails a five percent error. Thus the measuring burette was reconstructed as described in the description of the apparatus so that one-eighth of an inch vertically represents 0.2 ml. Now zinc ethyl volumes should be read accurately to 0.1 ml. which introduces only one percent error.

Experiment Eight

The apparatus used in this experiment is identical with that described in the earlier part of this thesis. Chemically this experiment is identical with experiment seven. Addition time was three hours and sweeping time was six hours. The volume of gas corrected to standard conditions was 4566 ml., a value which is 1.9 percent high. It was felt that this result reaches the limit of accuracy of this apparatus and method.

Experiment Nine

The remainder of the experimental work deals with the reaction of zinc ethyl with tertiary butyl chloride. The general method was to add the tertiary butyl chloride to the zinc ethyl and then to sweep to find the entire volume of gas from this reaction.

Sulfuric acid in butyl ether was then added and the gas produced was swept into the measuring apparatus. The reason for this last addition was to use up any zinc ethyl or ethyl zinc chloride present and find out how much was present.

For this experiment a huge dry ice-alcohol condenser having a gas capacity of approximately one liter was used instead of the Friedrich's condenser. The reason for this change was because it was believed that the tertiary butyl chloride might otherwise escape.

The quantities of zinc ethyl were doubled so that after about one-half of the "ethyl" is used to make 2,2-dimethylbutane there is still sufficient to give an appreciable gas volume for study. Thus 20.9 ml. (0.2 mole) of zinc ethyl was added to the reaction flask and then 43.7 ml. (0.4 mole) of tertiary butyl chloride was added dropwise. At first there was no reaction but after a bit had been added, gas evolution was violent and blew the mercury from the seal. Addition time was three hours and sweeping time was seven hours. The total volume collected was 6968 ml. corrected to standard conditions. Sulfuric acid in butyl ether was then added with very little gas evolution. Addition was complete in one hour, and two hours sweeping gave a corrected volume of 1542 ml. at standard conditions.

These total volumes are only 4.5 percent below the theoretical value for the total amount of gas attainable. In view of the fact that some of the gas was lost, it is logical to assume that no 2,2-dimethylbutane was formed. By reason of this, it was suspected that the "tertiary butyl chloride" was not that at all. It had been distilled several weeks previously and apparently had totally hydrolyzed. In further experiments this distillation was done just prior

to the use of the tertiary butyl chloride.

Experiment Ten

The dry ice-alcohol condenser described in the previous experiment was used also in this experiment. The quantities were the same as in the previous experiment. The freshly-distilled tertiary butyl chloride was added over a period of three hours and then the apparatus was swept for six and one-half hours. The volume of gas corrected to standard conditions was 4328 ml. This amount of gas is 3.4 percent below the value expected if one-half the ethyl radicals make gaseous products. Then the sulfuric acid in butyl ether was added over fifty minutes. During this addition a solid cake formed which then broke up into hard pellets and finally sticky gums which made mechanical stirring an impossibility. Finally, after sufficient butyl ether had been added, a homogeneous suspension was obtained. Five hours sweeping brought the volume of gas to 1804 ml. corrected to standard conditions.

Since it was anticipated that gases other than ethane were produced in the first part of this experiment, gas analysis was conducted on that first gas collected. The results were:

Percent carbon dioxide	0.8
Percent unsaturates	75.0
Percent oxygen	7.1
Percent hydrogen	3.0
Percent ethane	14.0

A low temperature, low pressure distillation was attempted on this gas produced in this experiment. The apparatus for this work has been described in an earlier part of this thesis. At the time of this work, however, the liquid air column was not constructed.

The dry ice-alcohol head would not condense a major portion of the gases so the non-condensables were drawn off into an ampoule by use of liquid air refrigerant. A small amount of gas which was condensed by the head temperature was left behind. However this gas was in insufficient quantity to wet the column although it did establish equilibrium in the head. Consequently, no distillation was possible but it seemed reasonable to assume that a fractionation between the C_2 fraction and the C_4 fraction had been effected. The reasoning becomes apparent when one considers the boiling points of the probable constituents as shown in Table I.

Table I

Compound	Boiling point	Melting point
Ethylene[27a]	-103.8° C.	-169.4° C.
Ethane[27b]	$- 88.3$	-172.0
Isobutane[27c]	$- 10.2$	-142.0
Butylene[27d]	$- 6.0$	
Normal butane[27e]	$+ 0.6$	-135.0

The C_2 fraction and the C_4 fraction were analyzed. The C_2 fraction analyzed:

Percent unsaturates (ethylene)	81.2
Percent oxygen	0.9
Percent ethane	16.1

The C_4 fraction analyzed:

Percent carbon dioxide	0.1
Percent unsaturates	3.7
Percent oxygen	0.9

Several combustions had to be carried out before a satisfactory result

was obtained. The error with the unsatisfactory ones apparently derived from the use of too large a gas sample for combustion, a procedure which caused incomplete combustion. Improvement of technique gave the following result:

Percent butane   84.8

Experiment Eleven

In this experiment it was desired to repeat experiment ten, producing sufficiently larger quantities of gas so that by low temperature, low pressure distillation the gases evolved could be more definitely characterized. The low temperature, low pressure apparatus was to be modified to include a liquid air column so that the ethane and ethylene might be identified as such.

The dry ice-alcohol condenser described in experiment nine which was used in the previous two experiments was replaced by the original Friedrich's condenser; however, this time ice cooled water was passed through the condenser.

Forty-one and six-tenths ml. (0.398 mole) of zinc ethyl was added to the reaction flask and 56.5 ml. of dry toluene was added as solvent to prevent the gum formation experienced previously. Then 87 ml. (0.796 mole) of tertiary butyl chloride was added dropwise over a period of ten hours. Eleven hours sweeping brought the volume of gas, corrected to standard conditions, to 3898 ml. This value is only 0.19 percent below the theoretical value. Then 21.4 ml. of concentrated sulfuric acid in 150 ml. of butyl ether was added over three hours with consequent slight gas evolution. The corrected volume of gas at standard conditions was 1522 ml. after six hours sweeping.

The gas collected on addition of the tertiary butyl chloride analyzed as follows:

Percent carbon dioxide   1.0

Percent unsaturates   50.6

Percent oxygen   1.1

Percent hydrogen   0.5

Percent ethane   11.9

Percent butane   29.9

The checks on the several combustion runs were not very satisfactory but these results represent the average of four combustions and we are probably reasonably correct.

The gas collected on addition of the sulfuric acid gave the following analysis:

Percent carbon dioxide   6.9

Percent unsaturates   5.5

Percent oxygen   2.3

Percent hydrogen   1.5

Percent ethane   13.1

Percent butane   60.9

Low temperature, low pressure distillation of the gas collected upon addition of tertiary butyl chloride was carried out. After an apparent air block or other uncondensable gas block was drawn off, the liquid air column settled into equilibrium and for about twenty minutes a gas was drawn off with the temperature rising from -89.9 to -89.6° C. uncorrected. The heat input into the distilling bulb was 150 watts on the lamp bank. The dropping ratio was about 100 drops per minute. Atmospheric pressure was 762.6 mm. of

mercury. Distillation was continued for 35 minutes at which time
the temperature had dropped to -35.5° C. and a cut was made. During
this time about two ml. of liquid were collected. Shortly after
taking this cut, the distilling flask broke off causing complete loss
of the remainder of the gas.

A freezing point was attempted with the small amount of
liquid collected. This was unfortunately unsuccessful for the reasons
that the stirrer stuck at about -150° C. when there was yet no cyrstal-
lization and too small a sample was present.

A further experiment was necessary to produce more gas to
further characterize the products.

Experiment Twelve

Since the object of this experiment was to prepare gas
and not necessarily attempt to obtain quantitative results, the
trap was only surrounded by ice water. A grievous mistake was made
at first in this experiment by replacing the Lubriseal stopcock
lubricant with a mixture of trimethylene citrate and tetramethylene
citrate. During distillation the zinc ethyl reacted with the
citrates with a consequent clogging of several of the stopcocks.
Finally the apparatus was reassembled using Lubriseal again at all
ground glass joints except the two stopcocks, j and k, where only
gases come in contact with the lubricant.

Eighty-three and six-tenths milliliters (0.8 mole) of zinc
ethyl was measured into the reaction flask. Then 120 ml. of dry toluene
was added at once and stirring begun. The temperature was lowered
to 0° C. and 175 ml. (1.6 moles) of tertiary butyl chloride was added
dropwise over nineteen hours. Six hour sweeping did not give micro-

bubbles, since so many volatile compounds were present in the
reaction flask. However, from past experience, it had proven
that six hour sweeping cleared the apparatus so sweeping was halted.
A thin layer of liquid had collected above the potassium hydroxide
solution by this time. The gas volume corrected to standard condi-
tions was 20.60 liters, a value about 15 percent above the theoretical.
This high result is not unexpected considering the volatile compounds
present in the system.

Then 42.8 ml. of concentrated sulfuric acid in 300 ml. of
butyl ether was added over one hour. Only the first 10-20 ml. of
this solution caused any gas evolution. Sweeping was carried out
for six hours at which time the volume of gas collected was 3320 ml.
at standard conditions. This quantity has no particular significance.

The gas collected from the reaction of zinc ethyl on tertiary
butyl chloride was condensed to about 20 ml. of liquid and placed in
the low temperature, low pressure distillation apparatus. It was very
difficult to establish equilibrium in the liquid air column and at
first it seemed that some non-condensable gas was present so considerable
bleeding off into the charcoal tube was carried out. The head tempera-
ture during the bleeding-off operation rose quite regularly and gradual-
ly from -159° C. to -90° C. There seemed to be some little hesitation
at about -102° C. which would indicate ethylene. After the tempera-
ture reached -140° C., it was decided to take the gas into an ampoule
instead of the charcoal tube. In this ampoule about 4 ml. of liquid
were collected. This fraction will be referred to as fraction one
later in the thesis. It would be desirable to repeat this distillation
to attempt better fractionation but this was not attempted because

time was short and liquid air in proper quantities was difficult to obtain.

Then the column settled down and for two hours a gas was distilled off at an average temperature of -84.1° C. The temperature during the course of the distillation rose from -39.3° C. to -79.5° C. Only about 2-3 ml. of liquid collected in the ampoule. This fraction is to be known as fraction two. The conditions for this distillation were 758.7 mm. pressure, dropping rate of 90 drops per minute, and a heat input of 100 watts.

After this out the temperature climbed gradually for four hours to -11° C. The column was stopped after trying to take off with the liquid air head. Pressure and consequently temperature varied too widely so the gas was shifted into the dry ice-alcohol column. At first the heat input was 150 watts but this caused flooding and that drove some water up into the head which formed a block. Finally, after warming up the column and starting over, equilibrium was reached at -11.8° C. Gas was taken off for one and a half hours with an average boiling point of -11.7° C. At the conclusion of this time the temperature rose immediately above 0° C. The conditions of this distillation were 755 mm. of mercury pressure, dropping rate of 36 drops per minute, and a heat input of 50 watts. This fraction will be spoken of as fraction three.

Freezing points were attempted for all three fractions. Fraction one never became solid down to temperatures of -171° in the freezing point tube. However, it was noticed that when the freezing point tube is in contact with the liquid air, the fraction becomes solid.

Fraction two likewise gave unsatisfactory results. The stirrer did not move vigorously enough to keep a solid shell from forming around the sides of the tube and thus stopping the stirrer. This happened a number of times; each time the temperature was about -160° C. Just what the temperature of freezing is, is therefore unknown. Many varied attempts were made to get the better of this situation but time did not permit an exhaustive search for a remedy.

Fraction three met with greater success. The freezing point curve is shown on the accompanying graph. The break represents supercooling and the freezing point is -143.7° C.

Gas analysis on fraction one gave the following results:

Percent carbon dioxide   0.3

Percent ethylene   75.0

Percent oxygen   0.6

Percent ethane   23.8

Gas analysis on fraction two gave the following results:

Percent carbon dioxide   0.9

Percent ethylene   60.8

Percent oxygen   0.7

Percent ethane   37.6

Gas analysis on fraction three was never carried out as it was felt that this fraction had already been sufficiently characterized.

The gas which was formed upon addition of the sulfuric acid in butyl ether was analyzed as follows:

Percent carbon dioxide   2.9

Percent unsaturates   2.9

Percent oxygen   1.5

Percent ethane   55.1

Percent butane   39.7

PLATE VIII

FREEZING POINT CURVE FOR

ISOBUTANE

TEMPERATURE (DEGREES CENTIGRADE)

10 SQUARES TO THE INCH
Made in U. S. A.

TIME (MINUTES)
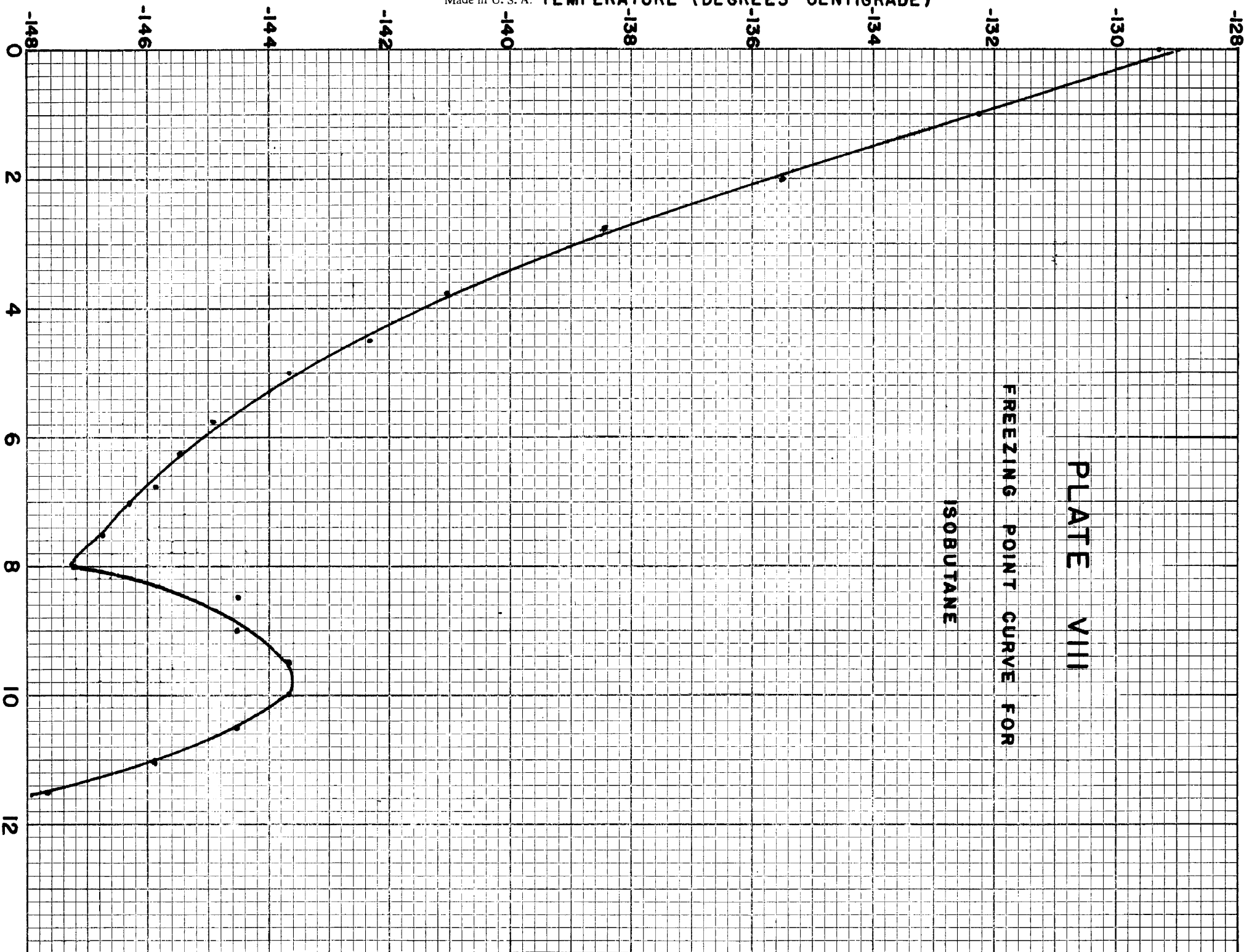
DISCUSSION OF RESULTS

Since the object of the first eight experiments was to construct and operate an apparatus satisfactory for running the reaction of zinc ethyl with other substances and in making a quantitative study of that reaction, that end was attained. It was found during the course of these experiments that the evolution of gas from the reaction of zinc ethyl upon an active hydrogen compound could be controlled by appropriate dilution of that compound. It was found after some incorrect conclusions that the gas evolved from this direct reaction was the pure paraffin expected, ethane. It was found that the evolution of this gas was quantitative when calculated on the basis of zinc ethyl added.

Such were the general results of these first experiments. From various of the experiments less general facts were observed. The reaction of zinc ethyl with acids is complete at 0° C., however with ethyl alcohol apparently the reaction proceeds only half way at 0° C. It seems probable then that the compound first formed is ethoxy zinc ethyl, $C_2H_5OZnC_2H_5$, which is stable to ethyl alcohol even at room temperature.

Just which one of the many possible contributing causes gave rise to the consistently high results is not known. It can be assumed that one consistent cause for high results is the entrained vapors of the various volatile components in the reaction flask. The other most probable reason was the continued evaporation of zinc ethyl from the measuring burette as the apparatus was first constructed. Both of these possible causes were easily obviated.

Experiment nine which was the first experiment involving the reaction with tertiary butyl chloride was a failure doubtless because the tertiary butyl chloride was of unsatisfactory purity. Of the 0.4 gram equivalents of ethyl radical added, 0.392 gram equivalents of them show up as ethane. Obviously little or no 2,2-dimethylbutane could be formed under these conditions.

Experiment ten, using good quality tertiary butyl chloride, produced the first evidence that the reaction,

$$Zn(C_2H_5)_2 + C_4H_9Cl \longrightarrow C_4H_9 \cdot C_2H_5 + C_2H_5ZnCl$$
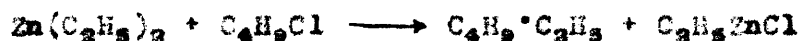
was incorrect. If this reaction as written were correct, there would be no gas evolved upon addition of tertiary butyl chloride and then there would be much ethane evolution upon addition of acid. However it was found that the volume of gas collected upon addition of tertiary butyl chloride was only 3.4 percent below the value determined from the amount of zinc ethyl used, assuming that one-half of the ethyl radicals react to produce ethane. The most important reason for believing that the reaction as written is incorrect is that only 1304 ml. of gas was collected upon addition of acid. According to information concerning the yields of the hydrocarbon from past literature references, there should be 0.2 mole of ethyl zinc chloride present which would give 0.2 mole of ethane.

The fact that the first gas collected in this experiment showed on analysis such a large percentage of unsaturated hydrocarbon, leads one immediately to the conclusion that the reaction has never been understood or written correctly before. A practical interpretation of the gas analysis would be to disregard the carbon dioxide and oxygen figures as due to solution of the gas in the reagents and also to assume that the hydrogen content was due to occlusion of gas within

the copper oxide tube. Thus we would be led to assume that the gas was a mixture of pure ethane and unsaturates. If these assumptions are true, an analysis showing 31.5 percent unsaturates and 13.5 percent ethane approximately should have been obtained.

The question naturally arose as to the identity of the unsaturated hydrocarbons. Two methods of attack suggested themselves. Either gas analysis in the elaborate fashion of Tropsch and Mattox[39] using various concentrations of sulfuric acid could be carried out, or a low temperature, low pressure distillation column and apparatus could be built. Both methods involved a great deal of work and of the two, the latter demanded the most. However the multiple advantages of setting up the low temperature, low pressure outfit overbalanced the objection of time, since the apparatus could furnish not only separation but also definite sound physical constants for the gases.

By means of the dry ice-alcohol column the combined gases of both fractions from this experiment were separated. There was insufficient gas to do very satisfactory work and having only a dry ice head at the time made it impossible to hold the ethane in the head and obtain a boiling point of it. However the column did effect a separation of the gases which boil below dry ice temperature and those which boil above dry ice temperature. The major portion of the gas was not held by the head and thus represents the ethane and ethylene, if any. The gas analysis of this fraction indicated there was 81.? percent unsaturates which can only be ethylene. The remainder analyzed for pure ethane. These results check beautifully with the analysis of the gas from the first fraction so it is tentatively assumed that the first fraction contains all the ethane and ethylene.

The gas which was held by the head was of insufficient quantity to obtain the boiling point but was sufficient for gas analysis. These analysis results showed some unsaturates, possibly butylene, and predominantly pure butane.

Experiment eleven was designed to make sufficient gas to obtain satisfactory physical constants using the liquid air column and freezing point tube which were constructed meanwhile. It did not attain that goal since during the liquid air distillation, the distilling bulb broke off and the gas was lost. By the time that happened, however, some information was obtained. Gas analysis was run on both fractions of the gas obtained directly from the reaction. The addition of toluene as a solvent has changed the character of the gases evolved. The gas collected upon the addition of tertiary butyl chloride had a good deal less ethylene but contained butane which was absent entirely in the previous experiment. The gas collected upon acid addition was predominantly butane as expected in the previous experiment but did contain 5.5 percent unsaturates and 18 percent ethane.

As far as the low temperature distillation had gone, it indicated ethane was present. Ethane boils at $-33.3°$ C.[27b] at 760 mm. pressure. Two ml. of liquid was collected which boiled from -89.9 to $-85.5°$ C. The fact that the attempted freezing point showed that the substance did not freeze above $-150°$ C. is a slight indication that the substance may be ethane.

The twelfth experiment gave an abundance of gas which was sufficient to allow exhaustive studies which were halted prematurely by lack of time. The distillation of the gas proved to be a difficult task. It was extremely difficult to establish equilibrium in the

column and it was supposed that due to the similarity of the substances being separated and their consequent solubility in one another that separation by a single fractionation was impossible. Podbielniak[37] found that the separation of a complex hydrocarbon mixture was a difficult task involving a very efficient column. The temperature during the distillation rose gradually from -159 to -90° C. with only the slightest pause at about -102° C. The gas coming off in this range gave an analysis for 75 percent ethylene and 24 percent ethane which gives an insight into what was happening. Despite the fact that the boiling points of ethane and ethylene are fifteen degrees apart, it appears that they cannot be separated by a single fractionation. The reflux ratio was not too fast as was shown a number of times by changing over to total reflux. The temperature never changed appreciably with this operation and it surely would have had the ratio been too low. Ideally this fraction should have been redistilled but it was felt that the gas analysis data satisfactorily identifies the constituents.

The next fraction came over in the ethane range. It is to be noted that here again the temperature gradually increases and although the increase was slower than before, it still indicates an impurity present. This fraction was not pure by a wide margin. Its analysis indicated 61 percent ethylene and 38 percent ethane. It is remarkable that this mixture would distil over at this particular temperature range. The freezing point which was attempted on this fraction was unsuccessful as was expected.

The next fraction was probably a conglomerate mixture of all the constituents and was saved for further work which never came

about. The temperature finally reached -11.8° C. and remained
constant for one and one-half hours. This gas must be isobutane
which has the recorded boiling point of -1C.2° C.[27] Just why the
big difference in boiling points occurred is not known. The slightly
lower than atmospheric pressure would not account for the wide
difference in boiling points. However this boiling point does point
directly to isobutane. The freezing point data verifies the fact
that this fraction is isobutane. The accepted value for the freezing
point is -145° C. and the result was -143.7° C. It is probable that
the isobutane has slight impurities but the question of its identity
is assured.

The analysis of the gas obtained upon addition of the acid
indicated 55 percent ethane, 40 percent butane, and a small amount
of unsaturates. It is doubtful that unsaturates are actually present
and it is believed that the amount dissolved simply represents the
solubility of the saturates in the reagent or the amount of toluene
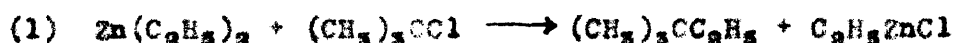vapor present in the gas.

CONCLUSIONS

The reaction between zinc ethyl and tertiary butyl chloride is not the simple reaction that has been written previously in the literature. Although the presence of some small amounts of ethyl zinc chloride as a product has not been disproven it seems unlikely that much of it is formed. The zinc ethyl and the tertiary butyl chloride which are not used in the reaction to produce 2,2-dimethyl-butane break down into hydrocarbons stemming from the two radicals involved. Significantly butylene was not a product which could be detected. The volume of gas liberated by the reaction closely approximates one-half the molar quantity of zinc ethyl used, however the gas is not pure ethane, nor even pure ethylene. The fact that isobutane is present suggests that possibly some sort of shift may be taking place between the ethyl and tertiary butyl radicals.

A similar shift is well known for some of the metal alkyls. For example, Calingaert[5,6,8] found that compounds such as R_4M and R'_3MX exhanged their alkyl groups to give all the possible compounds from R_4M to R'_4M and from R'_3MX to R_3MX. The metals used were lead, tin, mercury, and silicon. Calingaert[7] then studied the exchange within the system $R_4M-R'_4M$ and found that the exchange took place again and later[10] that $R_3MX-R'_3MX$ were involved in similar processes. However the study[9] of the zinc ethyl-zinc methyl system showed that no exchange took place. The exact counterpart of the system encountered in this research has not been studied, however it seems possible in light of this work of Calingaert, that an exchange of radicals might occur between zinc ethyl and tertiary butyl chloride or between ethyl-zinc chloride and tertiary butyl chloride.
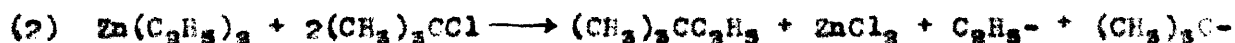
Even assuming this exchange, it is impossible to write any one equation to represent the reaction. Of the many equations which can be written, it is fairly certain that the following reaction, the one usually written, is incorrect.
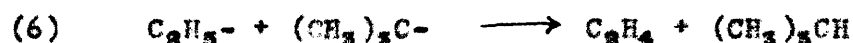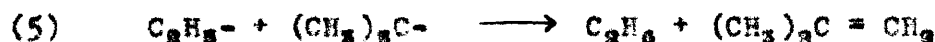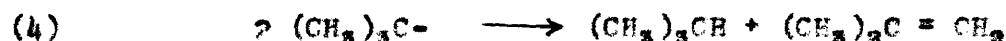
$$Zn(C_2H_5)_2 + 2(CH_3)_3CCl \longrightarrow 2(CH_3)_3CC_2H_5 + ZnCl_2$$

The first two reactions which can occur are:

(1) $Zn(C_2H_5)_2 + (CH_3)_3CCl \longrightarrow (CH_3)_3CC_2H_5 + C_2H_5ZnCl$

and

(2) $Zn(C_2H_5)_2 + 2(CH_3)_3CCl \longrightarrow (CH_3)_3CC_2H_5 + ZnCl_2 + C_2H_5- + (CH_3)_3C-$

The free radicals can then undergo several reactions. They can disproportionate:

(3) $2 C_2H_5- \longrightarrow C_2H_6 + C_2H_4$

(4) $2 (CH_3)_3C- \longrightarrow (CH_3)_3CH + (CH_3)_2C = CH_2$

(5) $C_2H_5- + (CH_3)_3C- \longrightarrow C_2H_6 + (CH_3)_2C = CH_2$

(6) $C_2H_5- + (CH_3)_3C- \longrightarrow C_2H_4 + (CH_3)_3CH$

They can combine:

(7) $2 C_2H_5- \longrightarrow n-C_4H_{10}$

(8) $2 (CH_3)_3C- \longrightarrow (CH_3)_3CC(CH_3)_3$

(9) $C_2H_5- + (CH_3)_3C- \longrightarrow (CH_3)_3CC_2H_5$
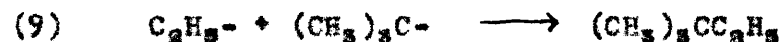
Of all these possibilities some can be eliminated. Equations (4) and (5) are out of the question because isobutylene was not present in the products. Equation (7) is impossible because no normal butane was detected in the gas from the reaction of zinc ethyl with tertiary butyl chloride. The remainder of the equations are possibilities.
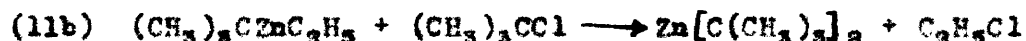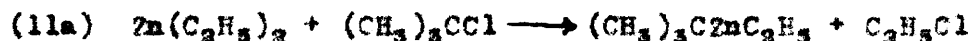
The reaction (1) is a definite probability and will be discussed later. Reaction (2) must take place in order to form the free radicals from which come the gaseous products. Reactions (3) and (6)

are quite probable since they offer a reasonable explanation of the
approximate percentages of the gases formed. Experimental data show
that the total percentage of ethane and butane closely approximate
the amount of ethylene. These two equations explain these facts.
Apparently (6) takes place more readily than (3) because the observed
percentage of isobutane was about 30 and the observed percentage of
ethane was about 15. Equations (3) and (9) are definite possibilities.
Reaction (9) has no way of being substantiated since it produces in
the same substance as do reactions (1) and (2). Reaction (3) could
be proven or disproven if an accurate liquid distillation were carried
out. Lack of time has prevented this distillation's being included
in this thesis, however, the distillation will be carried out in the
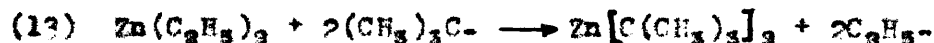near future.

As was discussed previously the ethylzinc chloride which
might be formed according to equation (1) may undergo alkyl exchange
with tertiary butyl chloride as follows:

(10) $C_2H_5ZnCl + (CH_3)_3CCl \longrightarrow (CH_3)_3CZnCl + C_2H_5Cl$
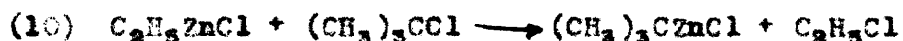
Or, it is possible that this exchange may involve zinc ethyl and
tertiary butyl chloride:

(11a) $Zn(C_2H_5)_2 + (CH_3)_3CCl \longrightarrow (CH_3)_3CZnC_2H_5 + C_2H_5Cl$

(11b) $(CH_3)_3CZnC_2H_5 + (CH_3)_3CCl \longrightarrow Zn[C(CH_3)_3]_2 + C_2H_5Cl$

It is even possible that the free radicals formed in (2) might react
directly with the zinc compounds:

(12) $C_2H_5ZnCl + (CH_3)_3C- \longrightarrow (CH_3)_3CZnCl + C_2H_5-$

(13) $Zn(C_2H_5)_2 + 2(CH_3)_3C- \longrightarrow Zn[C(CH_3)_3]_2 + 2C_2H_5-$
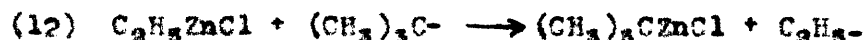
One way or another zinc tertiary butyl or tertiary-butylzinc chloride
is formed.

Upon addition of sulfuric acid the following reactions may take place:

(14) $Zn[C(CH_3)_3]_2 + H_2SO_4 \longrightarrow 2(CH_3)_3CH + ZnSO_4$

(15) $(CH_3)_3CZnCl + H_2SO_4 \longrightarrow (CH_3)_3CH + ZnSO_4 + HCl$

(16) $Zn(C_2H_5)_2 + H_2SO_4 \longrightarrow C_2H_6 + ZnSO_4$

(17) $C_2H_5ZnCl + H_2SO_4 \longrightarrow C_2H_6 + ZnSO_4 + HCl$
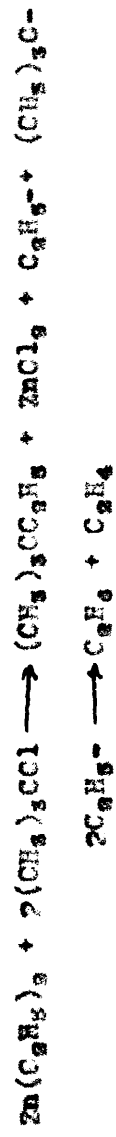
Either or both reactions (14) and (15) are necessary to explain the isobutane formation, and either or both of reactions (16) and (17) are necessary to explain the ethane formation. Although the gas which analyzes for butane was never characterized further, it cannot be normal butane because the only way normal butane can be formed is by equation (7) and there is no source of ethyl radicals at this stage of the process. In the earlier part of this thesis, the action of sulfuric acid on zinc ethyl was studied and it was found that only pure ethane in one hundred percent yield resulted. This furnishes further proof that normal butane is not a product of this reaction.

The relative amounts of the products indicate that equation (2) is about five or six times more probable than equation (1). Equation (6) is favored about two to one over equation (3). It would be expected that equation (10) would be more probable than equation (11a) and (11b) because of simplicity. Equations (12) and (13) are probably unimportant but do represent possibilities. Equation (13) is ruled out if (11a) and (11b) are discarded.

As a result of our study of the reaction of zinc ethyl with tertiary butyl chloride and subsequent addition of sulfuric acid, the following equations can be written to represent the reactions involved.

$$Zn(C_2H_5)_2 + (CH_3)_3CCl \longrightarrow (CH_3)_3CC_2H_5 + C_2H_5ZnCl$$

$$Zn(C_2H_5)_2 + 2(CH_3)_3CCl \longrightarrow (CH_3)_3CC_2H_5 + ZnCl_2 + C_2H_5{\cdot} + (CH_3)_3C{\cdot}$$

$$2C_2H_5{\cdot} \longrightarrow C_2H_6 + C_2H_4$$

$$C_2H_5{\cdot} + (CH_3)_3C{\cdot} \longrightarrow C_2H_4 + (CH_3)_3CH$$

$$C_2H_5ZnCl + (CH_3)_3CCl \longrightarrow (CH_3)_3CZnCl + C_2H_5Cl$$

$$(CH_3)_3CZnCl + H_2SO_4 \longrightarrow (CH_3)_3CH + ZnSO_4 + HCl$$

$$C_2H_5ZnCl + H_2SO_4 \longrightarrow C_2H_6 + ZnSO_4 + HCl$$
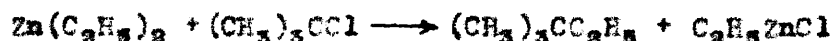
SUMMARY

1. Zinc ethyl reacts quantitatively with any active hydrogen compound to produce ethane.

2. Zinc ethyl reacts with tertiary butyl chloride to produce from 55 to 60 percent of the possible gas.

3. This gas is a mixture of ethane, ethylene, and isobutane in amounts approximately 15 percent, 50 percent, and 30 percent respectively.

4. Addition of an active hydrogen compound at the conclusion of the reaction of tertiary butyl chloride shows that some active zinc compound remains.

5. The gas produced by the reaction with the active hydrogen compound is predominantly isobutane, the remainder being ethane.

6. The equations for the overall reaction have been proposed.

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