

A STUDY  
of the  
UNSATURATION OF 2-BROMO BUTANE

Thesis  
by  
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In partial fulfillment of the requirements  
for the degree of Bachelor of Science  
in Chemical Engineering.

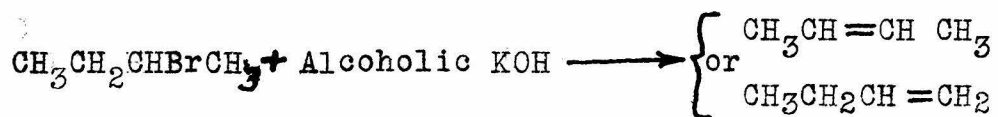
CALIFORNIA INSTITUTE OF TECHNOLOGY  
Pasadena, California.

~~1924~~  
1925

## INTRODUCTION

Although the unsaturation of secondary butyl iodide has been mentioned in the literature<sup>(1)</sup> no details have been given about the method of procedure or the quantitative results. It therefore seems desirable to further study the unsaturation of secondary butyl halides, and in this particular case 2-butyl bromide.\*\*

When 2-butyl bromide is unsaturated two butenes may be obtained as is illustrated by the following reaction.



The problem which concerns the author consists in determining the relative proportions of these butenes formed.

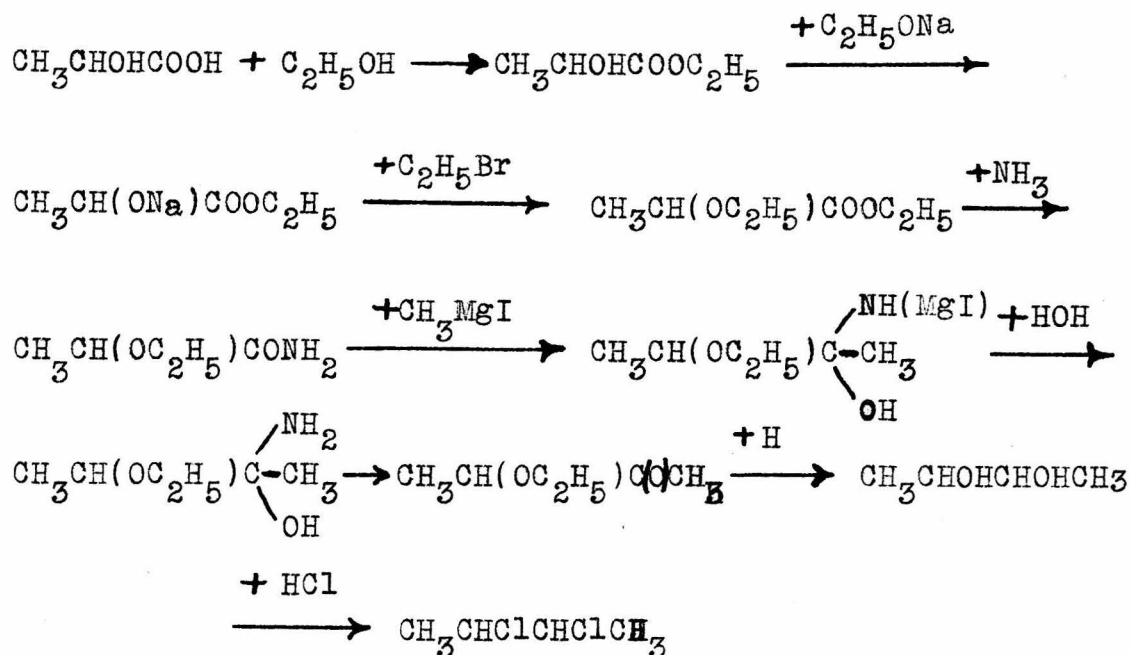
The unsaturation of 2-butanol offers the same possibilities and a problem of similar nature. Evers<sup>(2)</sup> has studied this problem, by unsaturating 2-butanol with phosphorus pentoxide and finds that 2-butene is obtained without even a trace of 1-butene.

\*\*Note. 2-bromo butane is the correct nomenclature and is intended wherever 2-butyl bromide occurs in this thesis.

## OUTLINE OF PROCEDURE

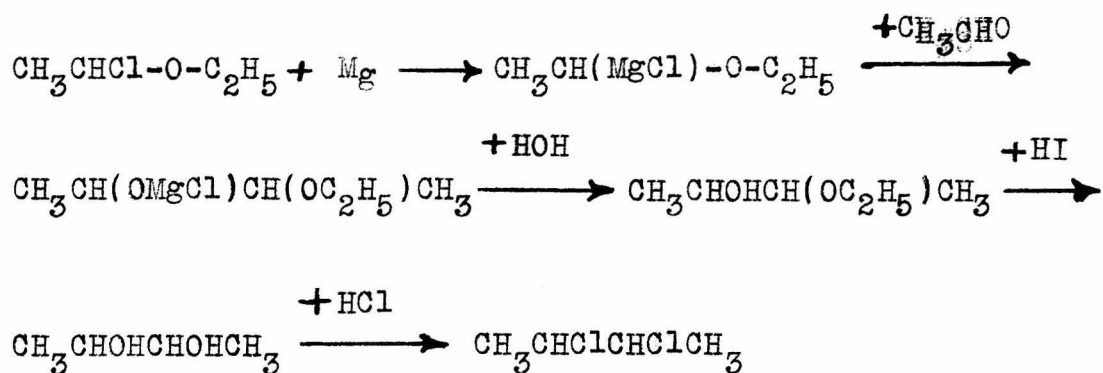
In order to determine the relative proportions of the 1-butene and 2-butene obtained by the unsaturation of the 2-butyl bromide it was deemed advisable to add chlorine to them thus giving 1,2-dichlor-butane and 2,3-dichlor-butane respectively. It is better to form the di-chlor rather than the di-brom compounds because they boil about 40° lower and can therefore be distilled with less danger of decomposition. In addition the chlor compounds are usually more stable than the brom. However the literature gives only meager and inconsistent data concerning the di-chlor compounds. It therefore seemed desirable to prepare them by synthesis and make a thorough investigation of their properties before proceeding with the unsaturation of the 2-butyl bromide.

The first method decided upon to prepare the 2,3-dichlor-butane was to proceed through the following reactions.



This method of attack was abandoned after two attempts to prepare the ethyl lactate by the method (3) of Gustrow failed to give satisfactory results.

The next method of attack decided on was to go through the following set of reactions.



This method was abandoned after two attempts to prepare chlor-ethyl ether by the method of Gauthier<sup>(4)</sup> failed to give a suitable yield or a product free from acid and water.

The next method was to prepare 2,3-di-hydroxy butane by the method suggested by L.Meunier<sup>(5)</sup> using magnesium amalgam and acetaldehyde. When the first attempt failed to give the results predicted a second was about to be made when it was found that more recent investigators<sup>(6)</sup> had disproved the work of Meunier. This method was therefore abandoned.

An attempt was then made to prepare 1,2-di-chlor butane by unsaturating normal butyl bromide with alcoholic potassium hydroxide and then adding chlorine to the butene thus obtained. However no di-chlor<sup>compound</sup> was obtained but a 63% yield of butyl ethyl ether was obtained.

Finally it was decided to determine the products of unsaturation of the 2-butyl bromide by forming the di-brom rather than the di-chlor compounds. The properties of 1,2 di-brom and 2,3 di-brom butanes are well established and since all investigators<sup>(7)</sup> seem to agree, it is justifiable to use their results without further investigation. This method yielded satisfactory results.

In addition one run was made adding chlorine to the products of unsaturation, and the results of this test checked those where bromine was added.

#### OUTLINE OF CONCLUSIONS.

By inspecting the results obtained in the fractionations as well as plots I and II made from them, it is evident that only the 2,3-dihalogen butanes are obtained by adding halogen to the products of unsaturation of the 2-butyl bromide. This implies that only 2-butene is formed in the unsaturation and completely eliminates the possibility of any appreciable amount of 1-butene being produced. This is a just conclusion because throughout the entire procedure of fractionation there was never any indication of the presence of a compound having a boiling point corresponding to those of the 1,2-dihalogen butanes.

These results also establish the boiling point for the meso form of 2,3-di-chlor butane as  $115.5^{\circ}$ - $116.5^{\circ}$  at 745m.m., and the racemic probably as  $118.0^{\circ}$ - $119.0^{\circ}$  at the same pressure. These figures check the results of Scheschukow<sup>(8)</sup> who gives  $115^{\circ}$ - $120^{\circ}$  for the boiling point of 2,3-di-chlor butane.

## EXPERIMENTAL PART.

The 2-butyl bromide was prepared by treating 2-butanol (obtained from the Standard Oil Company of New Jersey,) with hydrogen bromide. Hydrogen bromide prepared by treating sodium bromide with concentrated sulfuric acid, was passed into the 2-butanol until an excess of 25% over the theoretical amount necessary to react with it had been added. This mixture was then heated under pressure on a bath maintained at 65.-75.° for about ten hours. The 2-butyl bromide thus prepared was washed several times with water and dilute alkali, and then dried. The crude dry product was then distilled. The fraction distilling at 88.0-90.5°(uncorrected) was used ~~ex~~clusively in all the succeeding experiments. The yield was 70% of the theoretical.

The apparatus used for the unsaturation of the 2-butyl bromide and for adding bromine to the ~~unsat~~ unsaturated compounds obtained, is shown in Figure I.

The butyl bromide is unsaturated by dropping it from the dropping funnel C through the dropping tube B into the reaction chamber A containing a strong alcoholic potassium hydroxide solution. The

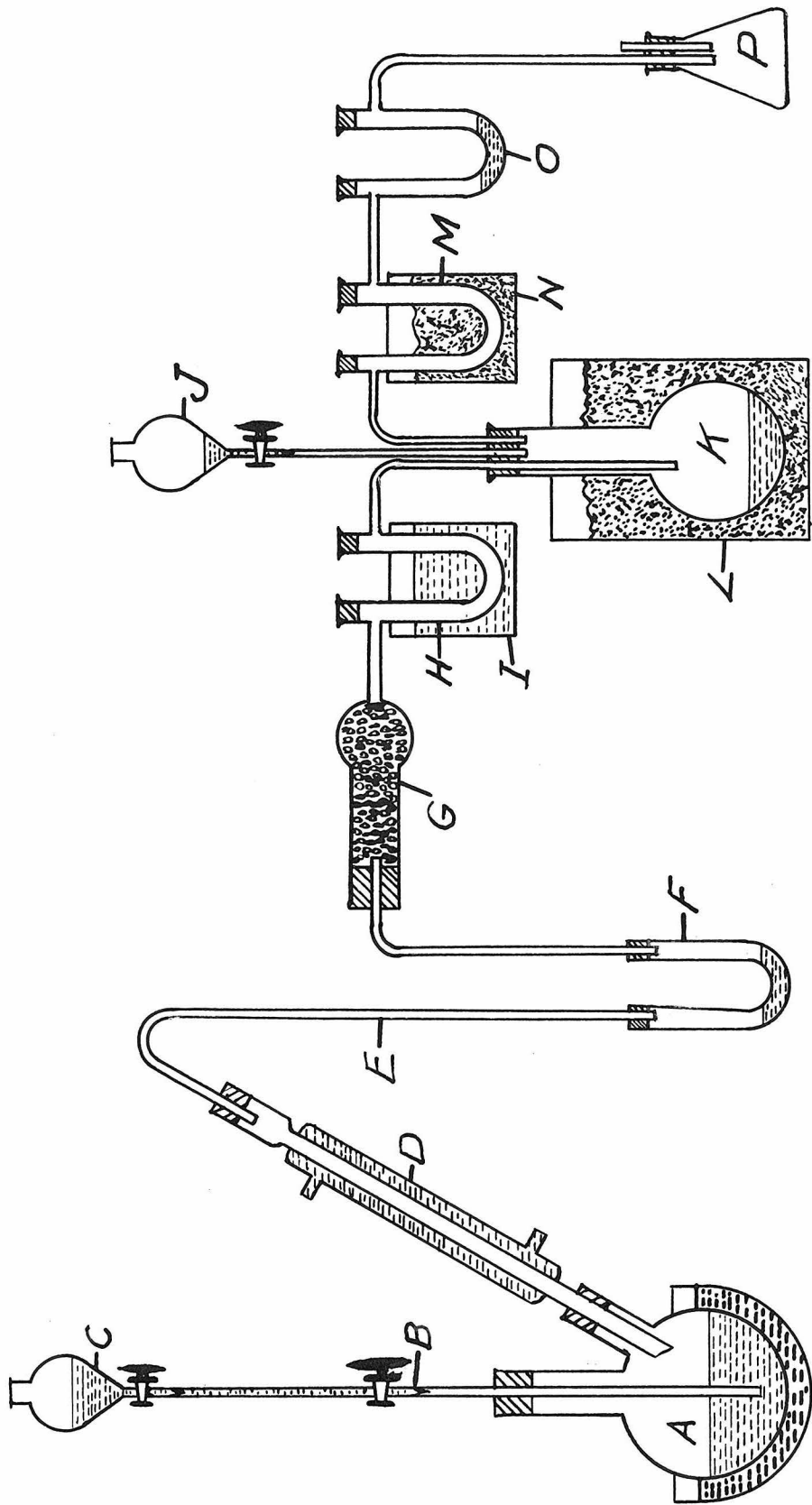


Figure 1.



chamber A has a volume of 300c.c. and is surrounded by an oil bath at  $120^{\circ}$ .- $140^{\circ}$ .. The butene generated by the reaction boils at  $+1^{\circ}$  to  $-5^{\circ}$  and is therefore gaseous at room temperature, and passes through the condenser D surrounded by tap water, then through the tube E into the tube F which contains a little water to wash out the alcohol. The gas then passes through the drying tube G containing calcium chloride, and then through the tube H surrounded by a bath I maintained at  $2.5^{\circ}$ - $5.0^{\circ}$ . The tube H serves to precool the gas and to condense out higher boiling substances in it. The gas then passes into the chamber K containing bromine and here the butene reacts with the bromine to form the dibrom compounds. K is surrounded by a bath L maintained at about  $-5.0^{\circ}$  at the start of a run, the temperature being gradually lowered as the amount of dibrom compound increases, until the minimum possible temperature obtainable with a mixture of ice and sodium chloride is reached. Thus K serves as a reaction chamber, and a condenser for the butene. Bromine is introduced into K by means of the funnel J. M is surrounded at all times by the bath N containing a mixture of ice and sodium chloride at the minimum possible temperature. M serves to condense out any butene that escapes reaction, and acts as a safety trap between K and O. O contains

carbon tetrachloride and acts as a pressure gauge to indicate how the apparatus is operating, <sup>also</sup> it dissolves any bromine that comes over and prevents it from escaping into the room. P is empty and is open to the atmosphere, it serves as a catch-all in case a sudden pressure increase should spurt some carbon tetrachloride out of O.

In the case where chlorine is added to the butenes, the chamber K is replaced by a large U tube with arms about 40.cms. long and a bore about 4cms.. This is kept as cold as possible with an ice and sodium chloride freezing mixture, throughout the entire procedure.

After the reaction in A is complete air is drawn slowly into the apparatus by applying suction at P and opening valves C and B. A little water is also introduced into A to reduce the solubility of the butene in the alcoholic potassium hydroxide. In this manner most of the butene is condensed into K or the large U tube as the case may be, and the losses are minimized.

In the case where chlorine is added, after the butene is all condensed the apparatus is separated between G and H, and H is shut off from the atmosphere.

Dry chlorine is then introduced through one side arm of the large U tube containing the butene. The chlorine is introduced at the rate of 40 to 60 c.f. per minute, but in any event ~~the~~ it should not be introduced more rapidly than it will be absorbed. The reaction is complete when the liquid obtains a yellow color, and the flow of chlorine is then shut off.

It takes about 3 hours for a run beginning with 50 grams of 2-butyl bromide when bromine is added and from 6 to 8 hours when chlorine is added.

In either case the crude di-halogen butane is washed with 1 to 3 normal sodium hydroxide solution to remove excess halogen, and then with water. It is then dried with calcium chloride and is ready for distillation.

The distillation was made with an Eastman fractionating column about 25 cms. high. That part of the liquid which could not be distilled with the column was removed to a small flask (about 15 c.c. in volume) and repeatedly fractionated.

Three runs were made adding bromine and one run adding chlorine to the butenes obtained in the unsaturation.

The results of the bromine runs are as

follows:

	Ist run	2nd run	3rd run	
Weight of 2-butyl bromide used <i>137</i>	50.0	50.0	65.0	<i>(0.47 mol)</i>
" " potassium hydroxide used	60.0	60.0	80.0	<i>(1.4)</i>
" " <i>Bromine</i>				
" " crude, dry $C_4H_8Br_2$ obtained	35.2	35.0	91.3	
Yield " " " " "	44.7%	44.5%	89.0%	

\* Note. The weights in the above table are in grams.

The alcoholic potassium hydroxide consisted of 2 parts by weight, of potassium hydroxide, to 3 parts by weight of 96% ethyl alcohol. It will be noticed in the above table that for each mol of potassium hydroxide there are approximately two fifths of a mol of 2-butyl bromide.

The yields are low in the first two runs because the apparatus had not been perfected and accidents occurred which caused much of the product to be lost. However the third run is representative and the apparatus used (Fig. I ) eliminates the possibility of the losses which occurred in the first runs.

Wislicenus<sup>(9)</sup> gives the boiling point of the meso form of 2,3-dibrom butane as 158° and that of the racemic form as 161°. All authors agree with these figures, and none have been found at variance. Furthermore all authors<sup>(7)</sup> seem to agree on the boiling point of 1,2-dibrom butane as 165.6° - 166.0°. It is well to keep these figures in mind while inspecting the following tables.

The products of the first two runs were combined and fractionally distilled. The fractionation was repeated about six times. The results of the first and last fractionations are as follows:

First fractionation.

Weight of fraction	156.0 - 157.5	corrected	746m.m.	3.0
" " "	157.5 - 159.0	"	"	60.0
" " "	159.0 - 162.0	"	"	4.0
" " "	162.0 - 175.0	"	"	1.0
" " "	175 plus residue			1.0

Last fractionation.

Weight of fraction	156.0 - 157.5	"	"	2.0
" " "	157.5 - 159.0	"	"	58.0
" " "	159.0 - 160.5	"	"	0.6
" " "	160.5 - 162.5	"	"	6.0
" " "	162.5 - 170.0	"	"	0.4
" " "	170 plus residue			00.5

67.5

The product from the third run was fractionated the same as the first runs. The results of the first and last fractionations are as follows:

First fractionation.

Weight of fraction up to	I56.0	corrected	746m.m.	I.0
" " "	I56.0 - I57.9	" "	" "	4.3
" " "	I57.9 - I58.9	" "	" "	75.2
" " "	I58.9 - I60.5	" "	" "	4.7
" " "	I60.5 - I65.0	" "	" "	2.0
" " "	I65.0 - I75.0	" "	" "	2.6
" " residue				I.5

Last fractionation.

Weight of fraction up to	I57.0	corrected	746m.m.	I.0
" " "	I57.0 - I57.9	" "	" "	4.0
" " "	I57.9 - I58.9	" "	" "	68.0
" " "	I58.9 - I60.5	" "	" "	0.7
" " "	I60.5 - I61.5	" "	" "	8.3
" " "	I61.5 - I63.5	" "	" "	2.3
" " "	I63.5 - I65.0	" "	" "	0.6
" " "	I65.0 - I67.0	" "	" "	0.2
" " "	I67.0 - I75.0	" "	" "	0.6
" " residue				I.3
				<u>87.0</u>

\* Note. The weights in all tables are in grams.



$C_4H_8Br_2$  FRACTIONATION


o Fractionation of 1st and 2nd runs mixed  
 x " " 3rd run

PLOT I.



The results of the chlorine run are given in the tables below. The fractionation was made in the same manner as in the bromine runs, and about the same number of times.

Weight of 2-butyl bromide used	27.0
" " potassium hydroxide used	34.0
" " crude, dry $C_4H_8Cl_2$ obtained	20.0
Yield " " " " " "	80.5%

This yield is smaller than that obtained in the third run using bromine because the amount of substance used is much smaller and the losses in the apparatus produce a much greater effect.

The results of the first and last fractionations are as follows:

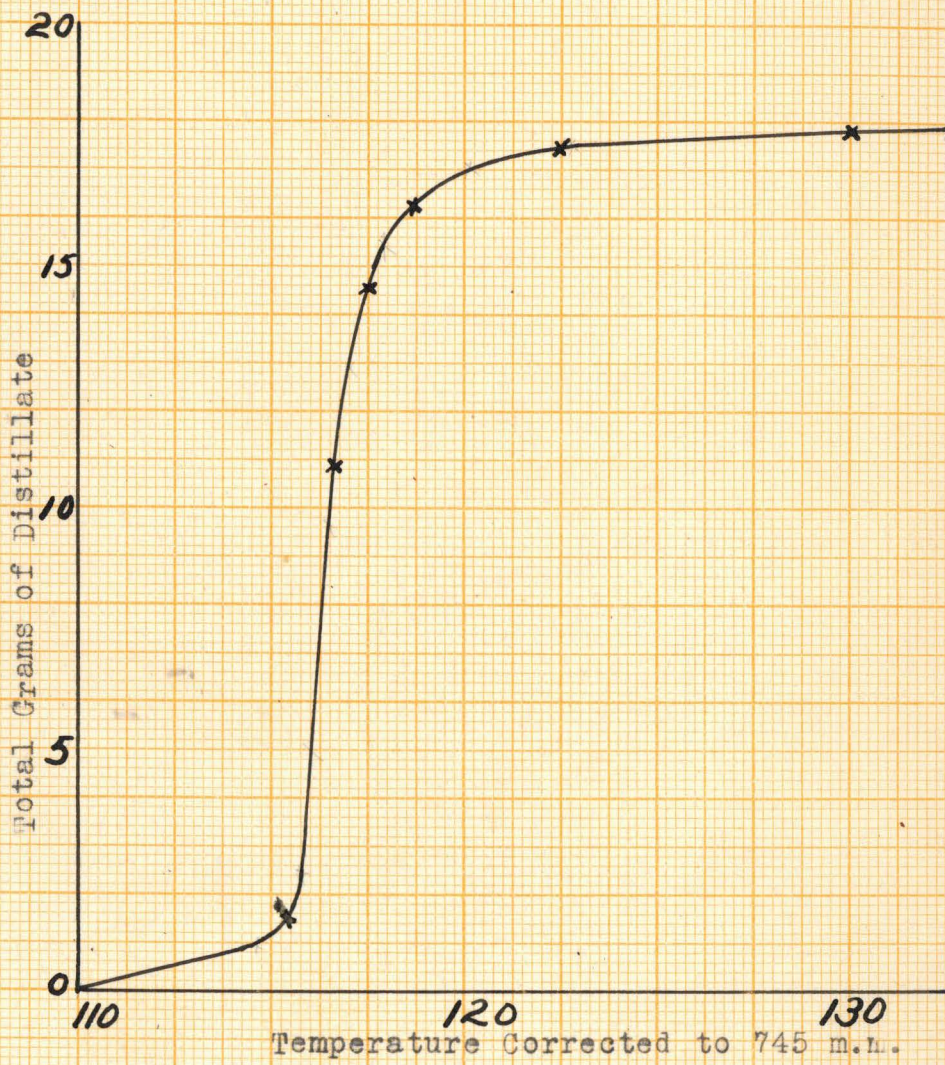
First fractionation.

Weight of fraction	110.0 - 115.5	corrected 745m.m.	1.9
" " "	115.5 - 117.5	" "	10.0
" " "	117.5 - 119.5	" "	4.0
" " "	119.5 - 124.0	" "	1.0
" " "	124.0 - 150.0	" "	1.0
" " residue			1.0

\*Note. The boiling points of 1,2 and 2,3-dichlor butanes are given as  $125^{\circ(10)}$  and  $115^{\circ} - 120^{\circ(18)}$  respectively.



$C_4H_8Cl_2$  FRACTIONATION



PLOT II.



Last fractionation.

	Actual values.	Corrected values.
Weight of fraction 110.0 - 115.5	1.8	1.5
" " " 115.5 - 116.5	8.0	10.3
" " " 116.5 - 117.5	2.8	3.6
" " " 117.5 - 118.5	1.4	1.8
" " " 118.5 - 122.5	1.0	1.3
" " " 122.5 - 130.0	0.8	0.4
" " residue	0.8	<u>1.0</u>

\*Note. All temperatures in the above table are corrected to 745m.m.. The column of corrected values is derived from the actual values by distributing the loss due to fractionation proportional to the size of each fraction. Plot II is made from the corrected values.

The results of the attempts to prepare the ethyl lactate are as follows:

First batch.

Weight of 90% lactic acid used	220. gms.
" " 96% ethyl alcohol used	160. "

Half of the alcohol was first saturated with hydrogen chloride and then the entire batch was mixed together.

Second batch.

Weight of 90% lactic acid used	236. gms
" " 96% ethyl alcohol used	170. "
" " Concentrated sulfuric acid used	80. "

Both batches were allowed to stand for two days and were then refluxed for about ten hours on a water bath. The mixture was then distilled using a fractionating device until the temperature of the distillate coming over reached 100°. Then distillation was then continued under a pressure of 25m.m.. The major portion of the distillate then came over between 35° and 45° and consisted almost entirely of alcohol and water. The residue remaining in the flask seemed to be a mixture of lactic and mineral acid and no evidence of ethyl lactate could be obtained. Further fractionation of the lower boiling fractions did not yield any ethyl lactate.

Although Gustrow<sup>(3)</sup> claims to have obtained a good yield of ethyl lactate by treating lactic acid with ethyl alcohol in the presence of mineral acid, the author was unable to do so because Gustrow's outline of procedure is only general and lacks the experimental details necessary for successful execution.

The results of one run in the preparation of alpha-chlor ethyl ether by the method of Gauthier<sup>(4)</sup> are as follows:

Weight of paraldehyde used	100. gms.
" " absolute ethyl alcohol used	104. "
" " hydrogen chloride used	110. "

The paraldehyde and alcohol were placed in a pressure bottle surrounded by a freezing mixture of ice and sodium chloride; the hydrogen chloride, generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid, was then introduced. The bottle was then closed and allowed to stand for about two weeks. The mixture was then distilled using a Hempel fractionating column about 35 cms. high. About 30. grams of distillate boiling at 95° - 100° was obtained, - this being the chlor ethyl ether which has a boiling point about 98°. This is a 15% yield. The product obtained could not be freed from hydrogen chloride, aldehyde or alcohol because it decomposes quite rapidly into these substances even in the cold. Consequently it could not be used in the subsequent procedure.

## SUMMARY

- I. 2-bromo butane was unsaturated by means of potassium hydroxide.
2. Bromine was added to the unsaturated compound produced by the unsaturation in one case while chlorine was added in another.
3. Only 2,3-dihalogen butanes are obtained by this procedure, thus proving that only 2-butene is produced by the unsaturation of 2-bromo butane.
4. The boiling point of the meso form of 2,3-dichlor butane has been established as  $115.5^{\circ}$  -  $116.5^{\circ}$  corrected to 745 m.m.
5. A suitable apparatus has been described for unsaturating 2-bromo butane, and for adding halogen to the butene thus obtained.

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\*Note. Abbreviations correspond to those in Richter or  
 Beilstein.



# Fractional Distillation of $C_4H_8Cl_2$

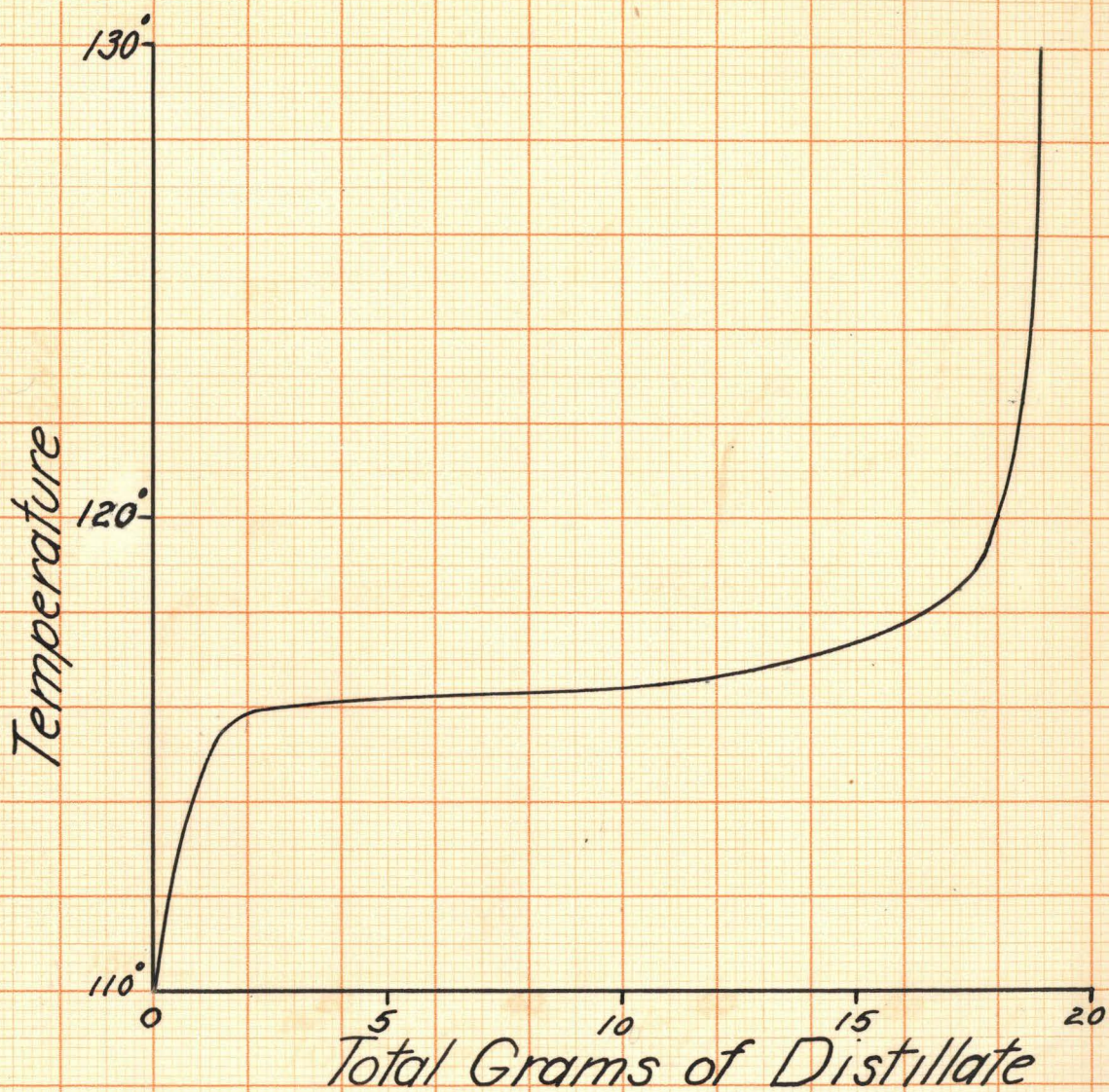
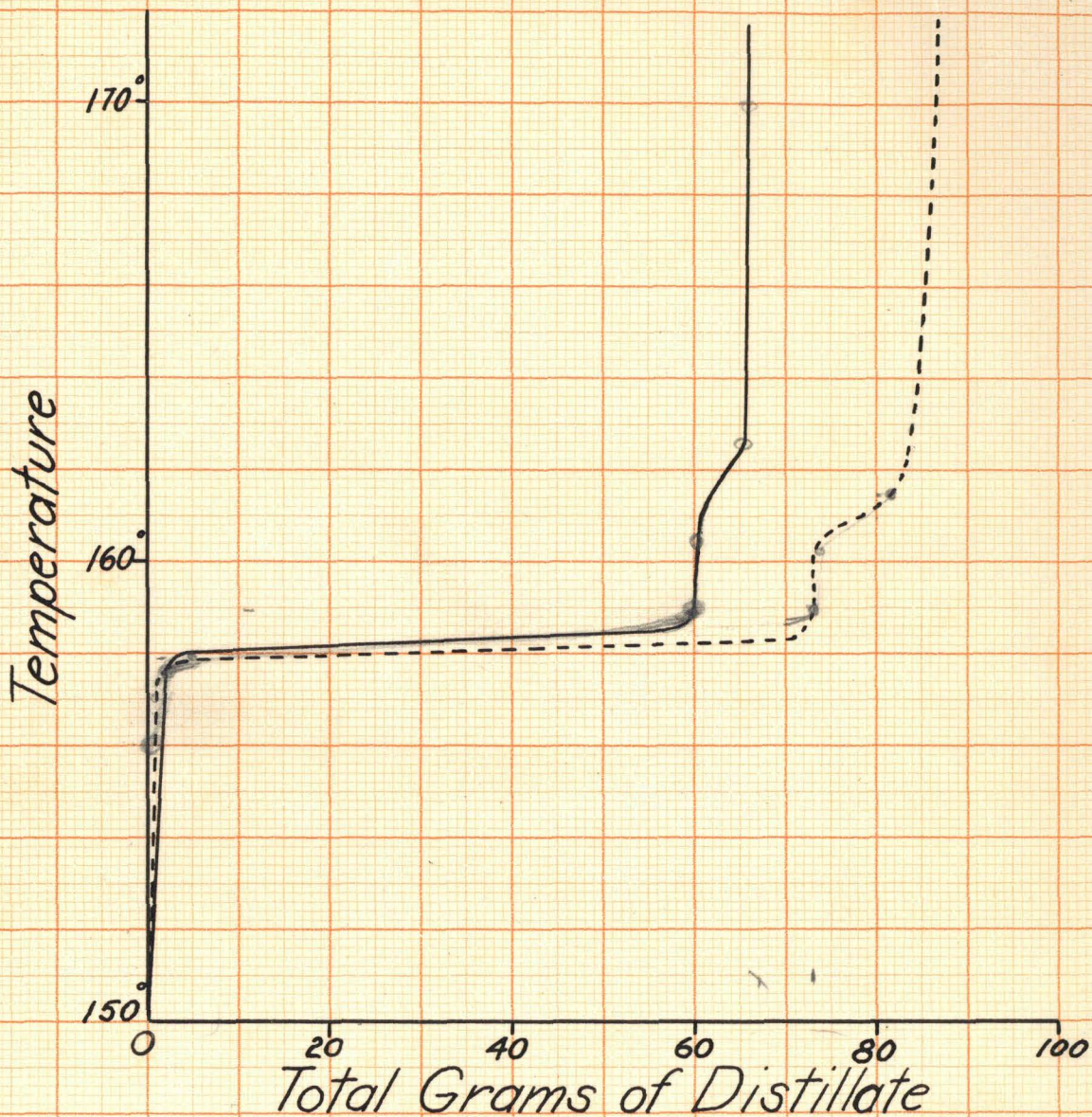


Figure II.

Electron Displacement in Carbon Compds II - Lucas Simpson and Carter Peterson + author



# Fractional Distillation of $C_4H_8Br_2$



First and Second Runs Combined ———

Third Run. - - - - -

Figure I.

Electron Supplement in Carbon Compounds III - Linn. Simpson and Carter  
Please return to authors - KEUFFEL & ESSER CO. N.Y.