

THE PREPARATION OF METHYLENE CYCLOBUTANE  
AND METHYL  $\Delta'$  CYCLOBUTENE

APPENDIX:

THE PREPARATION OF CERTAIN CYCLOBUTANE DERIVATIVES;  
ETHYL CYCLOBUTANE 1,1-DICARBOXYLATE,  
CYCLOBUTANE 1,1-DICARBOXYLIC ACID,  
CYCLOBUTANE MONOCARBOXYLIC ACID,  
CYCLOBUTANE MONOCARBOXYLIC ACID CHLORIDE,  
CYCLOBUTANE MONOCARBOXYLIC ACID AMIDE.

Thesis by

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In Partial Fulfillment of the Requirements  
for the Degree of Master of Science

California Institute of Technology  
Pasadena, California

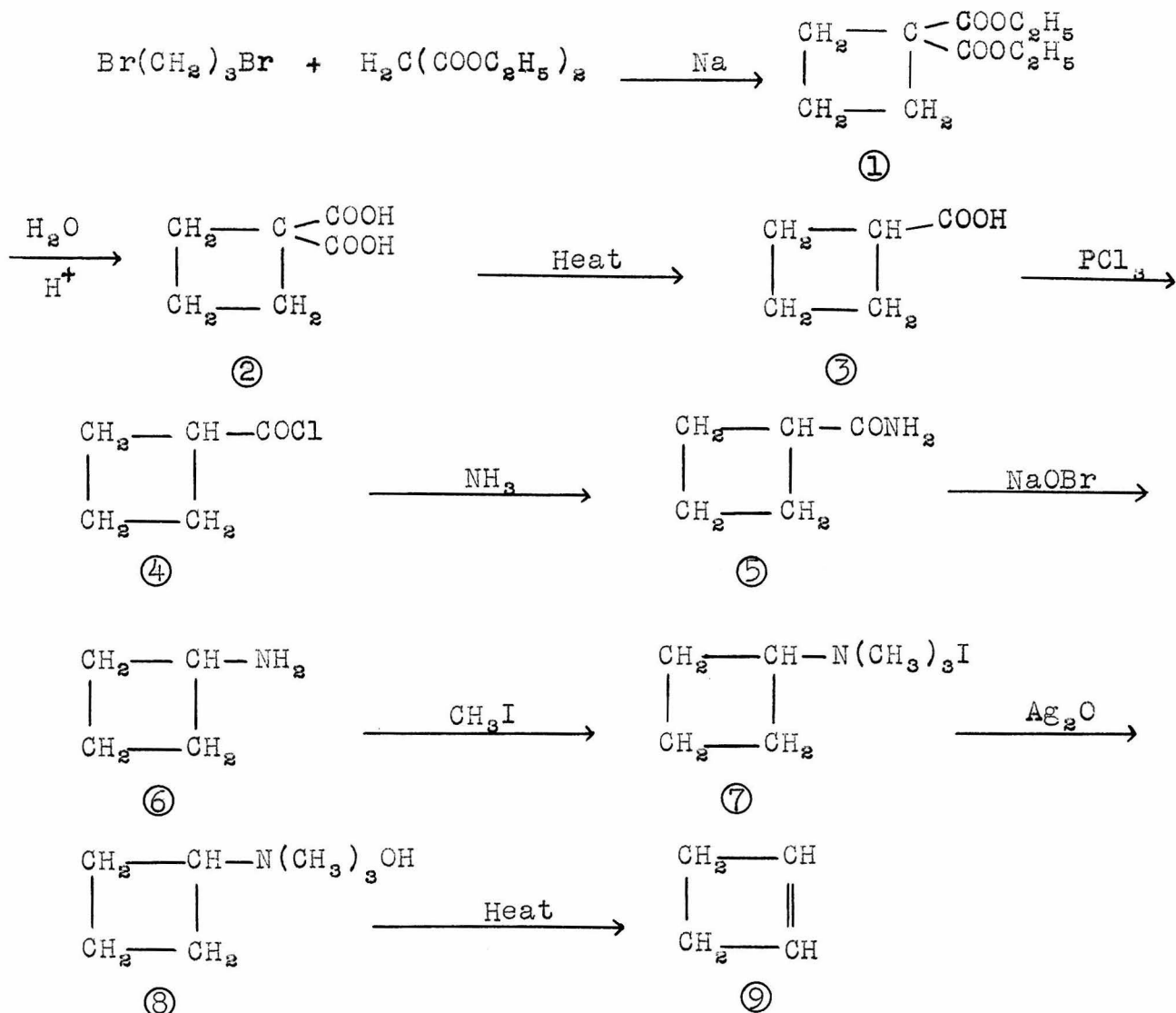
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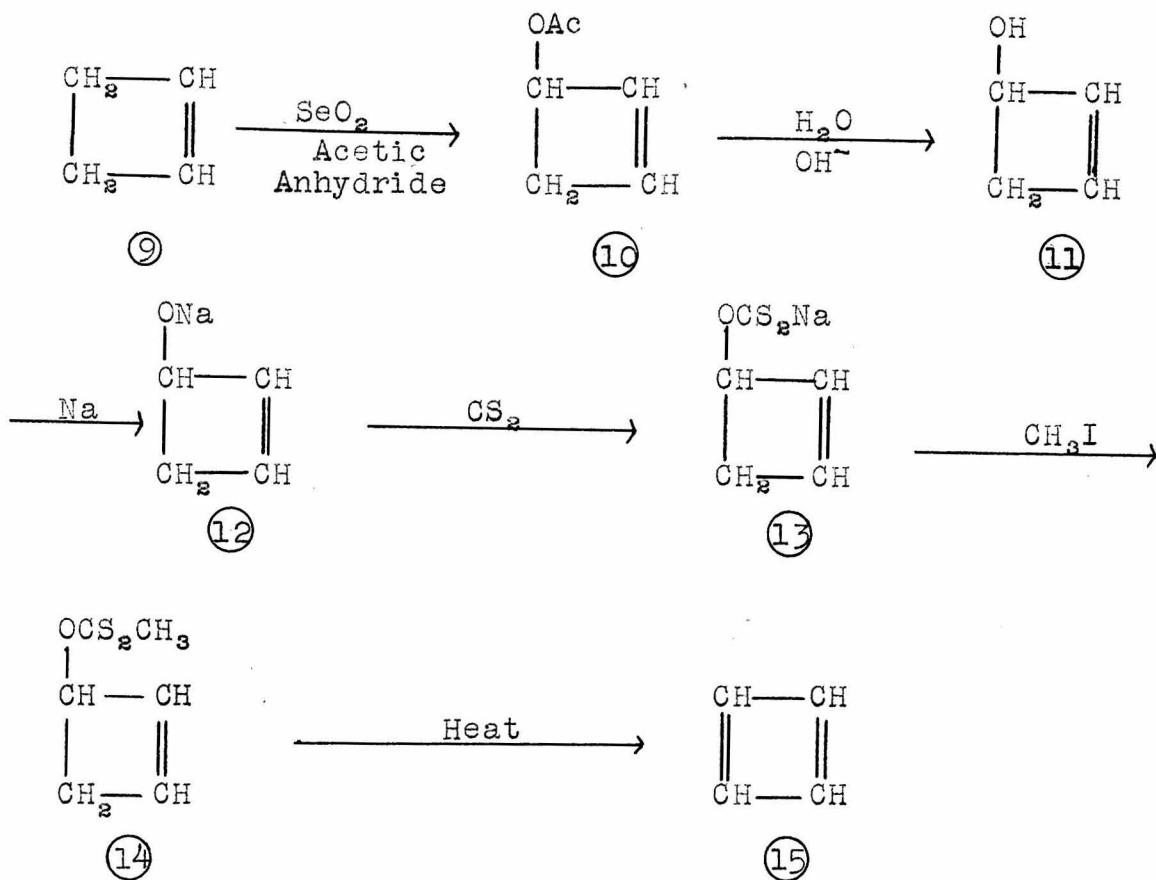
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THE PREPARATION OF METHYLENE CYCLOBUTANE  
AND METHYL  $\Delta'$  CYCLOBUTENE

Many attempts to synthesize cyclobutadiene have been made without success. In this laboratory, a broad research program, under the direction of Dr. Edwin R. Buchman, is being conducted on the cyclobutadiene problem. One phase of this program is the attempt to synthesize cyclobutadiene by the following series of reactions:

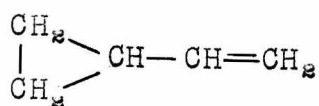




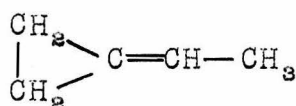
The various steps in the preparation of cyclobutane carboxamide (5) are described in the appendix. Due to the laborious procedure, resulting small yield, and expense involved in the preparation of cyclobutene (9), a suitable, more easily acquired, model compound, was sought, upon which all the preliminary experiments could be carried out.

Methyl  $\Delta'$  cyclobutene was first prepared by Gustavson<sup>1</sup> who treated pentaerythryl tetrabromide with zinc dust and obtained a hydrocarbon analysing for  $\text{C}_5\text{H}_8$ , to which he assigned structure (I) below. This compound when treated with HI in acetic acid yielded an iodide from which HI could be removed with KOH yielding a different hydrocarbon

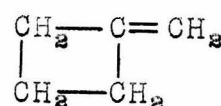
also analysing for  $C_5H_8$  to which Gustavson assigned structure (II) below. These isomeric hydrocarbons he named "Vinyltrimethylene" and "Ethylidenetrimethylene" respectively.



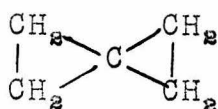
I



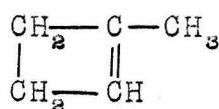
II



III



IV



V

Idzkowska and Wagner<sup>2</sup>, showed that Gustavson's Vinyltrimethylene was a mixture of methylene cyclobutane (III) and some cyclopentane. Later Fecht<sup>3</sup> proposed a structure consisting of two cyclopropane rings having one carbon in common, i.e., spiro bicyclo pentane IV.

Zelinsky and co-workers<sup>4</sup>, prepared a hydrocarbon from 1,1-di(bromomethyl) cyclopropane and zinc dust that had physical properties identical with those of Gustavson's Vinyltrimethylene, and thus apparently added experimental evidence to Fecht's hypothesis.

Philipow<sup>5</sup> carefully fractionated the hydrocarbon mixture obtained by the action of zinc dust upon pentaerythrityl tetrabromide and obtained two compounds, one boiling at 41.5-42° and the other 37.5°. To the higher boiling he assigned the methylene cyclobutane structure (III); to the lower boiling, (V), methyl  $\Delta'$ cyclobutene. His conclusions were based on careful oxidative studies of both

compounds. Furthermore, catalytic reduction of the mixture yielded pure methyl cyclobutane.

Demjanow and Dojarenko<sup>6</sup> were able to prove conclusively that the major constituent of Gustavson's "vinyltrimethylene" was methylene cyclobutane. This was accomplished by comparing, by means of a solid derivative, material obtained from pentaerythrityl bromide with methylene cyclobutane independently synthesized by a method indicative of structure.

Ingold<sup>7</sup> carried out oxidative studies upon the hydrocarbon prepared from 1,1-di(bromomethyl) cyclopropane and zinc dust and concluded that the substance was essentially methyl  $\Delta'$ cyclobutene, with the possibility of methylene cyclobutane being present also.

The procedure described by Philipow<sup>5</sup>, fractionation of the hydrocarbon mixture obtained from pentaerythrityl tetrabromide and zinc dust, was followed in the first attempt to prepare the model compound, methyl  $\Delta'$ cyclobutene. A total of 1340 grams of crude hydrocarbon mixture was fractionated. The column used was 6 1/2 feet long with inside diameter of 22 mm, packed with glass helices and fitted with total reflux, variable take-off head. The first fractionation yielded 234 g. of distillate boiling in the range 30-40°/750mm, (equals 18.3% of total), and 1042 g distillate boiling range 40-41.7°/750mm, (equals 81.7% of total). (See Plot 1). It was found in this investigation that pure methylene cyclobutane boils at

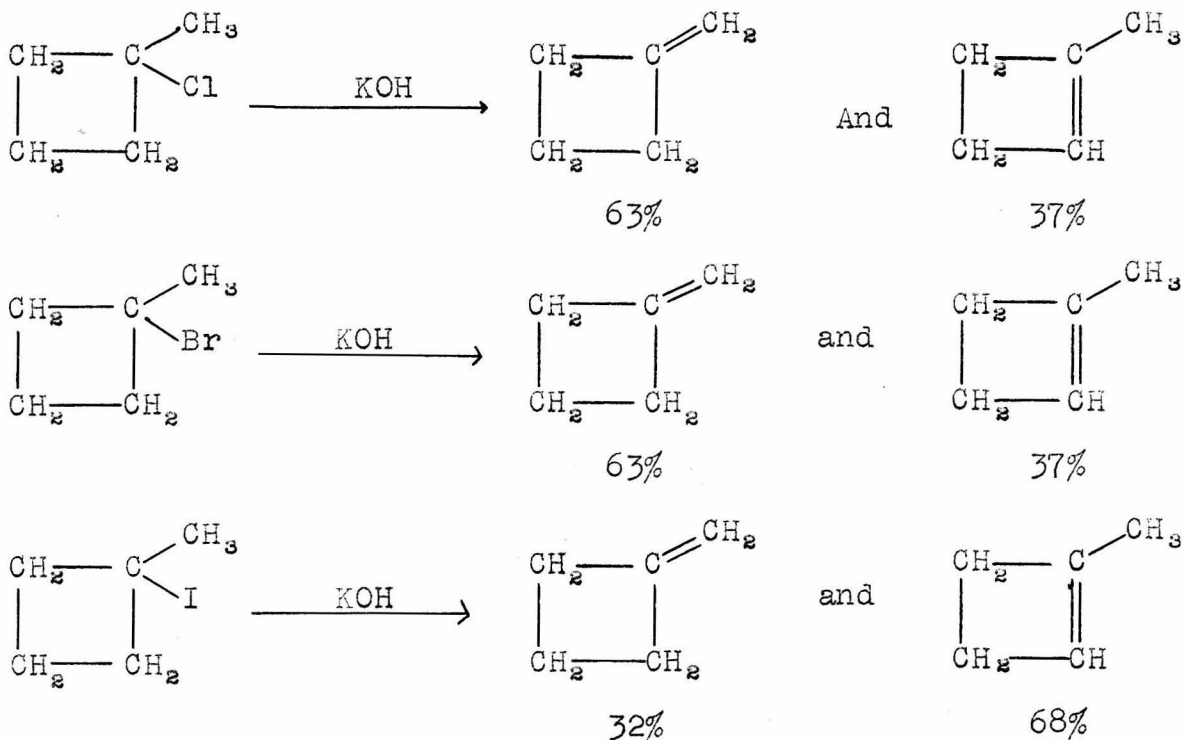
41.39°/750mm corrected, and methyl  $\Delta'$ cyclobutene at 37.10°/750mm corrected. A second fractionation through the same column seemed to give little further separation, the two distilling ranges being in ratio 16% to 84%. No definite break in the curve near the boiling point of methyl  $\Delta'$ cyclobutene was observed. (See plot 2).

While the research was in progress, a paper by Rogowski<sup>8</sup> appeared, claiming that the hydrocarbon prepared from pentaerythryl tetrabromide was really spiro bicyclopentane. The proof of structure was based on an electron diffraction study. This made it desirable to prepare reasonably pure samples of both methyl  $\Delta'$ cyclobutene and methylene cyclobutane for electron diffraction study in this laboratory. A portion of the methylene cyclobutane boiling at 41.2-41.3°/745mm from the second fractionation of the crude hydrocarbon mixture (Plot 2) was given a third fractionation through a 3 ft. column and a constant boiling middle portion of the distillate was used for the electron diffraction pictures. Physical properties of methylene cyclobutane: Boiling point 41.39°/750mm (corr.);  $n_D^{20} = 1.4210$ ;  $d_4^{20} = 0.7401$ . A preliminary examination of the material by Schomaker and Shand<sup>9</sup> yielded a max. and min. curve quite dissimilar to that of Rogowski<sup>8</sup>, but reasonably near the curve to be expected from methylene cyclobutane.

The conversion of methylene cyclobutane into methyl cyclobutene was then investigated. Gustavson<sup>1</sup> treated

methylene cyclobutane with HI forming the tertiary iodide. The iodide was then treated with alcoholic KOH yielding a different hydrocarbon, presumably methyl  $\Delta'$ cyclobutene.

In this research, methylene cyclobutane was treated with HCl, HBr and HI, forming the tertiary halide in each case. HX was then split out with KOH yielding a mixture of hydrocarbons. From the refractive indices and densities of the two  $C_5H_8$  hydrocarbons as found in this paper the ratio of methylene cyclobutane to methyl  $\Delta'$ cyclobutene was calculated.



Dojarenko<sup>10</sup> reports that methylene cyclobutane when passed over alumina at temperatures ranging from 300° to 400°C yields some methyl  $\Delta'$ cyclobutene along with by-products resulting from dehydrogenation, polymerization and hydrogenation. Several experiments were conducted, in which methylene



cyclobutane was passed over activated alumina, but in all cases, a very small amount, if any, of methyl  $\Delta'$ cyclobutene was formed. Unchanged methylene cyclobutane, low boiling hydrocarbons and high boiling polymers were found.

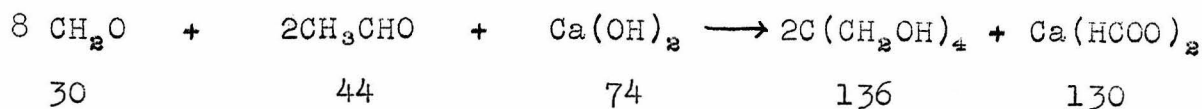
Attempts were made to dehydrate 1-methyl cyclobutanol-1, prepared by absorbing methylene cyclobutane in 66% sulfuric acid<sup>11</sup>. Heating the tertiary alcohol with sulfuric acid, anhydrous oxalic acid<sup>12</sup>, or with traces of iodine<sup>13</sup> did not yield methyl  $\Delta'$ cyclobutene. The alcohol darkened and polymerized when heated with sulfuric acid or oxalic acid but failed to react at all with iodine at atmospheric pressure, the unchanged alcohol being recovered.

The procedure finally used for the preparation of methyl  $\Delta'$ cyclobutene was essentially that of Gustavson<sup>1</sup>. 1-iodo-1-methyl cyclobutane was prepared from methylene cyclobutene and HI and reacted with KOH in ethyl cellosolve (ethylene glycol mono ethyl ether) yielding a mixture of hydrocarbons from which methyl  $\Delta'$ cyclobutene was separated by repeated fractionation. (See Plots 3, 4, 5, ). Physical properties of methyl  $\Delta'$ cyclobutene; Boiling point  $37.10^{\circ}/750\text{mm}$  (corr);  $N_D^{18} = 1.4088$ ;  $D_4^{20} = 0.7244$ ;  $D_4^{25} = 0.7188$ . These figures agree only moderately well with the previously reported data<sup>2,5</sup> on this compound. Gustavson<sup>2</sup> prepared this hydrocarbon in the same manner and found B.P.  $37.5^{\circ}/750\text{mm}$ ;  $d_4^{20} = 0.7235$ ;  $d_4^{18} = 0.7052$ ;  $N_D^{18} = 1.40255$ . Philipow<sup>5</sup> claimed to have obtained this compound by fractionation of the hydrocarbon mixture

resulting from the action of zinc on pentaerythryl bromide. His constants agree with Gustavson's only moderately well. B.P. 37-39°;  $d_4^{25} = 0.7075$ ;  $N_D^{25} = 1.4034$ . In spite of the poor agreement, it is felt that our constants are more nearly correct since highly refined fractionation techniques were employed which were not available to the previous investigators. A preliminary electron diffraction study of this material has also been made by Schomaker and Shand<sup>9</sup> and the pictures obtained here again do not correspond to those reported by Rogowski<sup>8</sup>.

Selenium dioxide has been used for the oxidation of unsaturated aliphatic and cyclic compounds. Some rules have been established as to the ease of oxidation of certain structures. A very extensive review has been published recently by Guillemonat<sup>14</sup>. He found that oxidation occurs primarily at the carbon atom alpha to the tertiary ethylenic carbon atom. If dissimilar groups are attached to the ethylenic carbon atom the ease of oxidation is in the following order:  $\text{CH}_2 > \text{CH}_3 > \text{CH}$ . Thus Dane and co-workers<sup>15</sup> have prepared  $\Delta^{2,3}$  cyclopentenol from cyclopentene, and 2-methyl  $\Delta^{2,3}$  cyclopentenol from methyl  $\Delta^1$  cyclopentene. Methylene cyclobutane therefore would be expected to yield methylene cyclobutanol-2. Using selenium dioxide in acetic anhydride solution, methylene cyclobutane readily reacted, resulting after hydrolysis, in a very high boiling liquid containing selenium but no active hydrogen as determined by the Zerevitinow method. This compound has not been further investigated.

## EXPERIMENTAL SECTION

Pentaerythritol:

800 g = 26.7 mols    210 g = 4.77    3.22 mols

Yield: 377 g melting range 247-249° (corr) equals 58% theory.

Procedure: The procedure outlined in Organic Synthesis<sup>16</sup>

was followed. In a twelve liter round bottom flask, 800 g of para-formaldehyde was dispersed in five liters of water. 210 g of freshly prepared acetaldehyde (paraldehyde distilled with trace of sulfuric acid) was added followed by 190 g of calcium oxide added portionwise over a period of one hour with vigorous stirring. Temperature of reaction mixture rises to 50-55°. After all the CaO was in, the solution was stirred and temperature held at 50° for three hours. The solution was then cooled, filtered using suction, acidified, and treated with 100 g of Norite and filtered. The solution, still somewhat colored, was evaporated on a hot water bath at 100 mm pressure, filtered warm and allowed to crystallize.

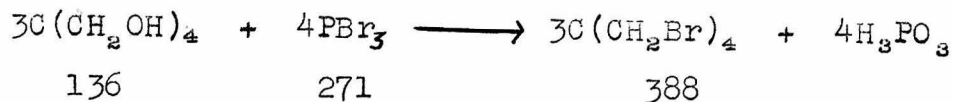
1st crop of crystals 184 g. M.R. 230-235° uncorrected.

2nd crop of crystals 226 g. M.R. 220-225° uncorrected.

3rd crop of crystals 44 g. M.R. 205-210° uncorrected.

4th crop of crystals 17 g. M.R. 210-215° uncorrected.

This material was recrystallized from the minimum amount of water containing 10 cc of HCl. Yield, 377 g. M.R. 247-249° corrected.

Pentaerythrityl Tetrabromide:

680 g = 5 mols      2,600 g = 9.6 mols

Yield: 1796 g of crude tetrabromide or 92% of theory.

Procedure: The procedure outlined in Organic Synthesis<sup>1,7</sup> was adapted to larger quantities. Apparatus consisted of a three liter three necked ground glass flask fitted with two 24/40 side arms and a 45/50 ground glass center opening. One side arm carried a 500 ml. ground glass dropping funnel, the other was loosely stoppered. The center opening carried a condenser, the outlet of which was connected through a calcium chloride guard tube to an HBr absorbing system. 680 g equals 5 mols pentaerythritol<sup>\*1</sup> M.P. 252° corr. was placed in the flask and 2600 g equals 9.6 mols of PBr<sub>3</sub> was added in portions over a period of four hours while heating on a steam bath. After all the phosphorus tribromide was in, an oil bath was substituted and the temperature raised gradually<sup>\*2</sup> to 170° and held there for 20 hours. The mixture was allowed to cool, scraped from the flask into a large volume of water, agitated, decanted and again washed. The material was then collected on a filter, washed with 1 liter of 95% ethanol and allowed to

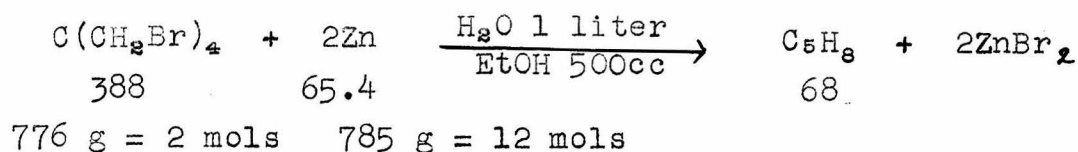
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<sup>\*1</sup>In part prepared as described in this paper, remainder purchased from Lemke Co.

<sup>\*2</sup>It is necessary to raise the temperature gradually since phosphorus compounds which spontaneously ignite are released if mixture is strongly heated.

to air dry. Yield, 1796 g of raw tetrabromide. Some of this crude material was extracted in a Soxhlet extractor using 95% ethanol and then recrystallized from acetone alcohol. Melting range 157-158° uncorrected. In this manner 4780 g (35 mols) of pentaerythritol plus 19,000 g (70 mols) of phosphorus tribromide yielded 12,024 g (31 mols) of tetrabromide for an average yield of 88.5%.

Hydrocarbon Mixture:



Yield: 115 g of crude hydrocarbons or 84.5% of theory.

Procedure: The apparatus consisted of a 12 liter flask fitted with a three necked adapter carrying a dropping funnel, mercury sealed stirrer, and a 38cm column without packing, fitted with a cold finger at the top and having the outlet attached to an ice water cooled condenser. The receiver was surrounded by ice. 776 g (2 mols) of pentaerythrityl tetrabromide<sup>\*1</sup> was crushed in a mortar and mixed intimately with 785 g (12 mols) of zinc dust. One liter of water was then cautiously added. (Note.-At times the reaction became very vigorous when water was added; in one instance the mixture caught fire). The mixture was then heated to 85° on a water bath with

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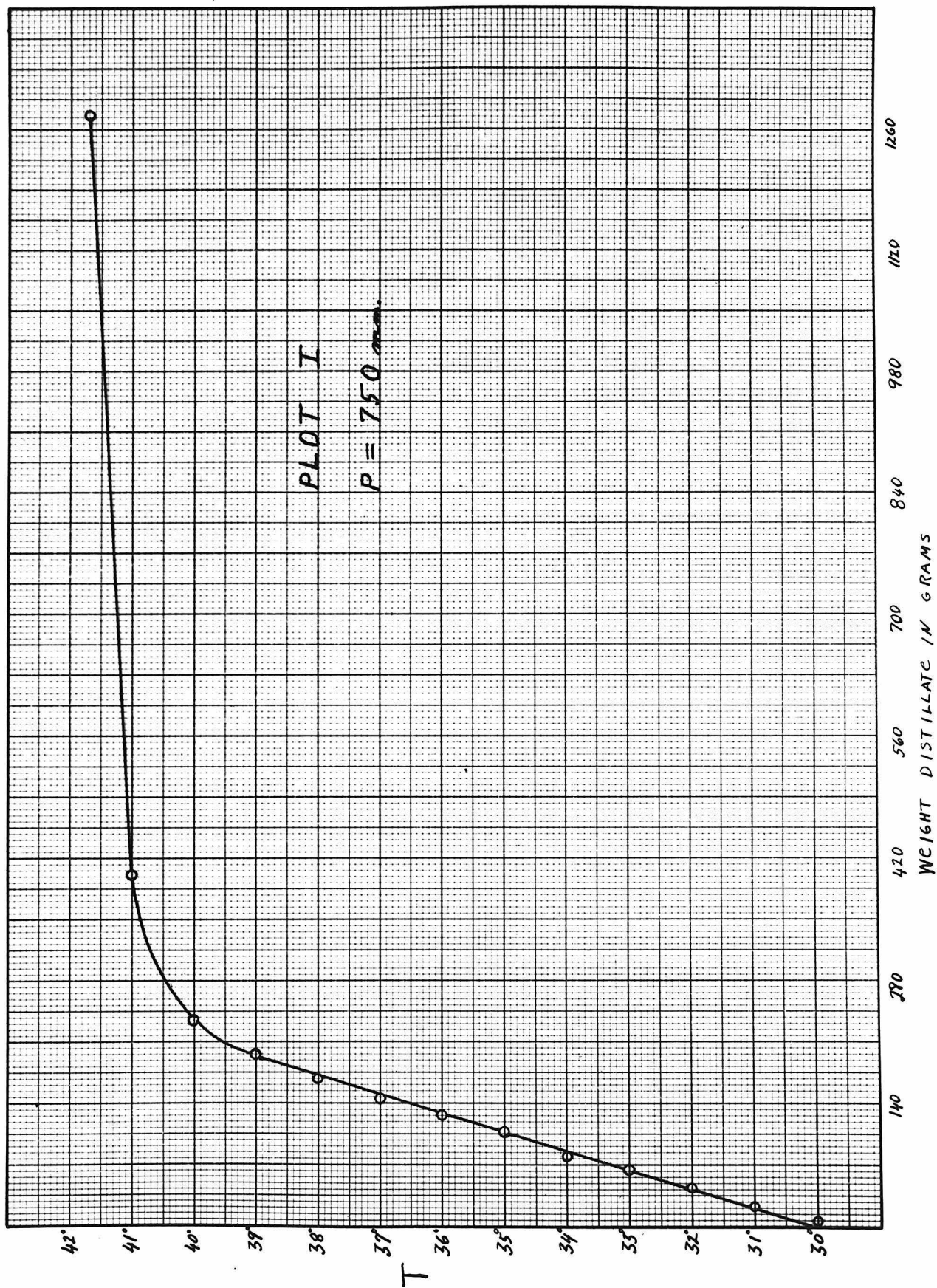
\*<sup>1</sup>In part supplied by Alf Reims.

stirring. 500 ml. of ethanol was then added portionwise from the dropping funnel over a period of two hours, or until no more hydrocarbon appeared to come over. Towards the end of the reaction the temperature was raised to 95° forcing the last traces of hydrocarbon over along with some alcohol and water. The mixture frothed considerably during the reaction and was controlled by raising and lowering the stirrer. The distillate was washed with two 100 ml portions of ice water and then dried over calcium chloride at 0°. The wash water was added to the next run. Crude dry hydrocarbon mixture weighed 115 g. In this manner 11,745 g (30.3 mols) of tetrabromide plus 11,879 g (182 mols) of zinc dust yielded 1425 g (21 mols) of hydrocarbon for an average yield of 69%. This included one run that was almost completely lost due to fire and several others where material was lost due to careless handling. Normal yields vary between 70 and 90%. The crude hydrocarbon mixture was fractionated using a column 6 1/2 feet long with an inside diameter of 22 mm. The column was packed with helices, insulated with asbestos cord with resistance wire wound between the turns for external heating; total reflux, variable take off type with ground glass connections.

First Fractionation Hydrocarbon Mixture. (See Plot 1)

Boiling range at 750mm.	Weight of Fraction	$\Sigma$ Weight
To 30°	6.6 g	6.6 g
30-31°	17.1	23.7
31-32°	19.8	43.5
32-33°	21.5	65.0
33-34°	13.6	78.6
34-35°	28.7	107.3
35-36°	19.1	126.4
36-37°	18.8	145.2
37-38°	22.6	167.8
38-39°	29.0	196.8
39-40°	37.2	234.0
40-41°	167.0	401.0
41-41.7°	875.0	1276.0

First Fractionation of Hydrocarbon Mixture from Tetrabromide.

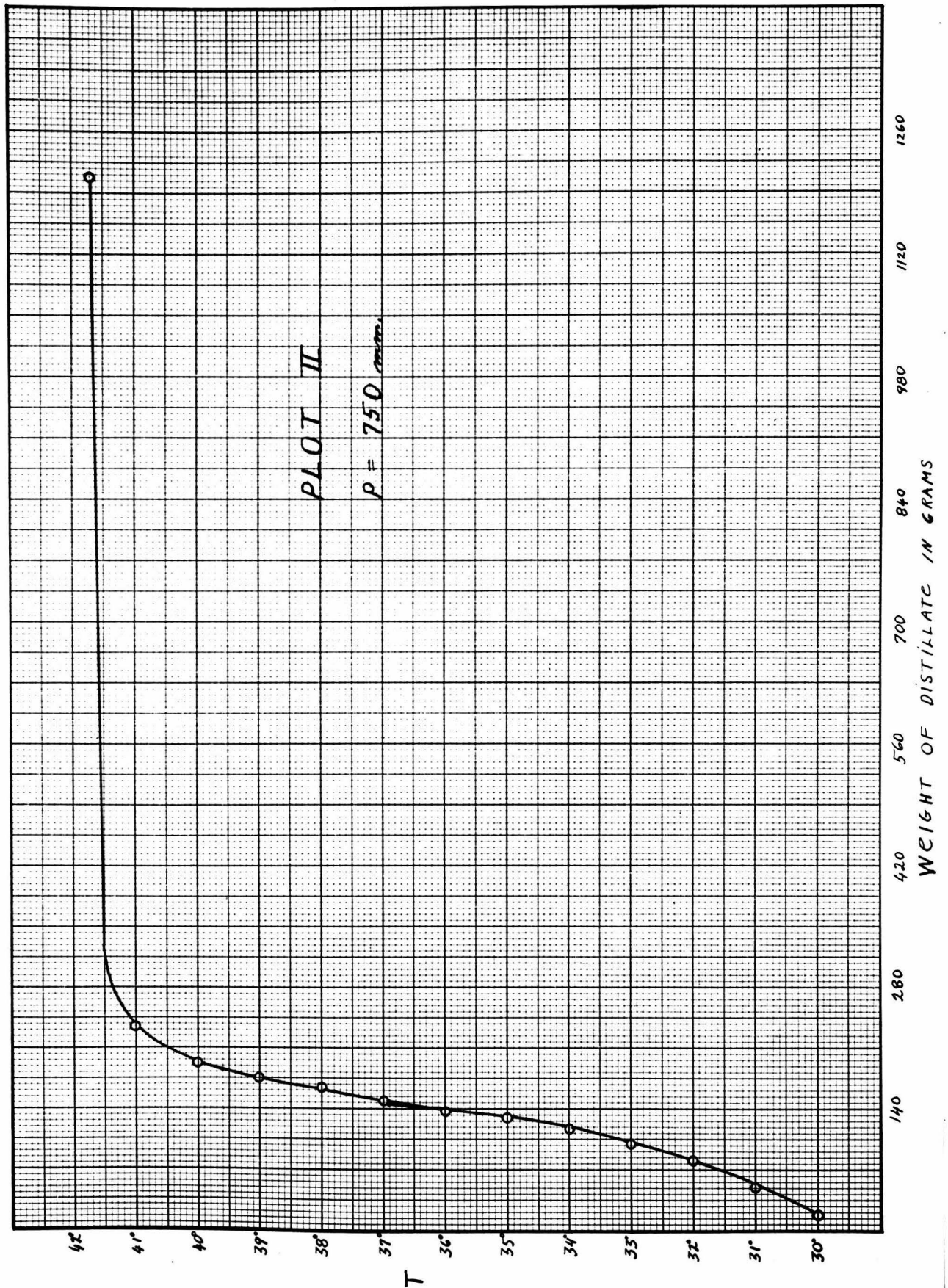




Second Fractionation Hydrocarbon Mixture. (See Plot 2)

Boiling range at 750mm	Weight Fraction	$\Sigma$ Weight
To 30°	18.0 g	18.0 g
30-31°	32.5	50.5
31-32°	30.5	81.0
32-33°	18.0	99.0
33-34°	17.0	116.0
34-35°	12.5	128.5
35-36°	10.0	138.5
36-37°	13.5	152.0
37-38°	12.5	164.5
38-39°	11.0	175.5
39-40°	17.5	193.0
40-41°	43.0	236.0
41-41.7°	974.0	1210.0

## Second Fractionation of Hydrocarbon Mixture from Tetrabromide.



Physical Properties of Second Fractionation Fractions.

Boiling range 750mm	Weight	Refractive Index $n_D^{18}$
To 30°	18.0 g	1.3798 g
30-31°	32.5	1.3810
31-32°	30.5	1.3832
32-33°	18.0	1.3869
33-34°	17.0	1.3905
34-35°	12.5	1.3930
35-36°	10.0	1.3968
36-37°	13.5	1.4000
37-38°	12.5	1.4049
38-39°	11.0	1.4084
39-40°	17.5	1.4139
40-41°	43.0	1.4180
41-41.7°	974.0	1.4218

Third Fractionation Hydrocarbon Mixture for Electron

Diffraction Sample:

A small amount of material boiling 41.2-41.3°/745mm was fractionated through a 3 ft. column packed with helices and the middle portion of distillate was given to Schomaker and Shand for electron diffraction study.

41.24-41.39°/750mm ..... 2.5 g.

41.39°/750mm ..... 7.0 g. Corrected

41.39-41.54°/750mm ..... 2.0 g.

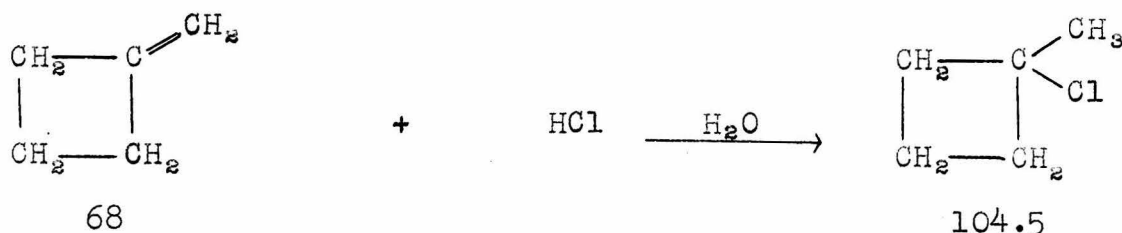
Physical Properties of Methylene Cyclobutane Fractionated from Hydrocarbon Mixture.

Boiling point at 750mm 41.39° corrected.

$$N_D^{20} = 1.4304; \quad N_D^{10} = 1.4266; \quad N_D^{15} = 1.4236; \quad N_D^{18} = 1.4220;$$

$$N_D^{20} = 1.4210; \quad d_4^{20} = 0.7401; \quad d_4^{25} = 0.7349.$$

1-Chloro-1-Methyl Cyclobutane.

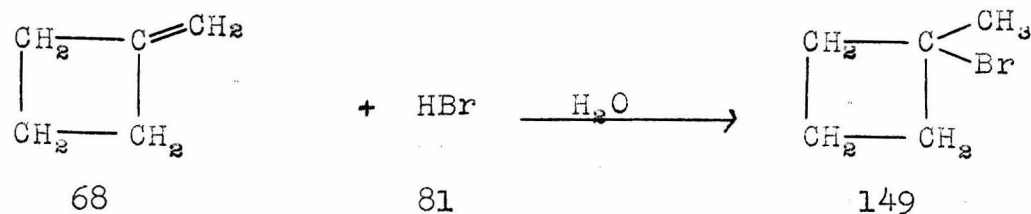


17 g = 0.25 mol

Yield: 21 g B.R. 90-91°/745mm equals 80%.

Procedure: 75 g of concentrated HCl, d. 1.19, was placed in a 250 ml. glass stoppered bottle and cooled to 0°. 17 g (0.25 mols) methylene cyclobutane  $N_D^{18} = 1.4218$  previously cooled to 0° was added and carefully mixed with the HCl. After most of the reaction was over (5 min.) the bottle was placed in a mechanical shaker and agitated for one hour. The tertiary chloride was then separated from the heavier aqueous phase, washed with sodium carbonate solution, then with water and put over calcium chloride to dry. Weight 25.5 g crude chloride. The second fractionation through a 40 cm column gave the following.-

85-90°/745 .....	1.2 g.	$N_D^{25} = 1.4275.$
90-91°/745 .....	21.0 g.	$N_D^{25} = 1.4288; N_D^{20} = 1.4311;$
		$d_4^{25} = 0.9444; d_4^{20} = 0.9495.$

1-Bromo-1-Methyl Cyclobutane.

34 g = 0.5 mol      130 g = 1.6 mols

Yield: 54 g B.R. 55-57°/100mm equals 72.5%.

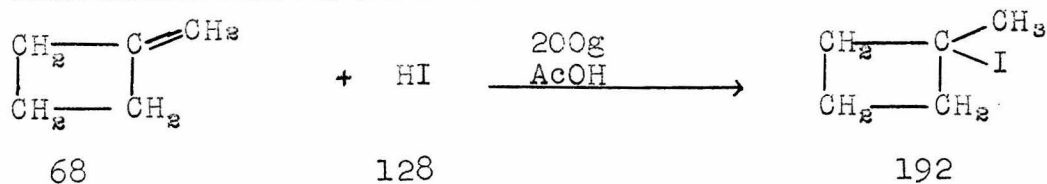
Procedure: 150 g 48% HBr was saturated at 0° with HBr making a 62% HBr solution. To the acid cooled to 0° was added 34 g (0.5 mol) methylene cyclobutane  $N_D^{15} = 1.4218$  also cooled to 0° and the two gently mixed by hand for about 10 minutes then put on a mechanical shaker for one hour. The tertiary bromide was separated from the aqueous phase, washed with sodium carbonate solution and water and then dried over calcium chloride. Weight, 71 g of crude bromide. The second fractionation through a 40 cm column gave the following.-

53-55°/100mm ..... few drops

55-57°/100mm ..... 54 g.  $N_D^{25} = 1.4673$ ;  $N_D^{20} = 1.4698$ .

$d_4^{25} = 1.3110$ ;  $d_4^{20} = 1.3179$ .

57-118°/100mm ..... 9 g.

1-Iodo-1-Methyl Cyclobutane.

68 g = 1 mol

154 g = 1.2 mols.

Yield: 150 g B.R. 40-42°/20mm equals 76.5%.

Procedure: The HI was prepared from I<sub>2</sub> and tetrahydro-naphthalene (tetralin). The iodine was added portionwise to the boiling tetralin by allowing the refluxing tetralin to trickle through solid iodine on the way back to the boiling flask. By controlling the amount of tetralin passing through the iodine the HI was generated smoothly and its rate of evolution easily controlled. The HI from the generator was passed over some moist red phosphorus then through phosphorus pentoxide and finally into glacial acetic acid cooled in ice water. By this procedure about 85% of the I<sub>2</sub> is converted into HI.

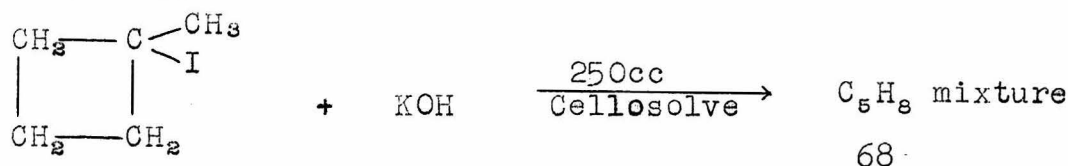
154 g (1.2 mols) of HI was absorbed in 200 g glacial acetic acid at 0°. 68 g (1 mol) of methylene cyclobutane  $n_D^{18} = 1.4218$  cooled to 0° was added to the cold HI solution in a glass stoppered bottle. After tying the stopper in, the bottle was carefully shaken until the main reaction was over, then placed on the mechanical shaker for half an hour. The reaction mixture was poured into one liter of water followed by separation of the two phases. The heavy iodide was freed of I<sub>2</sub> and HI by shaking with 1 f. sodium hydrogen sulfite, 1 f. sodium carbonate and finally with two washes of distilled water. Iodide was dried over calcium chloride, the crude material weighing 184 g. This material was then fractionated. The iodide was colorless when freshly distilled but colored

to 40°/20mm ..... 6 g.

40-42°/20mm ..... 150 g.  $n_D^{25} = 1.5215$ ;  $d_4^{20} = 1.604$ .

upon standing. Using the above procedure, 423 g (6.22 mols) of methylene cyclobutane was treated with 891 g (6.95 mols) of HI yielding 1143 g of crude iodide (5.84 mols) equals 94% theory.

Methyl  $\Delta'$  Cyclobutene.



98 g = .5 mol          56 g = 1 mol

Yield: 20.4 g of crude material equals 60%.

Procedure: The following procedure was worked out using tertiary amyl chloride<sup>18</sup> as a model compound. Ethyl cellosolve (ethylene glycol monoethyl ether) as solvent gave higher yields than ethanol or ethanol and water<sup>19</sup>, apparently because of its higher boiling point. Diethylene glycol was tried but the chloride remained as an immiscible phase. Higher boiling cellosolves such as butyl cellosolve gave about the same yield as ethyl cellosolve.

56 g (1 mol) of KOH was dissolved in 250 ml. cellosolve on the shaker (1/2 hour). This solution was heated to refluxing in a 500 ml. ground glass flask fitted with dropping funnel and with a reflux condenser as a column. Water in the reflux condenser was kept at 45°C. The outlet at the top of the reflux condenser lead to another condenser containing ice water and then into a receiver

cooled in a dry ice bath. 98 g (0.5 mol) of crude tertiary iodide was added dropwise over a period of two hours to the refluxing collosolve. The raw hydrocarbon mixture obtained was washed with ice water and dried over magnesium perchlorate. Weight, 20.4 g  $n_D^{18} = 1.4080$ . In this way a total of 1143 g (5.85 mols) of tertiary iodide yielded 223 g (3.29 mols) of hydrocarbon equal to 56% of theory.

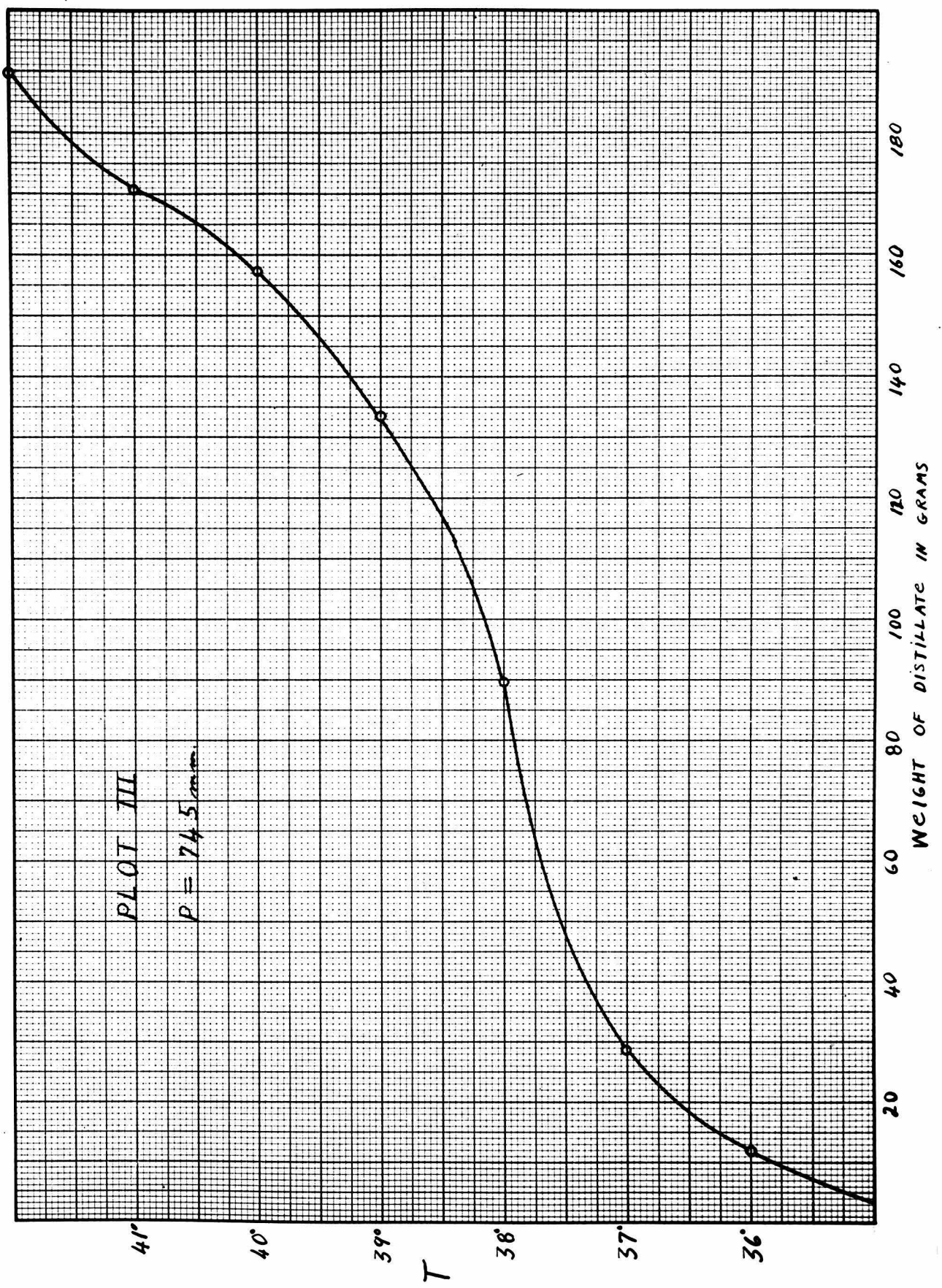
The crude hydrocarbon mixture was then fractionated. The 6 1/2 ft. column described previously (p. 12) was used for the first fractionation. Because of the small amount of material, a still-base was used. The still-base consisted of saturated aliphatic hydrocarbons boiling in the range 60-61°/746mm and was prepared by fractionation of 60-70° ligroin.

First Fractionation of Hydrocarbon Mixture from Tertiary Iodide. (See Plot 3)

Boiling range 745mm	Weight Fraction	Weight
32-36°	12 g	12 g
36-37°	16.7	28.7
37-38°	61.0	89.7
38-39°	44.0	133.7
39-40°	23.5	157.2
40-41°	13.7	170.9
41-42	19.0	189.9
42-47°	10.0	199.9



First Fractionation of Hydrocarbon Mixture from Tertiary Iodide.



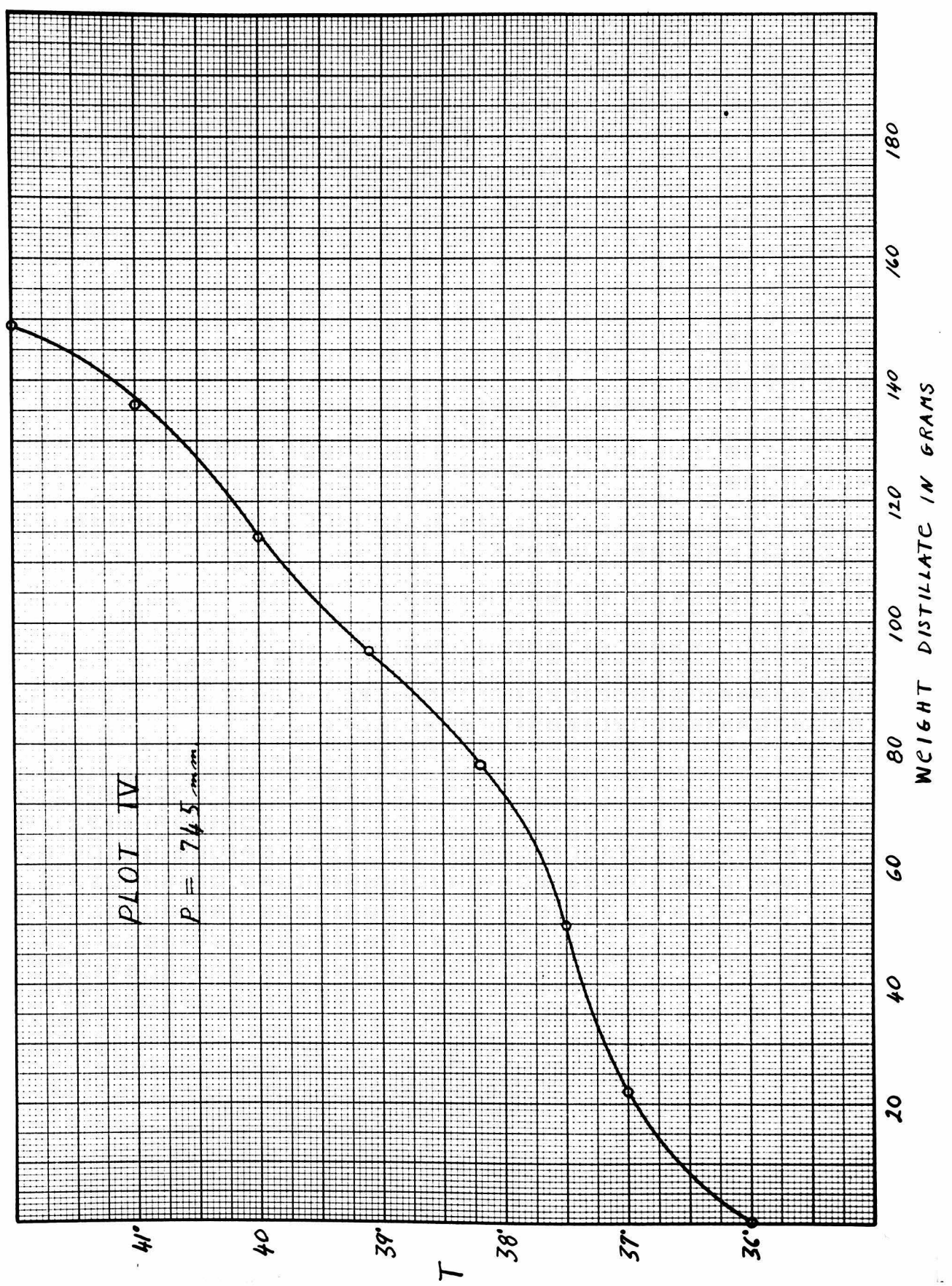
Second Fractionation of Hydrocarbon Mixture from Tertiary Iodide (See Fig. 4)

Only material boiling above 36°/745mm was refractionated using the same 6 1/2 ft. column.

Boiling range 745mm	Weight Fraction	Weight
36.0-37.0°	22 g	22
37.0-37.5°	27.8	49.8
37.5-38.2°	26.8	76.6
38.2-39.1°	18.5	95.1
39.1-40.0°	19.0	114.1
40.0-41.0°	22.0	136.1
41.0-42.0°	13.0	149.1
42.0-45.0°	6.0	155.1

For further fractionation the 6 1/2 ft. column was too large; instead, a spinning band column similar to the one described by Baker<sup>20</sup> was used. This column had the equivalent of 18 theoretical plates at the reflux rate and through put used.

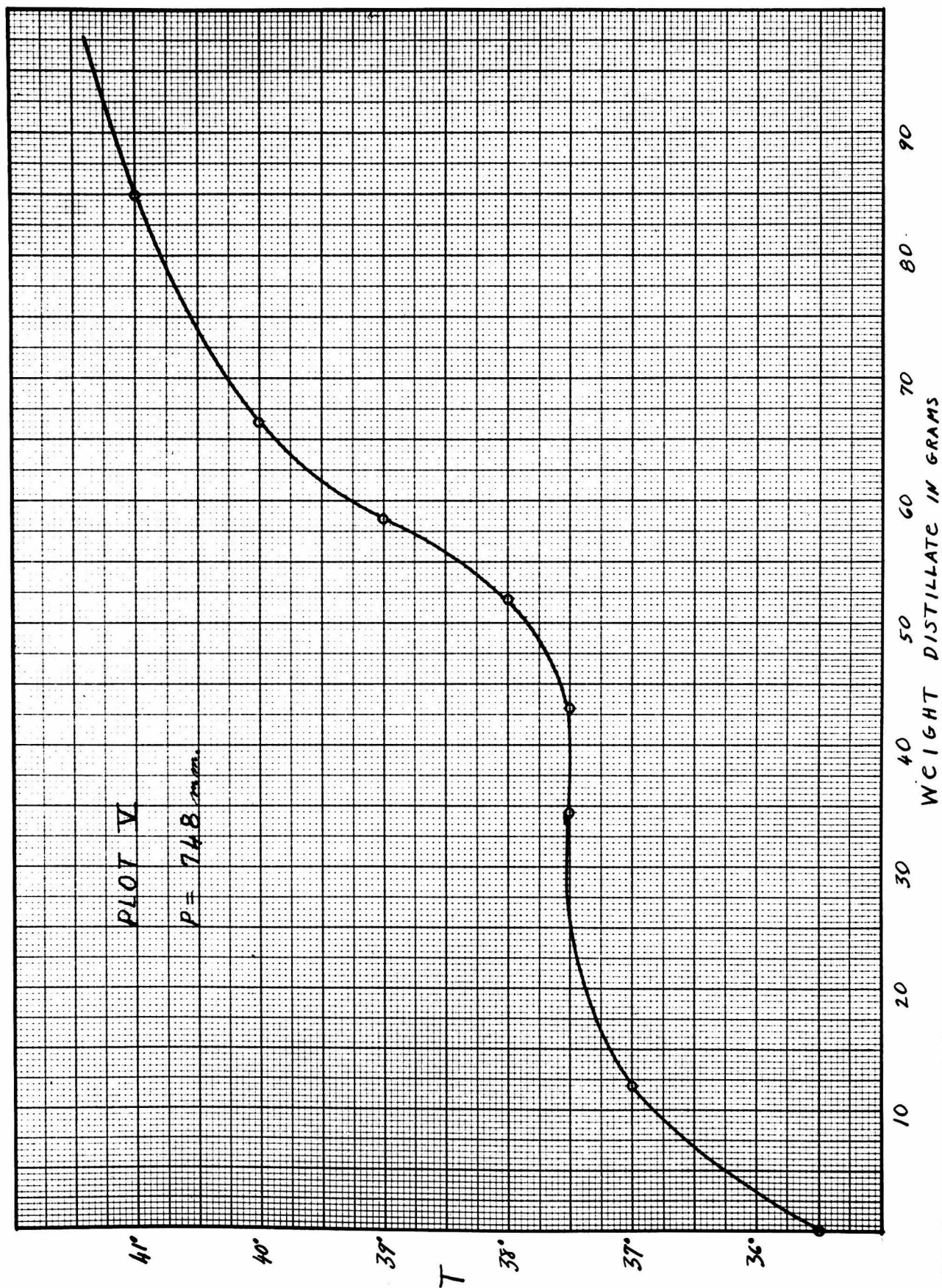
Second Fractionation of Hydrocarbon Mixture from Tert. Iodide.



Third Fractionation of Hydrocarbon Mixture from Tertiary  
Iodide. (See Plot 5)

Boiling range 748mm	Weight	Weight	$\frac{N^{18}}{D}$
35.5-37.0°	12.0g	12.0g	1.4100
37.0-37.5°	22.0	34.0	1.4091
37.5°	9.0	43.0	1.4110
37.5-38.0°	9.0	52.0	1.4118
38.0-39.0°	6.5	58.5	1.4149
39.0-40.0°	8.0	66.5	1.4170
40.0-41.0°	18.5	85.0	1.4190
41.0-42.0°	20.0	105.0	1.4210
42.0-45.0°	4.0	109.0	1.4128

## Third Fractionation of Hydrocarbon Mixture from Tert. Iodide.



The material boiling at  $37-38^{\circ}/748\text{mm}$  was put through the column again and divided into 5 ml. fractions.

Fraction	Boiling range 750mm	$n_D^{18}$
1	$33.2-35.9^{\circ}$	1.4051
2	$35.9-36.1^{\circ}$	1.4086
3.	$36.1-36.2^{\circ}$	1.4088
4	$36.2-36.6^{\circ}$	1.4085

Column shut off.-

5	$35.9-36.3^{\circ}$	1.4086
6	$36.3^{\circ}$	1.4087
7	$36.3^{\circ}$	1.4088
8	$36.3-36.4^{\circ}$	1.4089
9	$36.4-36.7^{\circ}$	1.4091
10	$36.7-38.2^{\circ}$	1.4108

Since there were small variations in pressure during the fractionation and also because the column when shut down was apparently not at equilibrium, refractive index was considered a better criterion than the boiling point. The 5 ml. fractions numbered 3, 6, 7, 8 were combined and considered to be the purest methyl  $\Delta'$ cyclobutene.

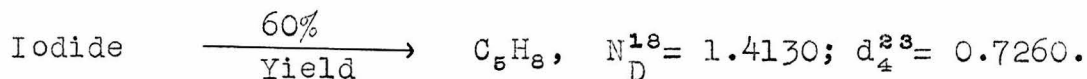
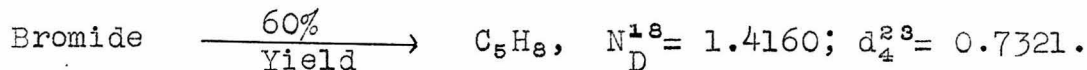
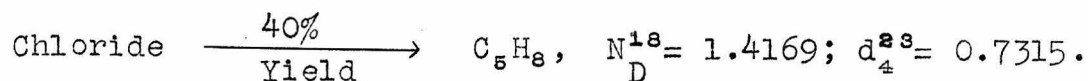
Physical Properties of Methyl Cyclobutene Fractionated from Hydrocarbon Mixture Prepared from Tertiary Iodide.

Boiling point at 750mm,  $37.10^{\circ}$  (corr.).

$$n_D^{18} = 1.4088; \quad d_4^{20} = 0.7244; \quad d_{\pm}^{25} = 0.7183.$$

Comparison of Hydrocarbon Mixtures Obtained from 1-Chloro-1-Methyl Cyclobutane, 1-Bromo-1-Methyl Cyclobutane, and 1-Iodo-1-Methyl Cyclobutane.

The chloride, bromide and iodide were treated identically. Approximately 100% excess KOH was dissolved in cellosolve and the halide added dropwise to the boiling alkali solution, the evolved hydrocarbon being collected in a dry ice cooled receiver.

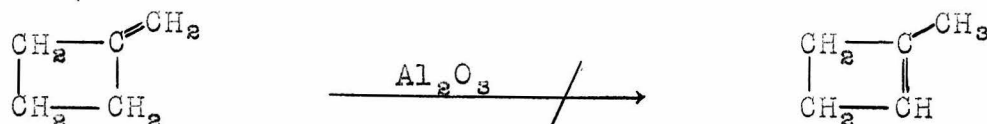


In this investigation the following physical properties were found: Methylene cyclobutane,  $N_D^{18} = 1.4220$ ;  $d_4^{23} = 0.7369$ ; methyl  $\Delta'$  cyclobutene,  $N_D^{18} = 1.4088$ ;  $d_4^{23} = 0.7210$ . The refractive indices of the two isomers differ by 0.0132; the densities by 0.0159. Using these values and assuming the hydrocarbon mixture contains only methylene cyclobutane and methyl  $\Delta'$  cyclobutene the following proportions of each isomer in the mixtures obtained from the halides can be calculated.

Halide	Proportions from Refractive Indices		Proportions from densities		Average	
	$\begin{array}{c} \text{CH}_2-\text{C}=\text{CH}_2 \\   \quad   \\ \text{CH}_2-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2-\text{C}-\text{CH}_3 \\   \quad    \\ \text{CH}_2-\text{CH} \end{array}$	$\begin{array}{c} \text{CH}_2 \\   \\ \text{R} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{R}_1 \end{array}$	$\begin{array}{c} \text{CH}_2 \\   \\ \bar{\text{R}} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \bar{\text{R}}_1 \end{array}$
Chloride	61%	39%	66%	34%	63%	67%
Bromide	55	45	70	30	63	67
Iodide	32	68	31	69	32	68

Actually, upon fractionating larger quantities of the mixture prepared from the iodide, roughly 40% was fractionated out as methyl  $\Delta^1$  cyclobutene and 28% as methylene cyclobutane.

Attempted Isomerization of Methylene Cyclobutane.



Apparatus: The catalyst chamber consisted of a pyrex tube 40 cm long with inside diameter of 3 cm. A thermometer well reached to the middle of the catalyst. Hydrocarbon was vaporized by dropping into a 50 ml. flask heated in an oil bath to 50-60°, and carried through the catalyst by a slow stream of dry CO<sub>2</sub>. Reaction products were collected in a dry ice trap.

Procedure: The catalyst used was Baker's "Hydralo" activated alumina. When heated for the first time some water was given off. The apparatus containing the alumina at 300°C was then evacuated for 1/2 hour in order to remove last traces of water.



Run A: 15 g of methylene cyclobutane  $N_D^{18} = 1.4218$  was vaporized and passed over the alumina at 300-305°C over a period of 3 1/2 hours. After all the hydrocarbon had been passed through, the apparatus was swept out with CO<sub>2</sub> for 1 1/2 hours. The dry ice cooled receiver was then removed, another receiver attached and the apparatus evacuated, forcing over several drops of high boiling polymer having a terpene like odor.

Low boiling material	7.2 g	$N_D^{18} = 1.4192$
High boiling polymer	.6 g	$N_D^{18} = 1.4722.$

The low boiling material was fractionated through a 20 cm column.

29.6-33.0°/745mm	..... .3 g.	$N_D^{18} = 1.4169$
33.0-34.0°/745mm	.....4.3 g.	$N_D^{18} = 1.4205$
34.0-35.2°/745mm	..... .8 g.	$N_D^{18} = 1.4214$
35.2-41.5°/745mm	.....3.0 g.	$N_D^{18} = 1.4222$

Run B: 17 g of methylene cyclobutane  $N_D^{18} = 1.4218$  was passed over the catalyst at 300-308°C over a period of 4 1/2 hours. Swept out apparatus for 1 hour with CO<sub>2</sub>, then replaced receiver and evacuated forcing over high boiling polymer.

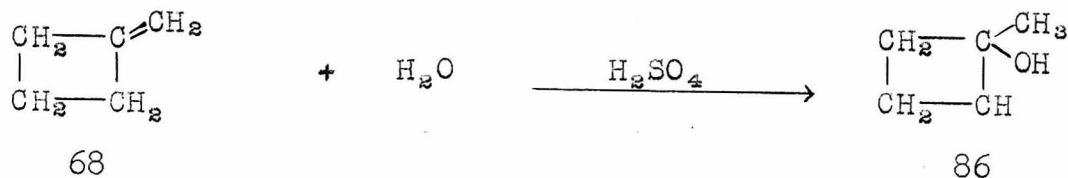
Low boiling material	13.3 g.	$N_D^{18} = 1.4218$
High boiling material	.5 g.	

Low boiling material was fractionated through a 20 cm column.

28-33°/747mm	..... .3 g.	
33-34°/747mm	..... 5.1 g.	$N_D^{18} = 1.4210$
34-35°/747mm	..... 3.2 g.	$N_D^{18} = 1.4215$
35-36°/747mm	..... 1.8 g.	
36-37°/747mm	..... .8 g.	

1-Methyl Cyclobutanol-1.

The procedure described by Demjanow<sup>11</sup> was used.



34 g = .5 mol.

Yield: 27.0 g B.R. 115-118°/748mm, equals 63%.

Procedure: In a 1 liter three necked flask fitted with stirrer, dropping funnel and surrounded by ice salt bath, 132 g of H<sub>2</sub>SO<sub>4</sub> was added to 66 g ice, the mixture cooled to 0° and 34 g (0.5 mol) of methylene cyclobutane, N<sub>D</sub><sup>18</sup> = 1.4218 added over a period of 15 minutes. Mixture was then stirred at 0° for 1 hour, made alkaline with 5N NaOH keeping the temperature below 20°, and then the sodium sulfate that had precipitated was filtered off, the solution being put on continuous ether extraction for 5 hours. The ether extract was dried with K<sub>2</sub>CO<sub>3</sub>, the ether distilled off, followed by fractionation of the residue.

85-115°/747mm..... 2 g.  
 115-118°/747mm ..... 27 g.  
 118-119°/747mm ..... 3 g.

The material boiling at 115-118°/747mm had the following properties: d<sub>4</sub><sup>20</sup> = 0.8971; N<sub>D</sub><sup>20</sup> = 1.4333; melting range -3 to -6°. The alcohol is soluble to the extent of 1 part in 6.5-7 parts of water at 25°. Miscible with ether. Phenyl urethane M.P. 139.9° (corr.) crystallized out of isopropyl ether.

Attempted Dehydration of 1-Methyl Cyclobutanol-1 Using  $H_2SO_4$ .

1-methyl cyclobutanol-1 was dropped into refluxing 60% sulfuric acid containing some diatomaceous earth. A dark insoluble phase, with terpene like odor separated out on top but no hydrocarbon was evolved. The experiment was repeated using 50% and 40% sulfuric acid with the same results.

Attempted Dehydration of 1-Methyl Cyclobutanol-1 using  $(COOH)_2$ .

The procedure described in D.R.P., 66, 866<sup>12</sup> was tested out first on tertiary amyl alcohol. The oxalic acid used was dehydrated by heating in an oven for 15 hours at 90°. Neutralization equivalent theory 46.0. Found 45.8. The tertiary amyl alcohol was added dropwise to the anhydrous oxalic acid heated on a steam bath giving a 75% yield of trimethylethylene.

The same procedure was followed using 1-methyl cyclobutanol-1 but no hydrocarbon was formed. The mixture darkened, resulting in a polymer similar to that obtained from the attempted sulfuric acid dehydration.

Attempted Dehydration of 1-Methyl Cyclobutanol-1 Using  $I_2$ .

Hibbert<sup>13</sup> has dehydrated tertiary amyl alcohol by heating at 100° with  $I_2$ . This same procedure was attempted with 1-methyl cyclobutanol-1. 6.7 g of the cyclic alcohol was refluxed with a small amount of  $I_2$  for 23 hours. 5.5 g unchanged alcohol was recovered and only a trace of hydrocarbon was formed.

Selenium Dioxide Oxidation of Methylene Cyclobutane.

Preparation of  $\text{SeO}_2$ : 100 g of powdered Se was placed in an evaporating dish and concentrated  $\text{HNO}_3$  added, (Hood). 200 ml. acid was added until no more oxides of nitrogen were evolved. The resulting yellow solution was evaporated on a steam bath; the crude dioxide then purified by sublimation from a dye pot on to a watch glass using a free flame. Yield 133 g of  $\text{SeO}_2$  equals 94%.

Guillemonat<sup>14</sup> describes the oxidation of trimethylethylene with selenium dioxide in acetic anhydride solution. Before working with the cyclic hydrocarbon, the procedure was tried out on trimethylethylene prepared by dehydrating tertiary amyl alcohol with oxalic acid. 2-methyl-2-butanol-1 was formed in accordance with Guillemonat's findings. Yield 3.2 g B.R. 134-135°/749mm;  $N_D^{24} = 1.439$ ; active hydrogen by Zerevitinow's method 1.3. Guillemonat<sup>13</sup> reports B.R. 136-138°;  $N_D^{24} = 1.441$ .

The attempt was then made to oxidize methylene cyclobutane using the same procedure. 10 g (0.147 mol) of methylene cyclobutane  $N_D^{18} = 1.4218$  plus 15 ml redistilled acetic anhydride was placed in a 200 ml. three necked flask fitted with stirrer, reflux condenser and thermometer. 9 g of selenium dioxide (0.081 mol) was added and the mixture heated on a steam bath with stirring for 1 3/4 hours. The temperature of the refluxing liquid rose from 48-65°. The reaction mixture was poured into water resulting in two phases. Oily phase (12 g) smelled of hydrocarbon, acetic acid and ester. This material was shaken

with 5N NaOH at room temperature, extracted with ether and the ether solution dried over  $K_2CO_3$ . The ether was distilled off leaving a residue which was then distilled at reduced pressure.

125-142°/1mm ..... 3.4 g.  $N_D^{25} = 1.5125$

142-147°/1mm ..... 4.0 g  $N_D^{25} = 1.5125$

above 147°/1mm ..... few drops  $N_D^{25} = 1.5235$

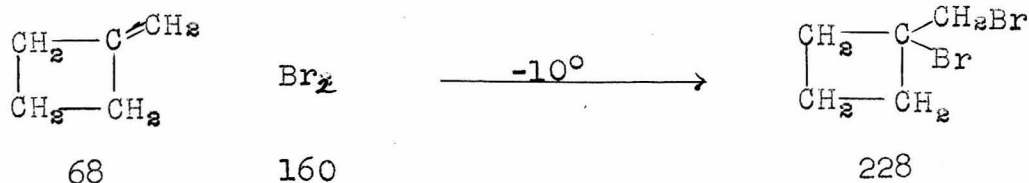
Attempts to make the benzoate, 3, 5 dinitro benzoate and phenylhydrazid of the material boiling 142-147°/1mm failed. Active hydrogen determination by Zerevitinow method gave absolutely no methane although reaction with the MeMgI did take place. 3.2 g,  $N_D^{25} = 1.5125$  of material boiling at 142-147°/1mm above was refluxed for 15 minutes with 5N NaOH, extracted with ether, the ether solution dried and the ether distilled off. The residue was then distilled.

120-140°/1mm ..... few drops,  $N_D^{23} = 1.5388.$

140-145°/1mm ..... 2.0 g,  $N_D^{23} = 1.5160.$

Both of these fractions were treated with MeMgI but no methane was evolved. Some of fraction 140-145°/1mm was heated on a spatula and left a residue of Se. From these results it was concluded that the expected compound, methylene cyclobutanol-2 was not obtained.

Methylene Cyclobutane Dibromide.



17 g = .25 mol      44 g = .27 mol

Yield: 54 g of crude, equals 95%. 35 g B.R. 84-85°/15mm equals 61%.

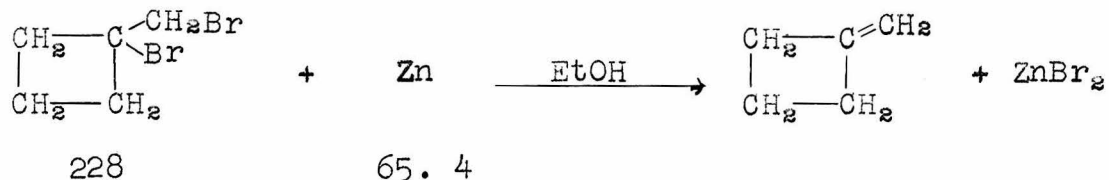
Procedure: 17 g (0.25 mol) methylene cyclobutane  $n_D^{18} = 1.4218$  plus 44 g (0.27 mol)  $Br_2$  added simultaneously with stirring into a 100 ml. three necked flask cooled to  $-10^\circ$ . The bromide was kept in slight excess and experiment was carried out in subdued artificial light. Product was washed with 1 f.  $K_2CO_3$  and water and dried over  $CaCl_2$ . Weight 54 g,  $n_D^{25} = 1.5410$ . After second fractionation through a 20 cm column

70-84°/15mm ..... 6.5 g.

84-85°/15mm ..... 35.0 g.  $n_D^{25} = 1.5369$ ,  $n_D^{20} = 1.5391$ .

85-88°/15mm ..... 1.0 g.  $d_4^{25} = 1.8203$ ,  $d_4^{20} = 1.8274$ .

Regeneration of Methylene Cyclobutane from Dibromide.



104 g = .445 mol      36 g = .55 mol.

Procedure: 36 g (0.55 mol) of 30 mesh zinc pellets was placed in a 200 ml. flask and 125 ml. absolute ethanol added. Heated to refluxing on a water bath and 104 g (0.445 mol) of methylene cyclobutane dibromide added slowly. When about 50 g had been added (1 hour) solution began to darken considerably and hydrocarbon ceased to come over. Contents of the flask was discarded and new zinc and ethanol replaced. The reaction then continued smoothly until the very end when again the mixture began to darken. Crude hydrocarbon weight

18 g,  $n_D^{18} = 1.4201$ ;  $d_4^{23} = 0.7326$  or roughly 90% pure methylene cyclobutane.

#### Acknowledgements

The author is greatly indebted to Dr. Edwin R. Buchman for his suggesting this problem and for his guidance throughout the course of the research.

The author wishes to express his appreciation to Alf Reims for his help in preparing certain of the compounds used in the investigation.

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APPENDIX

THE PREPARATION OF CERTAIN CYCLOBUTANE DERIVATIVES;

ETHYL CYCLOBUTANE 1,1-DICARBOXYLATE,

CYCLOBUTANE 1,1-DICARBOXYLIC ACID,

CYCLOBUTANE MONOCARBOXYLIC ACID,

CYCLOBUTANE MONOCARBOXYLIC ACID CHLORIDE,

CYCLOBUTANE MONOCARBOXYLIC ACID AMIDE.

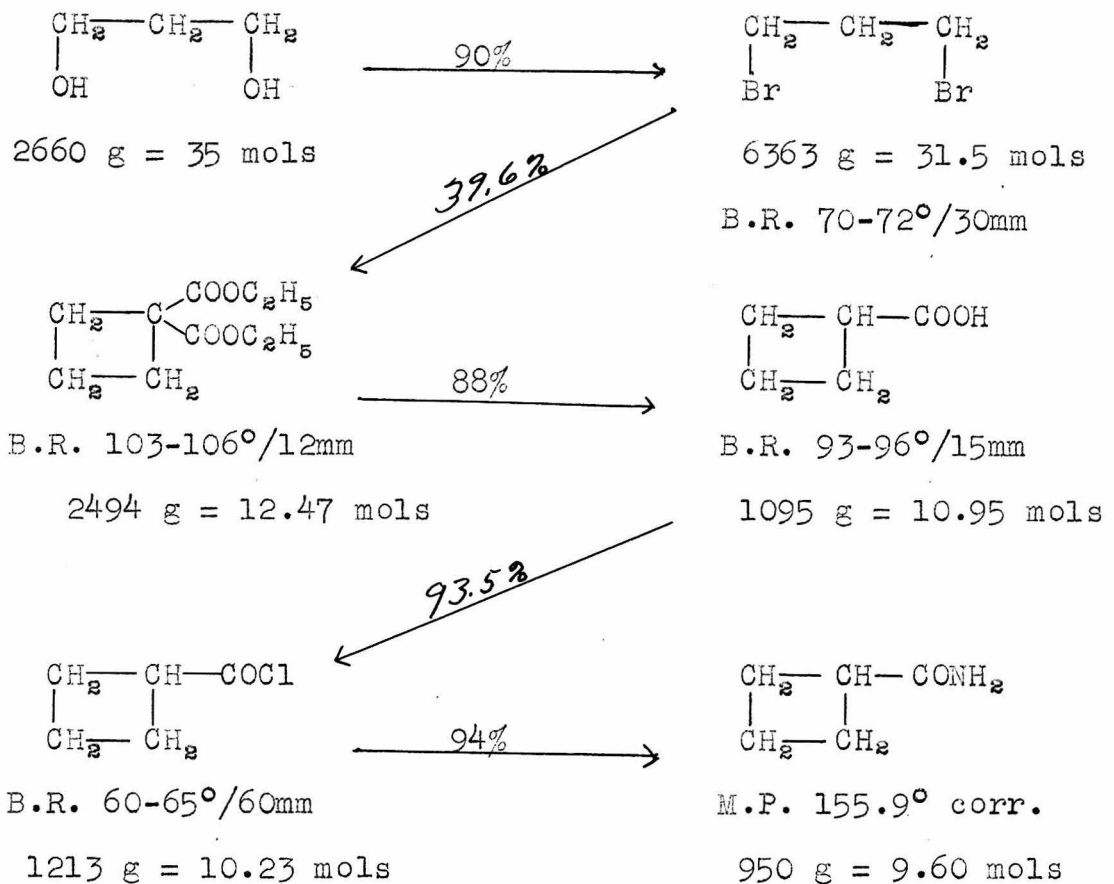
THE PREPARATION OF CERTAIN CYCLOBUTANE DERIVATIVES;  
ETHYL CYCLOBUTANE 1,1-DICARBOXYLATE,  
CYCLOBUTANE 1,1-DICARBOXYLIC ACID,  
CYCLOBUTANE MONOCARBOXYLIC ACID,  
CYCLOBUTANE MONOCARBOXYLIC ACID CHLORIDE,  
CYCLOBUTANE MONOCARBOXYLIC ACID AMIDE.

This research had several objectives: (A) A convenient procedure for the preparation of comparatively large quantities of cyclobutene; (B) Repetition of the preparation of cyclobutane derivatives for electron diffraction studies, corresponding to those of the cyclopropane series being prepared by Maurice J. Schlatter of this laboratory.

Results.

Thirty five mols of trimethylene glycol yielded 31.5 mols of trimethylene dibromide, B.R. 70-72°/30mm, equals 90% of theory. The dibromide was condensed with sodium malonic ester and yielded 12.47 mols of ethyl cyclobutane 1,1-dicarboxylate, B.R. 103-106°/12mm, equals 39.6% of theory. This ester was hydrolyzed to the 1,1-dicarboxylic acid which was decarboxylated to yield 10.95 mols of cyclobutane monocarboxylic acid, B.R. 93-96°/15mm, equals 88% of theory. The cyclobutane monocarboxylic acid was treated with phosphorus trichloride and yielded 10.23 mols of cyclobutane monocarboxylic acid chloride, B.R. 60-65°/60mm, equals 93.5% of theory. The acid chloride in turn was reacted with ammonia yielding 9.6 mols of cyclobutane mono-

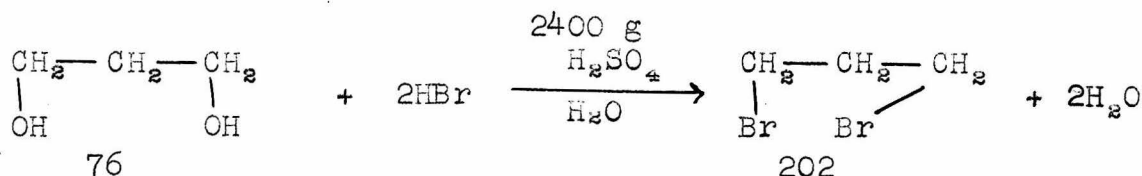
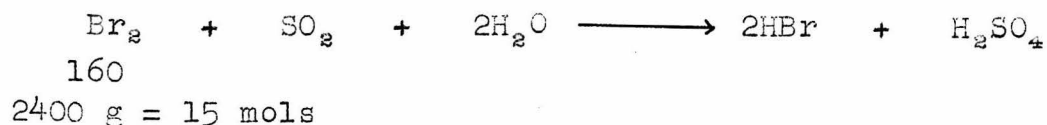
carboxylic acid amide M.P. 155.9° corrected, equals 94% theory. Over all yield from glycol to amide equals 27% theory.



A preliminary experiment on the cyclobutane mono-carboxylic acid amide, in which an attempt was made to convert it to cyclobutylamine using hypobromite, was not satisfactory and attention was then turned to the comparatively simple preparation of methyl cyclobutene in order to gain experience in the technique of handling these volatile, unsaturated, cyclic hydrocarbons. Various reactions could then be tried out first on the more easily obtainable methyl derivative. This research is described on pages 1-32 inclusive.

A detailed description of the experimental procedure follows:

Trimethylene Dibromide.



912 g = 12 mols

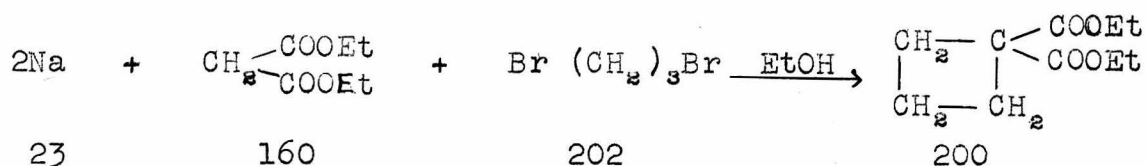
Yield: 2180 g of trimethylene dibromide, B.R. 70-72°/30 mm, equals 90 %.

The procedure outlined in Organic Synthesis<sup>2</sup> was followed rather closely. A typical run consisting of double quantities specified. A twelve liter round bottomed flask, surrounded by an ice bath and fitted with stirrer was used for the reduction of bromine to hydrobromic acid. 2400 g (15 mols) of technical bromine was poured over 2600 g of ice and sulfur dioxide passed in with agitation, at a rate adjusted for complete absorption. Time required, 2 hours. Reduction was considered complete when the deep red solution changed to a straw yellow. The solution of hydrobromic acid was then thoroughly cooled before attempting to add the glycol and sulfuric acid. 912 g (12 mols) of commercial trimethylene glycol and 2400 g (24 mols) of concentrated sulfuric acid were added to the cool solution with agitation. This mixture was refluxed for 5 hours and then distilled until no more dibromide

came over. Distilling time, 3 1/2 hours. The crude dibromide was separated from the water, washed twice with water, once with 400 g of concentrated sulfuric acid, once with one liter of 10% sodium carbonate solution and finally with water, then dried over 50 g calcium chloride. The crude, dry dibromide which weighed 2250 g was then distilled at reduced pressure.

up to 68°/30mm ..... 5 g.  
 68-70°/30mm ..... 45 g.  
 70-72°/30mm ..... 2180 g.  
 72-73°/30mm ..... 20 g.

Ethyl Cyclobutane 1,1-Dicarboxylate.



322 g = 14 mols, 1120g = 7 mols, 1414 g = 7 mols.

Yield: 598 g of crude ester B.R. 77-115°/2mm, equals 42.8% or 550 g redistilled ester, B.R. 103-106°/12mm, equals 39.2% of theory.

Procedure: A twelve liter flask was fitted with a three opening adapter carrying two Friedrich type reflux condensers, the center opening being used to add the sodium metal portionwise. The flask was placed in a bucket to provide for cooling should the reaction get out of hand. Calcium chloride guard tubes were used on the condensers. Six liters of absolute ethanol were placed in the flask and 322 g (14 mols) of sodium added in portions of about 25 g every fifteen minutes, just enough to keep the alcohol refluxing slowly. This solution of sodium ethylate

may be allowed to stand for a day if tightly stoppered. For the condensation between the dibromide and malonic ester another twelve liter flask was used. The flask was fitted with a three opening adapter carrying two reflux condensers, an inlet tube for the alcoholate solution and a mercury sealed stirrer in the middle opening. 1414 g of trimethylene dibromide (7 mols) B.R. 68-73°/30mm, plus 1120 g malonic ester (7 mols) of Eastman product, redistilled, B.R. 95-100°/20mm were mixed together in the flask and heated to 80° on a water bath, and then the sodium ethylate solution was forced in with vigorous stirring over a period of about one hour using dry air pressure to force the solution from one flask to the other through rubber tubing. The mixture was then refluxed and stirred for about half an hour, or until a small sample when diluted with water was neutral to litmus. The excess alcohol was distilled off on a boiling water bath using agitation to prevent bumping. About 5.5 liters of alcohol were recovered and re-used. After removing the alcohol, the mixture was cooled and two liters of cold water were added to dissolve the precipitated sodium bromide formed in the reaction. The oily phase was then removed in a separatory funnel and the aqueous phase extracted once, using about one liter of diethyl ether. This ether extract was combined with the bulk of the ester and the whole was dried over 60 g of anhydrous sodium sulfate. After drying, the ether solution was filtered, the sodium sulfate washed

with a small amount of ether, and the combined ether solutions added from a two liter separatory funnel to a three liter flask fitted with a short distilling head. The ether was distilled off on a steam cone using the aspirator to remove the last traces. An oil bath was then substituted for the steam cone and the oily residue distilled at reduced pressure. The thick, viscous residue, which sets to

up to  $77^{\circ}/4\text{mm}$  ..... 10 g.

$77-115^{\circ}/2\text{mm}$  ..... 598 g.

residue ..... 664 g.

a hard crystalline mass upon cooling, consists principally of ethyl pentane tetracarboxylate. The crude ester boiling at  $77-115^{\circ}/2\text{mm}$  was then refractionated using a 200 x 25mm column packed with helices.

$55-103^{\circ}/12\text{mm}$  ..... 12 g.

$103-106^{\circ}/12\text{mm}$  ..... 550 g.  $N_D^{26}=1.4325$

residue ..... 30 g.

Some of the fraction boiling at  $103-106^{\circ}/12\text{mm}$  was again fractionated for physical properties.

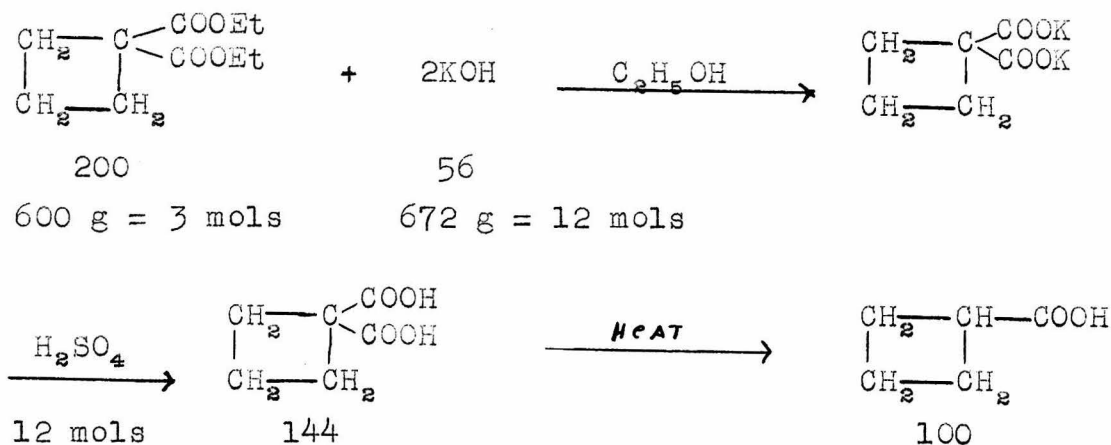
B.P.  $104.5^{\circ}/12\text{mm}$ ,  $N_D^{26}=1.4328$ ,  $N_D^{20}=1.4351$ .

The above procedure was found to be most convenient and to give the highest yields. Using methanol instead of ethanol seemed to result in a mixture of esters since a pure fraction could not be obtained by a simple fractionation. Ring closure using cyanoacetic ester instead of malonic ester gave no better yields and required a more careful fractionation. Using the procedure outlined by

Perkins<sup>3</sup>, yields averaging 32% were obtained as compared to the 39% by the procedure described here.

Cyclobutane 1,1-Dicarboxylic Acid,

Cyclobutane Monocarboxylic Acid.



Yield: 264 g of cyclobutane monocarboxylic acid B.R.

93-96°/15mm equals 88% of theory.

Procedure: The hydrolysis was carried out in a five liter three necked flask fitted with mechanical stirrer, condenser, inlet tube for alcoholic potassium hydroxide solution and surrounded by a water bath. 672 g (12 mols) Merk reagent potassium hydroxide was dissolved in three liters of 95% denatured ethanol and forced with vigorous stirring into 600 g (3 mols) of ethyl cyclobutane 1,1-dicarboxylate B.R. 103-106°/12mm,  $n_D^{26} = 1.4325$ . When about half of the alkali was in, the mixture set to a curdy semi-solid mass that was very difficult to break up. When all the potassium hydroxide solution had been added, the mixture was refluxed with stirring for 1.5 hours. The alcohol was then



taken off on an aspirator, one liter of water added and then evaporated to dryness, leaving a mixture of potassium salt of cyclobutane 1,1-dicarboxylic acid and excess potassium hydroxide. The dry salt mixture was dissolved in 500 cc of water and cooled before neutralizing the excess potassium hydroxide. 600 g of concentrated sulfuric acid was poured into 600 cc of water and the diluted acid was added slowly, with cooling to the salt solution. After the excess potassium hydroxide was neutralized, 600 g of concentrated sulfuric acid was added. This held the solution to a minimum volume. The solution was then filtered on a sintered glass funnel to remove the mixture of potassium sulfate and acid sulfate that had crystallized out. The clear solution was then put on continuous ether extraction for twenty four hours using about 1500 cc of alcohol-free diethyl ether. The mixture of potassium sulfate and acid sulfate was dissolved and extracted with a small amount of ether which was combined with the bulk of the ether in the continuous extractor. The ether solution, without drying, was added slowly to a 500 cc Claissen flask and the ether distilled off leaving a somewhat discolored crystalline mass of crude cyclobutane 1,1-dicarboxylic acid. The oil bath was then raised to about 200° where the mass melted and carbon dioxide was given off. The temperature of the bath was then lowered to 180° where the crude cyclobutane monocarboxylic acid slowly distilled at about 30mm pressure. It was found that if the decarboxylation was attempted at a temperature

higher than 200° much frothing resulted. Weight of crude cyclobutane monocarboxylic acid was 294 g. This crude material was then fractionated using a 200 x 25 mm column packed with helices. Some of the material boiling at

up to 93°/15 mm ..... 20 g.

93-96°/15mm .....264 g.

96-110°/15-10mm .. 5 g.

93-96°/15 mm was refractionated for physical properties.

B.P. 95.5°/15mm,  $N_D^{16} = 1.4450$

$N_D^{20} = 1.4437$

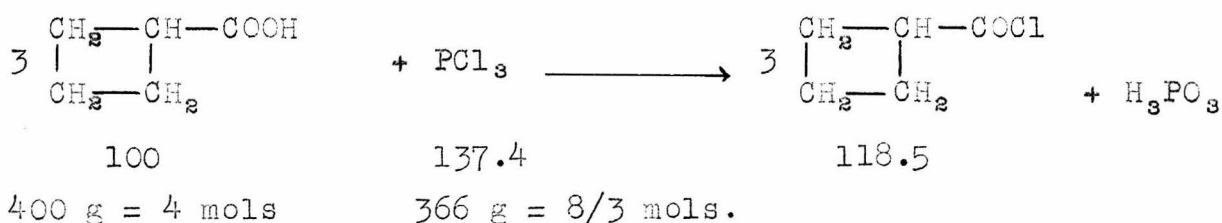
$N_D^{26} = 1.4424$

Pure cyclobutane 1,1-dicarboxylic acid may be prepared by evaporating the ether solution, obtained from the continuous extraction at room temperature using an aspirator. The crystalline mass thus obtained is pressed out on a porous plate to remove small amounts of cyclobutane monocarboxylic acid and perhaps some unsaponified ester, redissolved in ether and allowed to crystallize slowly by permitting the ether to slowly evaporate. In one instance recrystallization was repeated five times and resulted in crystals having a neutralization equivalent of 71.9. Theory for  $C_6H_8O_4$  equals 72.0.

The procedures outlined above were found to be most convenient of those tried. Potassium rather than sodium hydroxyde was used because of its greater solubility in

ethanol. Methanol may be substituted for ethanol with no bad effects, however, if water is used as solvent, a much longer period of refluxing is required for complete saponification. Aqueous 50% HCl was tried and gave fair yields in some cases but in one experiment, after having refluxed for fifteen hours, a very high boiling viscous yellow residue containing chlorine resulted and the yield of cyclobutane monocarboxylic acid was proportionally lower. B.P. of the chlorine containing residue was  $150^{\circ}/5\text{mm}$ .

Cyclobutane Monocarboxylic Acid Chloride.



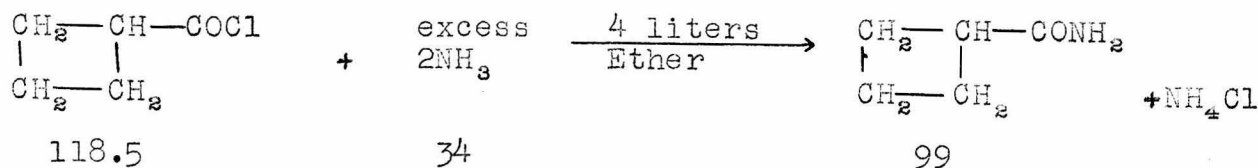
Yield: 427 g of cyclobutane monocarboxylic acid chloride B.R.  $60-65^{\circ}/60\text{mm}$ . By re-using the recovered phosphorus trichloride approximately 17 g of acid chloride is recovered making a total of 444 g equals 93.5% of theory.

Procedure: Ground glass equipment used throughout. 400 g of cyclobutane monocarboxylic acid (4 mols) B.R.  $93-96^{\circ}/15\text{mm}$  was placed in a one liter flask which was fitted with a reflux condenser and guard tube. 366 g of phosphorus trichloride (2.66 mols) B.R.  $73.5-75.5^{\circ}/750\text{mm}$ , freshly distilled, was added and the mixture heated on an oil bath at  $100-110^{\circ}$  for one hour. The temperature and length of heating are both critical. Above  $110^{\circ}$ , decomposition is

extensive, resulting in 30% yield of the acid chloride if reaction takes place at 130-140°. The reaction product was then cooled and the mixture of excess phosphorus trichloride and acid chloride was carefully decanted from the syrupy phosphorus acid into a one liter distilling flask. The syrupy residue amounting to about 125 g was washed with some phosphorus trichloride which was then combined with the bulk of the material. The distilling flask was connected to a 200 x 25mm fractionating column packed with helices, and the material fractionated using the aspirator. A dry ice trap was used in the vapor line to the aspirator. During the distillation the temperature was not allowed to rise above 110°.

35-60°/60mm .....	176 g.
60-65°/60mm .....	427 g.
trap .....	75 g.

trichloride was reused and yielded approximately 17 g more of the acid chloride making a total of 444 g, B.R. 60-65°/60mm. Using this procedure a total of 10.95 mols of cyclobutane monocarboxylic acid was converted to 10.23 mols cyclobutane monocarboxylic acid chloride. Acid chloride boiling at 60-65°/60mm was refractionated and the bulk of it came over at 65°/60mm or 62.5°/50mm. A sample of this refractionated material was given to Werner Schomaker for electron diffraction study.

Cyclobutane Monocarboxylic Acid Amide.

355.5 g = 3 mols

Yield: 279 g of cyclobutane monocarboxylic acid amide, M.P. 155.9° corrected, equals 94% of theory.

Procedure: Note- All apparatus was thoroughly dried and precautions taken against moisture entering the apparatus during the reaction. Apparatus used consisted of a dry five liter three necked flask fitted with a mercury seal stirrer, ammonia gas inlet tube, dropping funnel and gas exit tube and surrounded by an ice bath. Four liters of diethyl ether, previously dried for 48 hours over sodium wire was decanted from the sodium into the five liter flask and saturated with dry ammonia gas at 0°. About half an hour being required. 355.5 g of cyclobutane monocarboxylic acid chloride (3 mols) B.R. 60-65°/60mm was added over a period of half an hour in 50 g portions. If allowed to trickly in, the inlet tube clogged. The mixture was stirred and ammonia gas passed in for two hours after all the acid chloride was in. Completeness of reaction was tested by diluting a small amount of the mixture with water and testing with litmus. After ammonia was in excess, the stirrer was removed and a large bore capillary substituted. The capillary tube carried a calcium chloride guard tube. The ether was taken off on a steam cone using the

aspirator. The amide showed a tendency to sublime after all the ether had been removed. The dry mixture of amide and ammonium chloride weighed 465 g indicating that the acid chloride contained about 2.5% impurity calculated as phosphorus trichloride. The mixture of amide and ammonium chloride was scraped from the flask and placed in Soxhlet extractors and extracted continuously for 20 hours with chloroform. The second and third crops of crystals can be recrystallized if necessary and will yield about 120 g of cyclobutane monocarboxylic acid amide, M.P. 155.5° corrected.

First crop of crystals .... 160 g, M.P. 155.9° corr.

Second crop of crystals .... 100 g, M.P. 155.0° corr.

Third crop of crystals .... 25 g, M.P. 144-146° corr.

By this procedure a total of 11.21 mols of cyclobutane monocarboxylic acid chloride was converted to 10.25 mols of cyclobutane monocarboxylic acid amide, M.P. 155.5° corrected, equals 94% of theory.

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