

**THE CONSTITUENTS OF DIAMYLENE**

**by**

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## INTRODUCTION

Diamylene is a by-product formed in the chlorination of the pentane fraction of petroleum. Other by-products formed in this process are trimethylethylene, diamyl ether and some dichloropentanes<sup>1,2</sup>. The diamylene is formed by polymerization of the amylenes. The structure of the decene, or decenes, thus formed had not been established.

The literature relating to studies on olefins of this type has been summarized by Cooke<sup>3</sup> and the more recent contributions have been reviewed by Wheeler<sup>4</sup>.

Schindelmeiser<sup>5</sup> oxidised a dimer obtained by the polymerization of trimethylethylene. Several products were isolated, but acetic and succinic acids are the only compounds that were recognized. Even these were not characterized by the formation of suitable derivatives. Apparently disregarding the products of oxidation, Schindelmeiser ascribes the structure  $C_2H_5C(CH_3)_2C(CH_3):C(CH_3)_2$  to the dimer, based on its formation from trimethylethylene.

Norris and Joubert<sup>6</sup> attributed this same structure to a dimer obtained by the action of sulfuric acid on trimethylethylene. The published evidence favoring this structure is no more conclusive than that obtained by Schindelmeiser. The dimer was

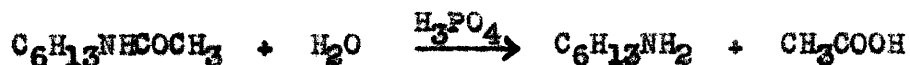
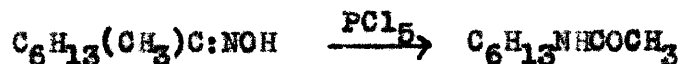
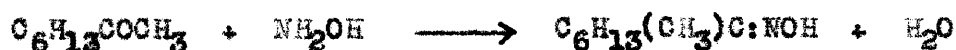
subjected to the action of ozonized air. The products resulting from the decomposition of the ozonide were formic and acetic acids, a substance that smelled like acetone and gave the nitroprusside color test, the silver salt of an acid  $C_5H_{11}COOH$ , believed to be dimethylethylacetic acid, and three equal fractions boiling  $130-150^\circ$ ,  $150-160^\circ$  and  $160$  to over  $200^\circ$ . These were believed to contain the methyl ketene corresponding to dimethylethylacetic acid, but the ketene was not isolated in the pure state and was not characterized by derivatives.

In the last two years, Whitmore and his students have investigated the structure of a number of olefins resulting from the dehydration of alcohols. The first of these studies<sup>7,8,9,10</sup> was a confirmation of the structure of the isomers of diisobutylene as 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, as reported by Butlerow<sup>11</sup> and McCubbin and Adkins<sup>12</sup>, and a study of the properties of these pure olefins. The dehydration of isopropyl-tert.-butylcarbinol<sup>13</sup> by sulfuric acid gave the same products as was obtained by heating the corresponding Grignard complex. The products include 2,4,4-trimethylpentene-1, and higher boiling olefins not yet identified. Dehydration of methylethyl-tert.-butylcarbinol<sup>14</sup> by heating with a trace of iodine gave mainly 2,2,3-trimethylpentene-3, and about 20% of a rearrangement product 2,3,3-trimethylpentene-1. Dimethyl-tert.-amylcarbinol<sup>14</sup> was similarly dehydrated to 2,3,3-trimethylpentene-1 and a small amount of a by-product not

yet identified. 2,3,4-trimethylpentanol-3, similarly dehydrated, yielded a mixture of 3-methyl-2-isopropylbutene-1 and 2,3,4-trimethylpentene-2 in the ratio of 1:2. Alcohols of the type  $R(CH_3)(iso-C_3H_7)COH$  were found to give mixtures of two olefins in each of the four cases studied<sup>15</sup>. Dehydration of pinacolyl alcohol by (1) oxalic acid (2) heating the  $-OMgBr$  derivative of the alcohol and (3) by heating with iodine in a sealed tube gave varying amounts of tetramethylethylene and unsymmetrical methylisopropylethylene<sup>16</sup>. Dehydration of pinacolyl alcohol with phosphoric acid on silica gel gave these rearrangement products, and the normal dehydration product, as well<sup>17</sup>. Substituted pinacolyl alcohols behaved similarly, except that no 2-methyl-3-butylheptene-3 was obtained from 3-methyl-3-butylheptanol-2<sup>18</sup>. Octanol-1 and octanol-2 both gave mixtures of octene-1 and octene-2<sup>19</sup>, on dehydration. Dehydration of several tertiary neopentyl alcohols<sup>20</sup> resulted in a normal dehydration, with little or no tendency toward the formation of rearrangement products. Dehydration of twenty-two aliphatic tertiary alcohols containing normal alkyl groups ranging in size from methyl to amyl<sup>21</sup> yielded only the normal dehydration products, and no products resulting from rearrangement. Dehydration of di-tert.-butylcarbinol<sup>22</sup> was found to give a 77% yield of trimethylethylene, due to rearrangements. The statement is made that part of the trimethylethylene is polymerized, but the nature of the polymer was not reported.

The decenes formed by the action of sulfuric acid on methylisopropylcarbinol have been under investigation in this laboratory for several years<sup>3,4</sup>. This polymerization is believed to proceed through the intermediate formation of trimethylethylene. The probable relationship of diamylene to the decenes formed from methylisopropylcarbinol led to the present investigation.

Two constituents of diamylene were separated by fractional distillation. The fractions thus obtained were subjected to the action of ozonized oxygen. The products of ozonolysis were acetaldehyde, identified by the formation of its p-nitrophenylhydrazone, and two ketones, namely 3,3-dimethylhexanone-5 and 2,2,3-trimethylpentanone-4. The structure of the former ketone was established by Kline<sup>27</sup>. That of the latter by the following transformations:

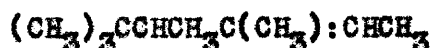


The amine  $\text{C}_6\text{H}_{13}\text{NH}_2$  was identified as 3-amino-2,2-dimethylbutane, by synthesis of the latter from pinacolone, and mixed melting point determinations of several derivatives.

This establishes the structure of the decenes as



and





### EXPERIMENTAL

It was proposed to subject the constituents of diamylene to the action of ozonized oxygen, and to characterize the fragments resulting from the decomposition of the resulting ozonide. Previous workers in this laboratory<sup>3,4</sup> had found it extremely difficult to separate the ketones resulting from the ozonization of a mixture of isomeric decenes. Hence it was deemed advisable to first separate the diamylene into the individual isomers present, as far as this was practicable by fractional distillation.

The diamylene used was obtained through the courtesy of the Sharples Solvent Corporation. The commercial product was refluxed over sodium for 12 hours, and was then distilled from the sodium. Two liters of this material was fractionated at the Bureau of Standards, through the courtesy of the late Dr. E. W. Washburn and Sylvester T. Schicktanz. The still used is of the total condensation type, and has been described by Schicktanz<sup>23</sup>. The results of this fractionation are given in the following table:

DISTILLATION A

Barometric Pressure = 215 mm.

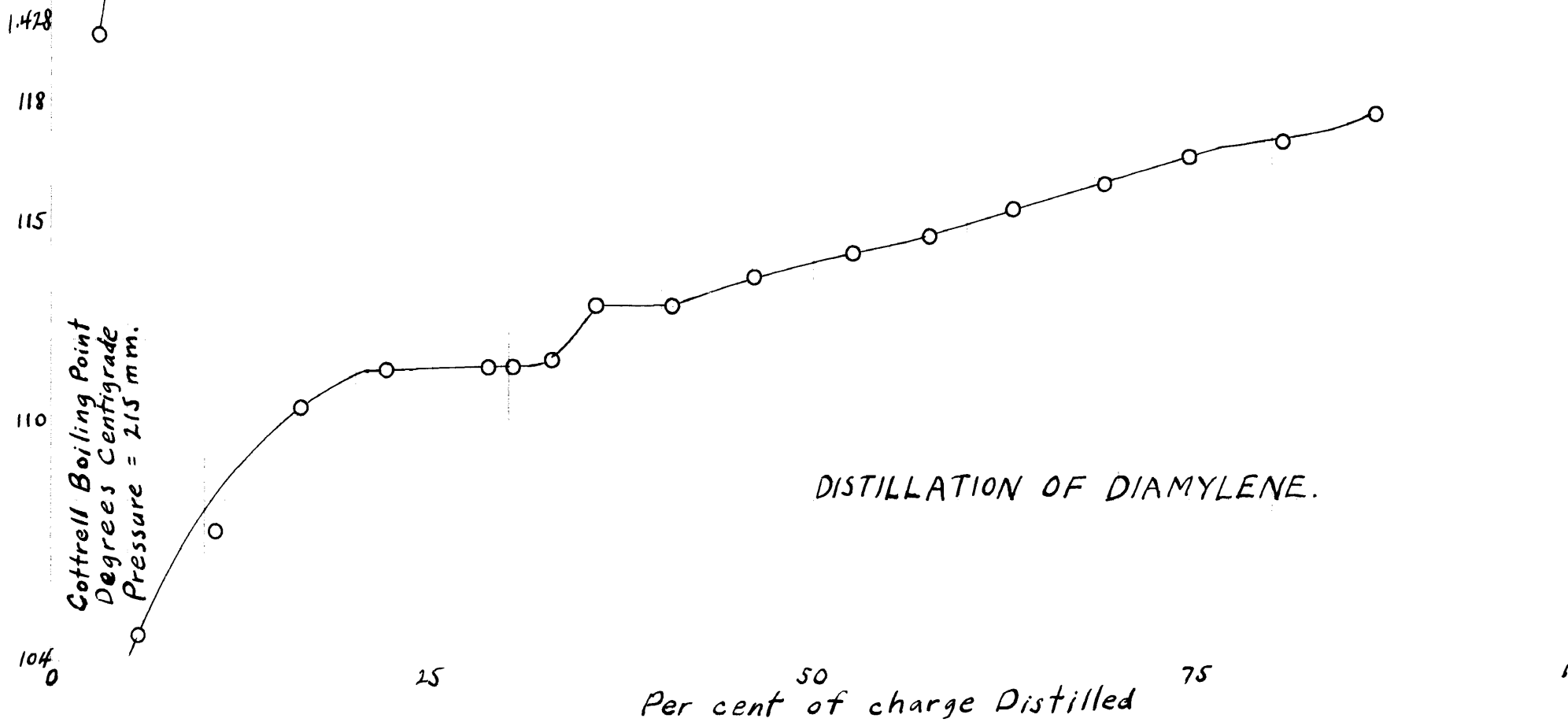
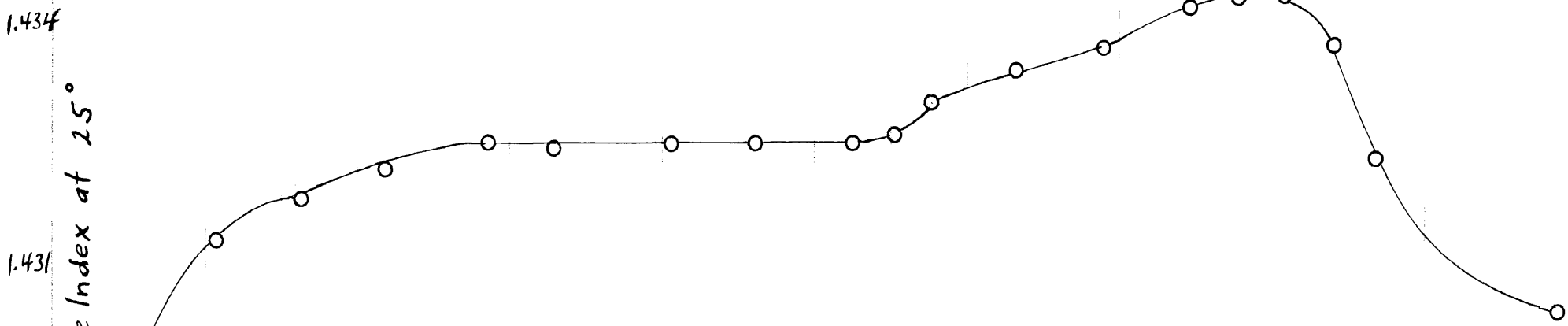
Fraction No.	Total Volume Distilled	Boiling Point <sup>a</sup>	n <sub>25°</sub>
1	54	100 °	1.4262
2	106	104.6	1.4278
3	163	104.9	1.4311
4	216	107.2	1.4313
5	269	106.7	1.4312
6	328	110.2	1.4318
7	385	110.5	1.4318
8	441	111.2	1.4322
9	500	111.3	1.4325
10	554	111.3	1.4325
11	607	111.3	1.4325
12	657	111.5	1.4324
13	707	112.8	1.4325
14	758	112.8	1.4325
15	812	112.8	1.4325
16	868	113.0	1.4325
17	922	113.5	1.4325
18	987	113.6	1.4325
19	1049	114.1	1.4325
20	1107	114.3	1.4326
21	1157	114.5	1.4330
22	1215	114.7	1.4333
23	1267	115.2	1.4334
24	1325	115.4	1.4337
25	1383	115.8	1.4337
26	1440	116.2	1.4341
27	1496	116.5	1.4342
28	1555	116.7	1.4343
29	1613	116.9	1.4343
30	1679	117.1	1.4337
31	1738	117.1	1.4322
Residue	1973		1.4304

a. The boiling point of the fractions was determined by a Cottrell boiling point apparatus built into the still and functioning under the same pressure at which the distillate was collected.

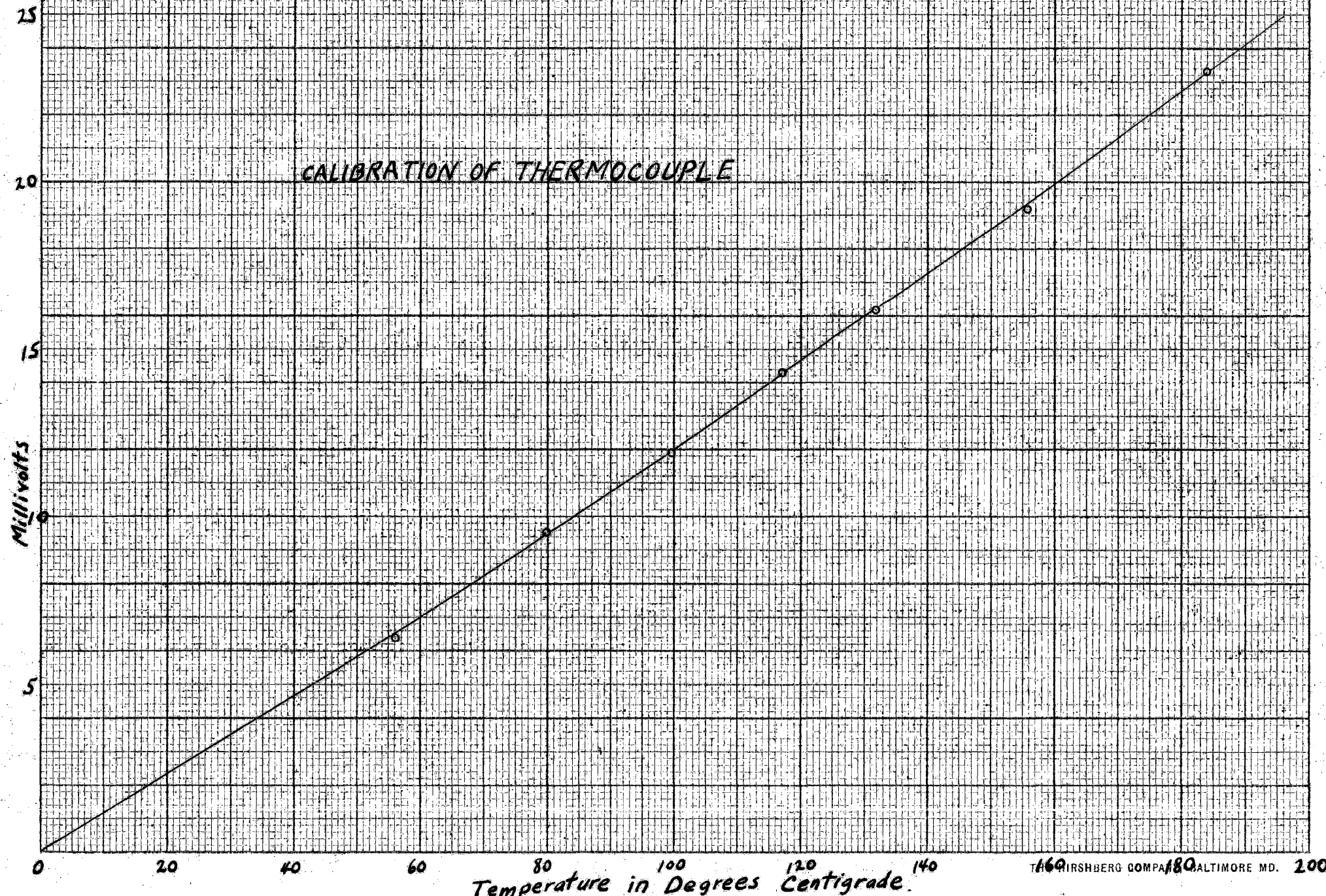
Graphical representation of these results, plotting boiling temperature and refractive index against per cent of the charge placed in the still pot is more informative. It will be observed (page 8) that fractions 9-19 have a constant refractive index, whereas the boiling point curve indicates two plateaus over this same part of the curve.

Fractions 1-5, 8-11, 13-15, 19-22, 28-30 and the residue were refractionated separately, using a still similar to that described by Podbielniak<sup>24</sup>. The still was constructed by the author, in this laboratory, with the exception of the quartz-pyrex vacuum jacket, the partial condenser and the receiver change block. An attempt was made to determine the boiling temperature of the distillate by means of a triple junction copper-advance thermocouple placed in a reentrant thermocouple well at the top of the column. The E. M. F. was determined by means of a Leeds and Northrup portable potentiometer.

The thermocouple was calibrated by distilling the following substances through the column, and observing the potentiometer reading. In each case, the distillation of the liquid was continued until no change in E. M. F. was observed, during the distillation of 10-15 cc. of the liquid.



CALIBRATION OF THERMOCOUPLE



CALIBRATION OF THERMOCOUPLE

Substance Distilled	E. M. F. (millivolts)	Accepted Boiling Point	Atmospheric Pressure mm.	B. F. Change for Pressure Changes <sup>a</sup>	Corrected Boiling Point
Acetone	6.39	56.20 <sup>b</sup>	756	0.12°	56.1°
Benzene	9.44	80.2 <sup>b, d</sup>	756	0.17	80.0
Water	11.88	100.0	762	0.09	99.9
n-Butyl Alcohol	14.26	117.7 <sup>c</sup>	786	0.19	117.5
Chlorobenzene	16.15	132.1 <sup>c</sup>	755	0.24	131.9
Bromobenzene	19.20	156.2 <sup>b, c</sup>	756	0.20	156.0
Aniline	23.28	184.4 <sup>c</sup>	755	0.27	184.1

a. Boiling points at 760 mm. pressure were corrected to the observed pressure during the distillation by means of the empirical relation  $e = .00012(760 - p)(273 + t)^{2.5}$

e = correction

p = observed pressure

t = boiling temperature

b. Young "Fractional Distillation".

c. International Critical Tables.

d. Tables Annuelles Internationelles de constantes et données numériques; 1925-6.

The accompanying graph (page 9) was prepared in order to make this data more readily available.

The efficiency of the still was tested by the distillation of a mixture containing 50 mol per cent each of benzene and symmetrical dichloroethane<sup>25</sup>. The distillation rate was 0.1 cc. per minute, the reflux ratio 30:1. The column used in this distillation had an internal diameter of 3.8 mm. and was packed with a single spiral of No. 26 monel metal wire. Other columns used in subsequent distillations had a diameter of 5.0-8.0 mm. and had a single coil of No. 20 monel metal wire, for packing.

TEST DISTILLATION OF PODBIELNIAK TYPE STILL

Charge = 75 cc. equimolar mixture of  $C_6H_6$  and  $CH_2ClCH_2Cl$

Fraction No.	cc. Distilled	Thermocouple Reading (MV)	$n_{25^\circ}$	Mol % $C_6H_6$
1	5	9.51	1.4839	76.5
2	10	9.53	1.4835	76.0
3	15	9.61	1.4829	75.0
4	20	9.51	1.4811	72.0
5	25	9.53	1.4798	70.0
6	30	9.58	1.4786	67.0
7	35	9.59	1.4764	63.5
8	40	9.61	1.4748	61.0
9	46	9.63	1.4729	57.0
10	50	9.63	1.4681	49.0
11	55	9.64	1.4670	47.0
12	60	9.73	1.4593	33.0
13	65	9.78	1.4501	15.5
14	70	9.40	1.4440	4.0
15	73.5	9.75	1.4422	1.0
16	Residue Ca 1.5 cc.-----		1.4414	0.0

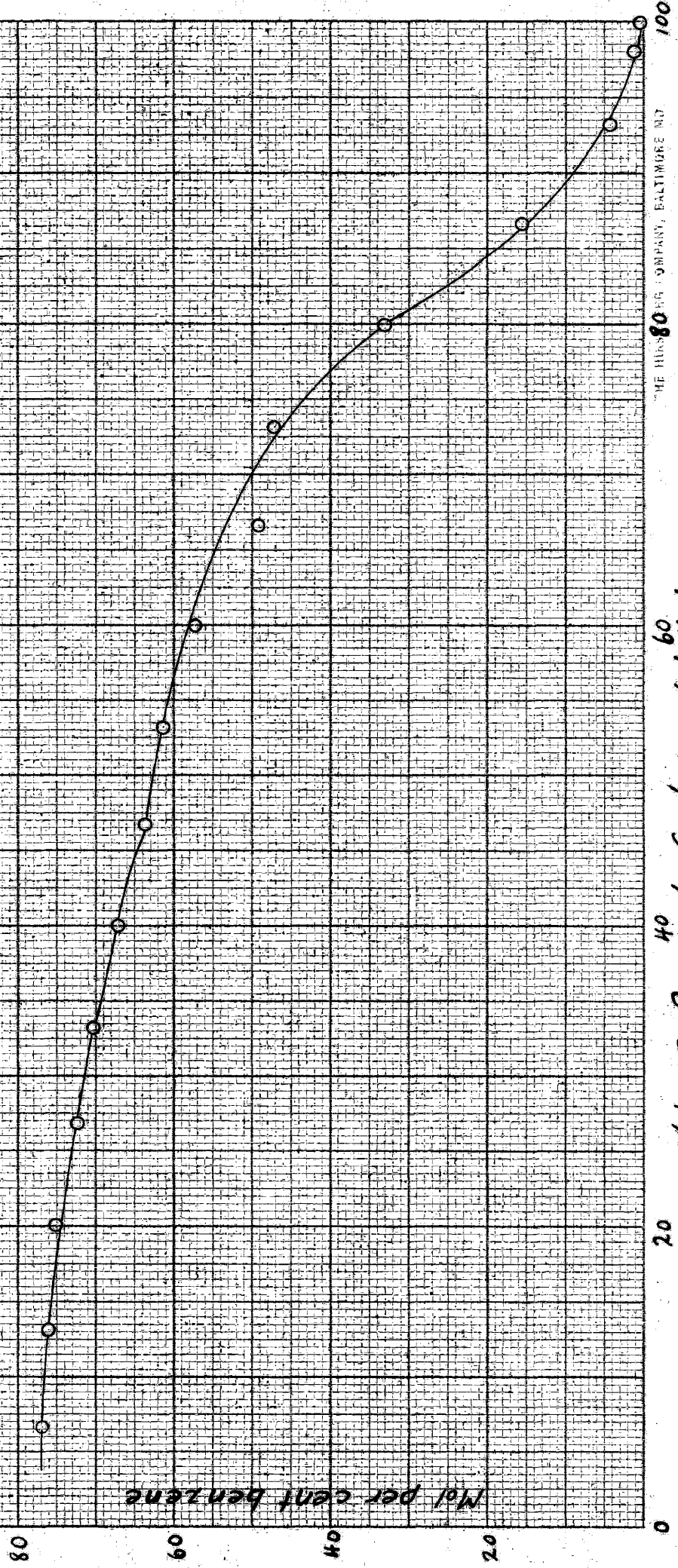
This data shows that a single distillation through the still, at a rate of 0.1 cc. per minute gives a distillate containing more than 70 mol per cent benzene, for about 20 mol per cent of the charge. The difference in the boiling points of the two substances is about  $3.5^\circ$ . This distillation also shows that for distillation rates of 0.1 cc. per minute, the thermocouple reading is not a reliable indication of the boiling temperature of the distillate.

A 125 cc. round bottom flask fastened to the column with a cork stopper, cemented with Le Page's glue, served as a still pot in the above test distillation. In the subsequent distillations, the still pot consisted of a Pyrex tube having a length approximately four times the diameter. This type of flask presented a smaller surface for evaporation, and tended to promote more regular distillation.

This distilling tube was sealed to the column by means of a side tube at the top of the distilling tube. A filling tube was provided at the top of the distilling tube. The filling tube was sealed, after introduction of the sample.



TEST DISTILLATION OF PODBIELNIAK TYPE STILL



THE HUBBARD COMPANY, BALTIMORE, MD

Volume Per cent of charge distilled

Mol per cent benzene

Redistillation of the fractions of distillation A required more than two hundred hours of actual distillation. Frequently, more than forty hours were required for the distillation of a single charge. Dr. Nathan L. Drake, Mr. Jos. R. Spies and Mr. Sterl A. Shrader were kind enough to assist with several distillations, to obviate the necessity of interrupting the distillation of an individual charge. Their assistance is gratefully acknowledged.

The data on the redistillation of the fractions of distillation A is best given in tabular form.

DISTILLATION B

Distillation of Fractions A-1, 2, 3, 4 and 5

Pressure = 200 mm.

Rate = 0.1 cc. per minute

<u>Fraction No.</u>	<u>cc. Distilled</u>	<u>Cottrell Boiling Point Pressure = 672 mm.</u>	<u><math>n_{25}^{\circ}</math></u>
1	20.2	121.1 <sup>o</sup>	1.4156
2	40.3	143.8	1.4246
3	61.1	149.4	1.4274
4	81.5	151.0	1.4288
5	101.5	151.9	1.4295
6	122.7	152.3	1.4304
7	145.8	153.2	1.4309
8	165.8	153.4	1.4314
9	185.8	153.6	1.4314
10	206.2	153.9	1.4314
11	226.6	154.4	1.4319
12	257.0	155.3	1.4325
Residue	ca.263.0	-----	1.4353

DISTILLATION C

Distillation of Fractions A-8, 9, 10 and 11

Pressure = 767-758 mm.

Rate = 0.1 cc. per minute

<u>Fraction No.</u>	<u>cc. Distilled</u>	<u>Cottrell Boiling Point Pressure = 763 mm.</u>	<u>n<sub>25°</sub></u>
1	20.0	153.8	1.4321
2	40.1	154.0	1.4323
3	60.1	154.2	1.4324
4	80.1	154.2	1.4324
5	100.4	154.2	1.4324
6	120.4	154.3	1.4324
7	140.4	154.4	1.4325
8	160.4	154.6	1.4325
9	180.4	154.6	1.4325
10	192.9	154.7	1.4328
Residue	ca.228.0	155.8	1.4329

DISTILLATION D

Distillation of Fractions A-13, 14 and 15

Pressure = 200 mm.

Rate = 0.1 cc. per minute

<u>Fraction No.</u>	<u>cc. Distilled</u>	<u>Cottrell Boiling Point Pressure = 765 mm.</u>	<u>n<sub>25°</sub></u>
1	8.0	-----	1.4324
2	28.0	155.9	1.4325
3	48.0	155.9	1.4325
4	68.8	156.0	1.4326
5	88.8	156.0	1.4326
6	109.0	156.0	1.4326
7	129.0	156.4	1.4326
8	140.3	157.3	1.4326
Residue	ca.148.0	-----	1.4334

DISTILLATION E

Distillation of Fractions A-19, 20, 21 and 22

Pressure = 200 mm.

Rate = 0.1 cc. per minute

<u>Fraction No.</u>	<u>cc. Distilled</u>	<u>Cottrell Boiling Point Pressure = 757 mm.</u>	<u>n<sub>D</sub><sup>25°</sup></u>
1	20.2	156.9	1.4324
2	40.2	157.1	1.4325
3	60.3	157.4	1.4327
4	80.9	157.4	1.4328
5	101.2	157.4	1.4328
6	121.5	157.6	1.4328
7	141.5	157.6	1.4328
8	161.9	158.1	1.4328
9	184.0	158.4	1.4329
10	204.1	158.8	1.4329
11	216.9	158.8	1.4334
Residue	ca.222	-----	1.4368

DISTILLATION F

Distillation of Fractions A-28, 29 and 30

Pressure = 200 mm.

Rate = 0.1 cc. per minute

<u>Fraction No.</u>	<u>cc. Distilled</u>	<u>Cottrell Boiling Point Pressure = 765 mm.</u>	<u>n<sub>D</sub><sup>25°</sup></u>
1	23.6	160.6	1.4344
2	44.1	160.6	1.4344
3	64.2	160.6	1.4344
4	85.0	160.6	1.4344
5	105.3	160.8	1.4345
6	125.3	160.8	1.4345
7	145.3	161.0	1.4345
8	165.8	162.0	1.4335
9	173.6	-----	1.4322
Residue	179	-----	1.4297

DISTILLATION G

Distillation of Fractions A-Residue

Pressure = 197 mm.

Rate = 0.1 cc. per minute

<u>Fraction No.</u>	<u>cc. Distilled</u>	<u>Cottrell Boiling Point Pressure = 771 mm.</u>	<u><math>n_{25}^{\circ}</math></u>
1	20.4	163.3	1.4282
2	40.4	163.5	1.4274
3	60.6	163.8	1.4265
4	80.7	164.6	1.4256
5	111.0	165.3	1.4251
6	131.1	166.2	1.4248
7	151.7	167.8	1.4268
8	171.7	168.0	1.4304
9	191.7	170.6	1.4362
10	202.2	172.4	1.4384
11	218.9	177.3	1.4357
Residue	ca.229	-----	1.4456

At least two isomers are indicated by these distillations, but the data on the intermediate fractionations, distillations D and E, is not conclusive. It was determined to investigate the possibility of the existence of additional isomers in the intermediate fractions by ozonolysis of representative fractions.

The ozonizer used was the same as that used by Cooke<sup>3</sup> and Wheeler<sup>4</sup>. During the course of the ozonolysis experiments, it became necessary to clean the Berthollet tubes. When these tubes were replaced in the containing jar, they were held in place by a glass rod, to which they were fastened with a cord, instead of being held in place by a wooden holder. The Berthollet tubes were then sealed to each other, instead of being connected by mercury-sealed cups. This resulted in a 10-15 per cent increase in the yield of

osone. The ozonizer generated ozone at a rate of .0432 - 0.497 mole per hour, when oxygen was supplied at a rate of 16.3 liters per hour (6.0-6.8 per cent ozone).

The decene was ozonized in solutions of ethyl acetate of petroleum ether, (boiling range 30-40°), the concentration being 1 mol of decene per liter of solution. For the ozonolysis of a small sample of the decene (10-20 cc.), the solution was placed in a pyrex tube 2 cm. in diameter and 35-40 cm. in length. The ozonized oxygen was admitted through an inlet tube sealed in at the bottom of this tube. Larger samples (50-100 cc.) of decene were ozonized in a specially constructed flask of 500 cc. capacity, having a bubbler tube sealed to the top of the flask. In each case, the container was connected to the ozonizer by means of a mercury-sealed cup, and was immersed in a mixture of chloroform and carbon tetrachloride, maintained at -15 to -25° by means of solid carbon dioxide.

Ozone was determined by bubbling the ozonized oxygen through a 5% solution of potassium iodide, acidifying with hydrochloric acid, and titrating the iodine liberated with standard sodium thiosulfate solution. The ozonized oxygen was bubbled through the decene solution for the time theoretically required, based on the ozone determination just described.

The ozonide was decomposed by two methods. The catalytic method recently described by F. G. Fisher<sup>26</sup> was the first to be tried. The ozonide was readily reduced by this method, when ethyl acetate was used as solvent. However, very little reduction was effected by

this method, when petroleum ether was used, because the water formed in the reduction was insoluble in the petroleum ether, and caused the catalyst to form small moist balls that remained in the bottom of the flask, and possessed no catalytic activity. The zinc, water-catalyst method described by Whitmore and Church<sup>9</sup> was found to give slightly better yields of ketone, less high boiling residue, and could be used equally well with petroleum ether or ethyl acetate as solvent. In one experiment, part of the ozonide decomposed violently, blowing the stopper out of the flask, during the removal of the solvent. Subsequently, the ozonide was reduced without the removal of the solvent. This method gave equally good results and apparently obviated the danger of an explosion.

More than 950 cc. of material was ozonized. Only three products of ozonization were found, i.e., an aldehyde, yielding a p-nitrophenylhydrazone that melted at 125.5-126.0°, and two ketones, giving semicarbazones melting at 148.5° and 168.6-168.8°. Each ozonization also yielded a high boiling fraction. Very careful fractionation failed to indicate any homogeneous product in this fraction. The results of the ozonizations may be summarized in tabular form.

<u>Reference No.</u>	<u>Material Ozonized Fraction No.</u>	<u>Vol. cc.</u>	<u>Method Used for Reduction of Ozonide</u>	<u>Amount of Ketone Obtained (cc.)</u>
1	A-6,7	110	catalytic	32.5
2	A-12,16	106	catalytic	21.6
3	B-11 <sup>a</sup>	10	catalytic	2.0
4	B-6,7,8,9,10,11 <sup>a</sup>	106	zinc-water <sup>b</sup>	35.5
5	C-1,2,3 <sup>a</sup> , Residue, D-1,7,8	108	zinc-water <sup>c</sup>	
6	C-3 <sup>a</sup> ,4,5,6,7,8 <sup>a</sup>	96	catalytic	31.5
7	D-2,3,4,5,6	94	catalytic	30.0
8	E-2,3,4,6 <sup>a</sup>	58	catalytic	19.0
9	F-1,2,3,4,5,6 <sup>a</sup>	109	catalytic	45.0
10	F-6 <sup>a</sup>	10	catalytic	3.5
11	Unfractionated decene	100	zinc-water	41.0
12	Unfractionated decene	100	zinc-water	42.0

- a. Only part of this fraction was used.
- b. Ozonized in petroleum ether. Attempted catalytic reduction was not successful.
- c. Part of the ozonide was lost by violent decomposition, after removal of the solvent.
- d. Ketone fractions of the two experiments were united before distillation.

The ketone fraction obtained from ozonizations nos. 1-7 gave only one semicarbasone, melting at 148.5°. The main fraction boiled at 147.2°, in the Cottrell boiling point apparatus, under a barometric pressure of 766 mm. The refractive index at 25° was found to be 1.4136, and the density at 20° was 0.8263. Ozonizations 9 and 10 gave a ketone boiling at 154°. The semicarbasone of this ketone melted at 168.6-168.8°. The ketone had a refractive index of 1.4183. These same two ketones were obtained by Wheeler<sup>4</sup> and Kline<sup>27</sup> from the dimer resulting from the action of sulfuric acid on methyl-isopropylcarbinol. The identity of these ketones with those obtained by Kline was established by mixed melting point determinations on the semicarbasones. The higher boiling ketone from these ozonolysis experiments was given to Mr. Gordon M. Kline, in connection with his work<sup>27</sup> on the structure of this substance.



Ozonization 8 gave a mixture of these two ketones. Ozonizations 11 and 12 were carried out in an endeavor to determine the relative amounts of the two ketones obtained from the unfractionated decene, since this could not be readily obtained from the decene fractionation, especially since the refractive index of the original decene mixture is lower than that of either of the pure constituents. Distillation of the ketone fractions of ozonizations 11 and 12 indicated that approximately equal quantities of each ketone were obtained.

Ozonization (11 and 12) of the original decene mixture was also designed to see whether or not products of ozonolysis could be obtained other than those obtained from the various decene fractions ozonized. No products were obtained, other than the three described above. Tests for formaldehyde<sup>28</sup> and acetone<sup>29</sup> on the distillate from the reduction of the ozonide formed in petroleum ether solution showed the absence of even traces of these substances. The same tests on the distillate from the reduction of the ozonolysis of the unfractionated decene in ethyl acetate solution gave very weak positive tests for the presence of both formaldehyde and acetone.

THE PRODUCTS OF OZONOLYSIS

The aldehyde giving a p-nitrophenylhydrazone melting at 125.5-126.0° was shown to be acetaldehyde by a mixed melting point determination with the p-nitrophenylhydrazone of acetaldehyde obtained from the Eastman Kodak Company.

The higher boiling ketone was shown to be  $C_2H_5C(CH_3)_2CH_2COCH_3$  by Kline<sup>27</sup>.

The lower boiling ketone was obtained by Wheeler<sup>4</sup> and was characterized by the formation of a semicarbazone. Analysis of this semicarbazone showed the ketone to have the formula  $C_8H_{16}O$ .

Part of the ketone used in the determination of structure to be described below was obtained by Mr. Gordon M. Kline, of this laboratory, in his investigation of the decenes obtained from methylisopropylcarbinol.

The ketone had a density of 0.8262 at 20° and a refractive index of 1.4136 at 25°. The ketone was characterized by the formation of a 2,4-dinitrophenylhydrazone that melts at 109.5°, prepared according to the directions of Allen<sup>30</sup>. The p-nitrophenylhydrazone, prepared from p-nitrophenylhydrazine in the same way, melted at 73,0°.

The action of alkaline hypiodite on the ketone indicated it to be a methyl ketone, although the formation of iodoform was very slow indeed. The ketone was accordingly oxidized with alkaline hypobromite, in accordance with the directions for the oxidation of pinacolone to trimethyl acetic acid<sup>30</sup>. Ninety-nine grams of

sodium hydroxide was dissolved in 840 cc. of water, and the solution cooled to 0°. Forty-six cc. bromine was added to the stirred, cooled solution at such rate that the temperature did not rise above 10°. This addition required about half an hour. The cold solution was stirred an additional hour, but the solution was not decolorized. The cooling mixture was removed, and stirring was continued for 6 hours at room temperature. After standing over night, the solution was still not decolorized. The solution was only decolorized after heating and stirring for half an hour. Neutral products of the reaction mixture were removed by steam distillation, the reaction mixture was made acid, and the resulting acid obtained by steam distillation, and ether extraction of the distillate. 12.5 g. of acid, boiling 103-104° at 20 mm., was obtained. This is equivalent to 35% of the amount theoretically possible.

The non-acidic products of the reaction included a large amount of carbon tetrabromide. Since the amount of bromine used corresponded to that theoretically required for the formation of bromoform, it was believed that the yield could be improved by increasing the amount of bromine used. In a subsequent preparation of this same acid, 80 g. of sodium hydroxide and 40 cc. of bromine were used for the oxidation of 28.7 g. of the ketone. This corresponds to 12% more bromine than that theoretically required. There was apparently a large excess of bromine in this oxidation, however, since bromine was liberated, on acidification of the reaction mixture, after removal of the non-acidic reaction products. The yield of

acid from this run was 5.5 g. that boiled at 76° at 5 mm. This is 19% of the amount theoretically obtainable.

The acid melts at 24.5°, and has a refractive index of 1.4182 at 25°. It yields an amide that melts at 106.0°, an anilide that melts at 104.5° and a p-phenylphenacyl ester that melts at 68.5°. The p-nitrobenzyl ester was an oil. Analysis of the acid, and the three solid derivatives showed it to have the composition  $C_6H_{13}COOH$ .

No acid possessing these properties has been described in the literature. An attempt was made to oxidize this acid to the next lower acid in the series, through esterification of the acid, the action of phenylmagnesiumbromide on the ester, and oxidation of the resulting tertiary carbinol.

Nine grams of this acid was refluxed for three hours with 30 cc. methyl iodide and 20 g. of silver oxide. The reaction mixture was filtered, and excess methyl iodide recovered from the filtrate. The silver oxide-silver iodide mixture on the filter was then washed with methyl alcohol, and the washings added to the filtrate, from which the excess methyl iodide had been removed. Distillation of this solution gave 6 g. of the ester boiling at 46° at 18 mm. pressure.

This ester was added, drop by drop to the Grignard reagent prepared from 2.4 g. magnesium in 50 cc. ether, and 15.0 g. of bromobenzene. After all the ester was added, the reaction mixture

was heated under reflux for half an hour, and let stand over night. The next morning it was refluxed an additional two hours, most of the ether was distilled off, and the residue was heated one hour more. The residue was poured into 100 g. of ice to which 6 cc. concentrated sulfuric acid had been added. This mixture was ether extracted, dried and the ether removed. There remained 9 g. of residue, which probably contained some ether.

This residue was oxidized with chromic anhydride and acetic acid, according to the method followed by Wieland, Schlichting and Jacobi<sup>32</sup> for the oxidation of the tertiary carbinol obtained from nor-cholanolic acid. The 9 g. of carbinol were dissolved in 10 cc. of glacial acetic acid. The solution was warmed on a steam bath, and to the warm solution there was added during the course of two hours, 16 g. of chromic anhydride dissolved in 15 cc. water and 20 cc. acetic acid. The reaction mixture was then heated on the steam bath six hours longer, cooled, and sulfur dioxide bubbled through the cooled solution, to reduce any excess of the oxidizing agent.

The reaction mixture was distilled with steam until about 800 cc. of distillate was obtained. The distillate was made alkaline, and extracted with ether. The aqueous layer was boiled to remove ether, made acid to congo by addition of sulfuric acid, and extracted with petroleum ether. Benzophenone was obtained from the extraction of the alkaline solution. Acetic acid was the only acidic organic constituent of the reaction mixture.

The next attempt at degradation of the ketone was a direct oxidation of the ketone with an aqueous solution of chromic anhydride and sulfuric acid. 16.5 g. of ketone was suspended in 25 cc. of water in a 500 cc. flask provided with a mechanical stirrer, reflux condenser and a dropping funnel. The stirrer was started, and a solution of 28.6 g. of chromic anhydride in 75 g. of 30 per cent sulfuric acid was slowly added through the dropping funnel. The stirred mixture was then heated under reflux for 8 hours. The material was then distilled with steam. The steam distillate was extracted with ether and the ether layer was extracted with sodium bicarbonate solution. The bicarbonate extract was acidified and extracted with ether and dried with sodium sulfate. Removal of the ether left but a minute residue that was too small to be distilled. This acidic residue was converted into the amide, and recrystallized once from petroleum ether. It melted at 97-99°. A mixed melting point determination of this material and the amide (melting at 106°) of the acid  $C_6H_{13}COOH$ , obtained by the hypobromite oxidation of the ketone, showed the mixture to melt at 100-101°. A mixture of this amide (melting at 97-99°) with the amide (melting at 103-104°) of dimethyl ethyl acetic acid melted at 70-75°. 5.5 g. of the original ketone was recovered from the neutral ether extract of the reaction mixture.

### BECKMANN REARRANGEMENT OF THE KETOXIME

More fruitful results were obtained by carrying out a Beckmann rearrangement of the ketoxime. The best yield of oxime was obtained in the following way. 26 g. of ketone was dissolved in 165 cc. of ethyl alcohol. To the solution was added 28.4 g. of hydroxylamine hydrochloride dissolved in 50 cc. of water and 47.5 g. of potassium hydroxide in 47.5 g. of water. The solution was refluxed on the steam bath for two hours, 100 cc. of water was added to dissolve the potassium chloride that precipitated from the cold solution, and the resulting solution was ether extracted and dried over sodium sulfate. Removal of the ether and distillation of the residue yielded 24.5 g. of oxime, boiling at  $113^{\circ}$  at 37 mm. This oxime boiled at  $79.0-79.5^{\circ}$  at 5 mm. pressure. It has a density of 0.9343 at  $20^{\circ}$ , and a refractive index of 1.4548 at  $25^{\circ}$ . The oxime is a viscous oil. It solidifies to a glass at the temperature of solid carbon dioxide, but could not be obtained in crystalline form.

Rearrangement of the oxime was effected by means of benzenesulfonylchloride<sup>33</sup>, in dry pyridine and by treatment of an absolute ether solution of the oxime with phosphorous pentachloride<sup>34</sup>. The latter method was favored, because the yields of amide from the rearrangement of the oxime were better.

Four grams of oxime was dissolved in 20 cc. pyridine, and the solution cooled to  $0^{\circ}$ . 5.85 g. of benzenesulfonylchloride was added to the cooled solution, drop by drop. When the solution

was removed from the cooling mixture, crystals were deposited on the walls of the flask. The solution warmed up very rapidly, and the crystals dissolved. Cooling the solution failed to cause the crystals to be reprecipitated. The solution was allowed to stand over night. The next morning it was poured into 100 cc. ice water containing 10 cc. concentrated sulfuric acid. This solution was extracted with ether, dried with sodium sulfate, the ether removed, and the residue distilled. The yield amounted to 2 g. of product boiling at 124-125° at 16 mm. This product solidified on cooling. It melted at 59.5-60.0°.

The following is typical of the experiments on the rearrangement of the oxime by means of phosphorous pentachloride. 11.6 g. oxime was dissolved in 125 cc. ether. The solution was cooled to -5°, and 19.0 g. of phosphorous pentachloride was added, in small portions, during the course of half an hour. Care was exercised to keep the solution below 0°, during the addition of the phosphorous pentachloride. The reaction mixture was allowed to warm up to room temperature gradually, and allowed to stand for 8 hours. Most of the ether was then boiled off. A white solid formed during the addition of phosphorous pentachloride to the ether solution of the oxime dissolved, after most of the ether was removed. The residue was poured into 100 cc. of ice and water and the cold solution was neutralized with sodium hydroxide solution. The neutral solution was ether extracted and the ether extract dried with sodium sulfate. Distillation of the residue, after



removal of the ether, gave 9 g. of amide boiling at 130-131° at 20 mm.

It was believed that the oxime had rearranged according to the scheme  $C_6H_{13}(CH_3)C:NOH \longrightarrow C_6H_{13}NECOCH_3$ . Accordingly, a literature search was made for the acetyl derivatives of the primary hexyl amines. Only three have been reported, and these all melt above 110°.

The first attempts to hydrolyze the amide were unsuccessful. Refluxing the amide with alcoholic alkali for 3 hours caused no hydrolysis. The same result was found on refluxing for 2 hours with 50% sulfuric acid. Refluxing with 1:1 sulfuric acid for 20 hours effected a partial hydrolysis, but there was also much carbonization. Attempts to hydrolyze the amide by Gattermann's modification<sup>35</sup> of Bouveault's method<sup>36</sup> of hydrolyzing difficulty hydrolyzable amides, and by Bouveault's original method (l.c.) were also unsuccessful.

Heating the amide in a sealed tube with 1:1 sulfuric acid effected hydrolysis, but there was also much carbonization. Three grams of the amide were heated with a solution of 4 cc. sulfuric acid in 4 cc. of water at 200°, for 3 hours. 1.2 g. of amine was obtained from this hydrolysis.

Heating 3 g. of the amide with 4 cc. 85% phosphoric acid and 4 cc. of water in a sealed tube at 200° for 4 hours also yielded 1.3 g. of amine. There was no carbonization in this experiment. In a subsequent experiment, 9 g. of the amide was hydrolyzed in two equal portions in sealed tubes, each of which

contained 15 cc. of a solution of equal volumes of 85% phosphoric acid and water. The tubes were heated at a temperature of 220-240°, for 5 hours. The reaction products from the two tubes were combined, and ether extracted to remove the neutral and acidic reaction products. The aqueous layer was then cooled, and saturated with potassium hydroxide. This mixture was then distilled, until about 50 cc. of distillate was collected. This distillate was again saturated with solid potassium hydroxide, and the water-insoluble layer was separated in a separatory funnel. This material was dried with potassium hydroxide, and distilled. 5.5 g. of amine was obtained. It boils at 101-103°, at 756 mm. pressure.

The amine had a marked ammoniacal odor, and reacted with the carbon dioxide of the air to form a solid carbonate. 0.1 g. of the amine dissolved in 5 cc. of water containing 6 drops concentrated hydrochloric acid reacted with 5 cc. of a 10% solution of chlorauric acid<sup>37</sup>, to give an insoluble chloraurate that melted, after one recrystallization from water, at 189°. Decomposition began at 195°. This agrees with the properties of the chloraurate of 3-amine-2, 2-dimethylbutane obtained by Markownikoff<sup>38</sup>, by reduction of the nitro compound obtained from 2,2-dimethylbutane, and synthetically (l.c.) by the reduction of pinacolone oxime with sodium and alcohol. In addition to the chloraurate, the 3-amine-2,2-dimethylbutane was characterized by Markownikoff by the formation of a chlorplatinate, and a hydrochloride.

In order to compare the amine obtained by hydrolysis of the amide with synthetic material, the amine was prepared from pinacolene oxime. 6.5 g. of pinacolene was dissolved in 20 cc. of alcohol. To this solution was added 9 g. of hydroxylamine hydrochloride in 9 cc. of water and 15 g. of potassium hydroxide in 15 cc. of water. The resulting solution was refluxed for 3 hours, part of the alcohol was distilled off, and the solution was cooled. The oxime crystallized as the solution cooled. Six grams of pinacolene oxime was obtained in this way. Subsequently 36 g. of oxime was obtained from 40 g. of pinacolene, using the same procedure.

Very poor yields of amine were obtained by the reduction of the oxime, with sodium amalgam<sup>39</sup> or with sodium and alcohol, in acetic acid solution<sup>40</sup>. Five grams of the oxime was dissolved in 30 cc. of alcohol and the solution was placed in a flask provided with a mechanical stirrer and a reflux condenser. The solution was warmed to 50°, the stirrer was started, and 205 g. of 2% sodium amalgam was added gradually, during the course of half an hour. 16.0 g. of acetic acid were added during the course of the reaction, at such a rate that the solution was always acid to phenolphthalein. After all the sodium-amalgam and acetic acid were added, the solution was warmed for 15 minutes, cooled, and the acid solution was extracted with ether to remove unreduced oxime. The reaction mixture was then made alkaline, and extracted with ether. The ether extract was dried with sodium hydroxide, the ether removed, and the residue distilled from a small flask, immersed in an oil bath. About

1 g. of material distilled with the bath temperature 120-130°.

12.5 g. of pinacolone oxime were dissolved in 300 cc. alcohol, placed in a flask fitted with a reflux condenser, and a mechanical stirrer. The contents of the flask were warmed to 70°, and 30 g. of sodium were added in small cubes about 0.5 cm. on each side. 200 cc. glacial acetic acid were added, during the course of the reaction. This large excess of acid over the amount needed to maintain an acidic reaction mixture was necessary in order to prevent the reaction mixture from becoming thick.

The solution was made alkaline, and distilled with steam until unreacted pinacolone oxime began to distill. About 250 cc. distillate had then been collected. The distillate was collected in dilute hydrochloric acid, to prevent loss of amine. The resulting amine hydrochloride solution was evaporated to dryness, dissolved in 5 cc. of water, and the cold solution was saturated with potassium hydroxide. Distillation of this mixture gave 2.5 g. of amine. Attempts to reduce the pinacolone oxime by means of hydrogen, at a pressure of 55-60 pounds, in the presence of platinum black were unsuccessful. Ether, acidulated with hydrochloric acid, acetic acid, and acetic acid containing hydrochloric acid were used as solvents, in these hydrogenation experiments.

The identity of the amine obtained by the hydrolysis of the amide, with the 3-amino-2,2-dimethylbutane prepared synthetically was established by the preparation of the picramide, the benzene sulfonamide, and the acetyl derivative of the amine from both sources.

Mixed melting point determinations of all these derivatives established the identity of the two amines.

0.2 g. of the amine was added to 4 cc. 5% sodium hydroxide solution. To this solution was added 6 drops of benzenesulfonylchloride. Gentle warming of the mixture resulted in a clear solution, in which a white precipitate formed almost immediately. The melting point of the benzenesulfone amide was 96.0°, after recrystallizing from 50% alcohol, and from petroleum ether.

The picramide of 3-amino-2,2-dimethylbutane was prepared by the addition of 0.1 g. of the amine to 10 cc. of a 2% solution of picryl chloride. On shaking the solution for a short time, a bright yellow precipitate appeared. This was recrystallized from 95% alcohol to a constant melting point of 107.0°.

The acetyl derivative of the synthetic 3-amino-2,2-dimethylbutane was prepared by heating the amine with an excess of acetic anhydride. The excess acetic anhydride was removed by distillation, and the amide was then distilled under diminished pressure. It was purified by subliming in vacuo (3 mm.) at 85-90°. Sublimation of the amide obtained by a Beckmann rearrangement of the oxime yielded a product that melted at 54°. It could not be recrystallized satisfactorily, because it was readily soluble in most solvents, and because of its low melting point. Recrystallization from petroleum ether (boiling range 60-67°) yielded a small amount of a product that melted at 127-128°, and the more soluble residue that melted at 56-58°.

Fractional sublimation of this residue at a temperature of 75-85°, and a pressure of 3 mm. did not raise the melting point. A second sublimation was also ineffective. A mixture of this material with the synthetic amide melted at 64-65°.

It was believed that the amide from the rearrangement of the ketoxime contained some of the other rearrangement product. Thus the rearrangement occurred mainly in the sense



but partly in the sense



and that the presence of the second product was responsible for the low melting point of the amide resulting from the rearrangement. The identity of the amide from the synthetic oxime with that obtained through the oxime was established by preparing the acetyl derivative of the latter. It melted at 68.0-68.5°, after sublimation. A mixed melting point determination of this material and the amide obtained from the synthetic oxime showed no depression. Analysis of the rearranged oxime was the same as that of the acetyl derivative of the amine obtained by hydrolysis of the former. This indicates that an isomeric amide was responsible for the low melting point of the amide obtained by rearrangement of the oxime.

The melting point determinations reported in this research were made with Anschütz thermometers that were calibrated at the U. S. Bureau of Standards, in a mechanically stirred oil bath. No corrections were applied, since the corrections were negligible, with thermometers of this type.

The analytical data of compounds not previously reported in the literature can best be presented in tabular form.

<u>Substance</u>	<u>Wt. of Sample</u> <u>MG.</u>	<u>Wt. of CO<sub>2</sub></u> <u>MG.</u>	<u>Wt. of H<sub>2</sub>O</u> <u>MG.</u>	<u>% C</u>	<u>% H</u>
Semicarbazone of 2,2,3-trimethyl- pentanone-4 <sup>a</sup>	4.041 2.392	8.672 5.093	3.687 2.228	58.53 58.07	10.20 10.42
Theoretical composition of C <sub>9</sub> H <sub>19</sub> N <sub>3</sub> O				58.33	10.34
p-Nitrophenyl- hydrazone of 2,2,3- trimethylpentanone-4	3.051 3.155	7.178 7.439	2.122 2.248	64.16 64.30	7.78 7.97
Theoretical composition of C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub>				63.83	8.04
2,4-Dinitrophenyl- hydrazone of 2,2,3- trimethylpentanone-4	3.180 3.763	6.381 7.512	1.852 2.158	54.73 54.45	6.52 6.41
Theoretical composition of C <sub>14</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub>				54.51	6.54
Oxime of 2,2,3-trimethyl- pentanone-4	3.152 4.239	7.740 10.430	3.287 4.482	66.97 67.10	12.22 11.83
Theoretical composition of C <sub>8</sub> H <sub>16</sub> NO				67.07	11.97
Methyl-tert.- butylacetic acid	3.275 3.381	7.762 7.945	3.154 3.208	64.64 64.09	10.73 10.62
Theoretical composition of C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>				64.54	10.84
Amide of methyl- tert.-butylacetic acid	3.174 3.293	7.533 7.833	3.199 3.482	64.73 64.84	11.28 11.80
Theoretical composition of C <sub>7</sub> H <sub>15</sub> NO				65.05	11.71

<u>Substance</u>	<u>Wt. of Sample</u> <u>mg.</u>	<u>Wt. of CO<sub>2</sub></u> <u>mg.</u>	<u>Wt. of H<sub>2</sub>O</u> <u>mg.</u>	<u>% C</u>	<u>% H</u>
Anilide of methyl- tert.-butylacetic acid	3.590 2.533	10.080 7.122	2.960 2.112	76.57 76.68	9.22 9.32
Theoretical composition of		C <sub>13</sub> H <sub>19</sub> NO		76.04	9.33
p-Phenylphenacyl ester of methyl-tert.- butylacetic acid	3.986 2.650	11.351 7.504	2.598 1.787	77.67 77.41	7.29 7.55
Theoretical composition of		C <sub>21</sub> H <sub>24</sub> O <sub>3</sub>		77.73	7.46
Benzene sulfoneamide of 3-amino-2,2- dimethylbutane	3.391 3.665	7.396 7.967	2.395 2.505	59.76 59.29	7.90 7.65
Theoretical composition of		C <sub>12</sub> H <sub>19</sub> NO <sub>2</sub> S		59.70	7.94
Picramide of 3-amino-2,2- dimethylbutane	3.378 4.330	5.734 7.352	1.494 1.979	46.29 46.30	4.94 5.12
Theoretical composition of		C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub>		46.13	5.16
Acetyl derivative of 3-amino-2,2- dimethylbutane	3.262 2.173	8.088 5.335	3.450 2.248	67.57 66.96	11.83 11.57
Theoretical composition of		C <sub>8</sub> H <sub>17</sub> NO		67.07	11.97
Amide formed by rearrangement of oxime	2.794 2.789	6.888 6.825	2.905 2.880	67.23 66.74	11.63 11.95
Theoretical composition of		C <sub>8</sub> H <sub>17</sub> NO		67.07	11.97

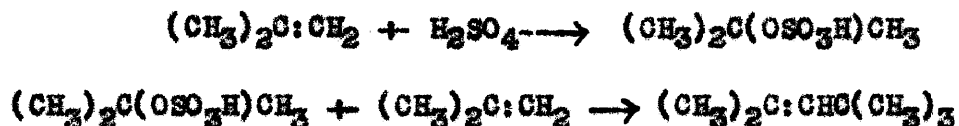


<u>Substance</u>	<u>Wt. of Sample</u> <u>mg.</u>	<u>Wt. of CO<sub>2</sub></u> <u>mg.</u>	<u>Wt. of H<sub>2</sub>O</u> <u>mg.</u>	<u>Wt. of Au</u> <u>mg.</u>	<u>% C</u>	<u>% H</u>	<u>% Au</u>
Chloraurate of	4.056	2.392	1.395	1.821	16.08	3.85	44.88
3-amino-2,2- dimethylbutane <sup>c</sup>	10.505	6.348	3.493	4.697	16.48	3.72	44.71 <sup>b</sup>
Theoretical composition of							
			$C_8H_{16}$	$HAuCl_4$	16.31	3.69	44.67

- a. Analysis of this substance was reported by Wheeler<sup>4</sup>.
- b. The author wishes to express his gratitude to Mr. J. B. Spies, of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, for this analysis.
- c. The gold content of this salt was reported by Markownikoff<sup>38</sup>.

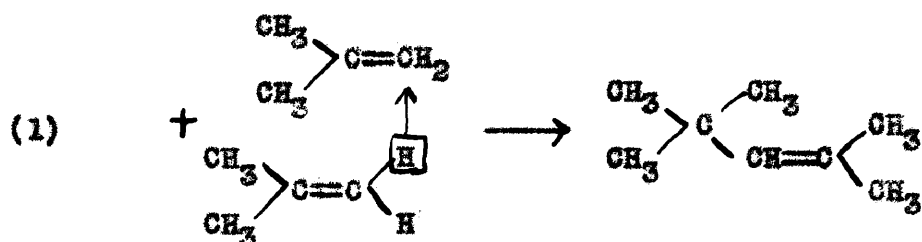
### DISCUSSION

Several theories have been advanced to explain the polymerization of olefins. Berthelet is said to have been the first to attempt an explanation of polymerizations of this type. The theory of Berthelet was used by Butlerov<sup>11</sup> and by Kondikov<sup>41</sup> to explain the results obtained by them in their studies on hydrocarbons. This theory postulates the intermediate formation of an alkyl sulfuric ester. This ester then condenses with a second molecule of the original olefin, to form the resulting dimer, with the loss of sulfuric acid. Thus,

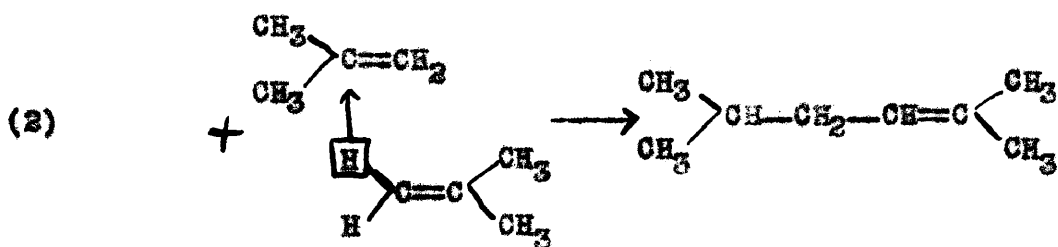


This mechanism never gained general acceptance, but more satisfactory mechanisms were not forthcoming. In the first place, this theory postulates the formation of but one diisobutylene, whereas there is abundant proof<sup>7,8,9,10,11,12</sup> that this reaction results in the formation of two isomeric octenes, namely, 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. Another objection that has been raised to this theory is the fact that other agents, such as aluminum chloride, zinc chloride, fuller's earth, light and heat, effect the same polymerization. This theory would not lead one to expect this.

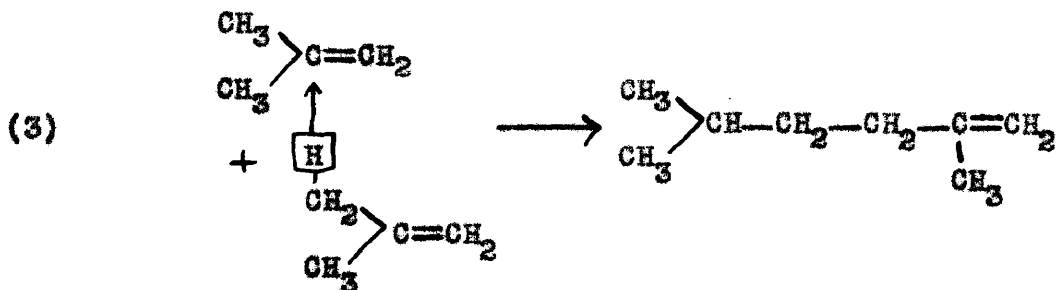
McCubbin and Adkins<sup>12</sup> explained the formation of these two octenes from isobutyl alcohol on the basis of the activated hydrogen theory of Bergmann. Thus, an active hydrogen atom of the methylene group or of the methyl group can add to one of the ethylenic carbons in one of several ways, the rest of the molecule then adding to the other ethylenic carbon. These transformations may be represented:



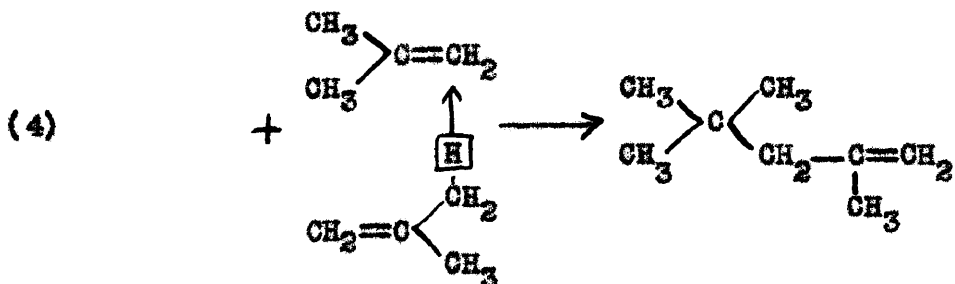
or



Or, again, the hydrogen atoms of the methyl group may be activated



or

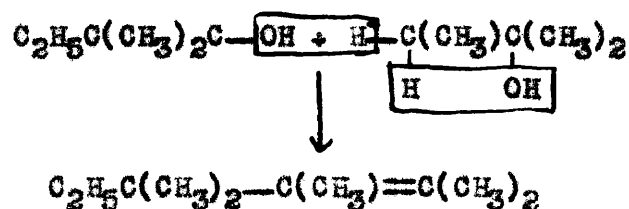


The compounds produced by reactions (1) and (4) are the only ones formed by the polymerization of isobutylene. Thus, the theory predicts the formation of four isomeric octenes; very careful investigations, using large quantities of material, showed the presence of but two isomers<sup>7,8,9,10</sup>. A more serious objection is to be found in the postulation of an active hydrogen atom in the methyl group. The interpretation of the experimental results of this polymerization in this way would indicate the hydrogens of the methyl group to be four times as active as those of the methylene group, since the amount of octene formed by reaction (4) is found to be four times that of the octene formed by reaction (1). This is inconsistent with the facts observed

in such reactions as chlorination and nitration. All of the recent work of Whitmore (cf. the many references in the bibliography) shows that the hydrogens of the methyl groups are the least labile.

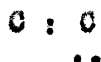
Morrell<sup>42</sup> postulated a mechanism for the polymerization of unsaturated hydrocarbons, on the basis of Thiele's partial valence theory, and the assumption of a mobile or labile hydrogen. This theory differs from that used by McCubbin and Atkins to explain the formation of the diisobutylenes, only in the introduction of the concept of partial valence.

Norris and Joubert<sup>6</sup> found that polymerization of the amylenes occurred most readily with the isomers which have two radicals in combination with a carbon atom of the olefinic bond, namely, trimethylethylene and unsymmetrical methylethylene. They concluded that these two amylenes do not form a sulfuric acid ester when they are dissolved in sulfuric acid solutions, of various concentrations, because the tertiary alcohol is precipitated, when the solution is saturated with ammonium sulfate. This led them to postulate a mechanism of polymerization that involves the formation of the alcohol, and its subsequent dehydration. They typified this mechanism by polymerization of trimethylethylene. According to their view, the first step in the polymerization involves the formation of tertiaryamyl alcohol. Two molecules of the alcohol are then dehydrated, as follows:

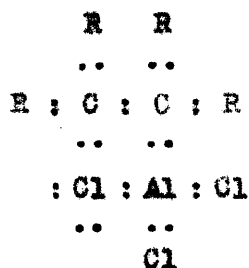


The theory does not account for the formation of the two isomers that were found in this investigation, and does not explain the polymerization of olefins by such agents as fuller's earth, light and heat.

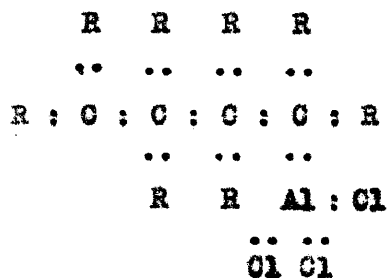
Hunter and Iche<sup>43</sup> studied the polymerization of unsaturated hydrocarbons by means of aluminum chloride. An activated olefinic bond is represented as one in which one carbon atom has acquired the second electron pair, thus:



An activated double bond then combines with a molecule of aluminum chloride, forming the complex



which then combines with another molecule containing an activated olefinic double bond, to form



This molecule can then undergo further addition, resulting in the formation of a trimer, etc.

This theory of Hunter and Yohe is similar to one previously postulated by Whitmore<sup>44,22,45</sup>, in that the modern concepts of atomic structure are utilized. Thus, the second of two pairs of shared electrons, constituting an olefinic linkage, is held closer to one of the olefinic carbons than to the other. The theory is based on the conceptions of atoms and molecules introduced by G. N. Lewis, Arthur Michael, Julius Stieglitz, W. A. Noyes, Hans Meerwein, H. J. Lucas and Charles Prévost. The theory was first applied to explain the mechanism of the Hofmann, Lossen, Curtius, Beckmann, pinacol-pinacolone and the benzil-benzilic acid rearrangements, as well as the rearrangements frequently observed in the dehydration of alcohols, or the replacement of an hydroxyl group by halogen, or some other atom or group. It has more recently<sup>45</sup> been applied to explain the rearrangements that occur during polymerization.

The following assumptions are the basis of the theory.

"1. A non-ionic attachment between an atom like carbon or nitrogen and an electronegative atom or group is broken during the reaction.

2. At the instant of removal of the electronegative group, it takes a completed octet of electrons with it.

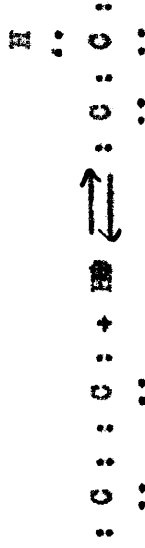
3. The atom which had shared an electron pair with the electronegative group is thus left with only a sextet of electrons.

4. This deficiency of two electrons may induce a migration of an electron pair from an adjacent atom, thus giving rise to 'abnormal' or rearranged products.

5. In the case of carbonyl compounds, a carbon with an open sextet may be formed by the addition of a positive ion to the oxygen. In this case, also, the presence of the open sextet induces rearrangement."

The additional assumptions of the theory as applied to the polymerization of olefins<sup>45</sup> have been stated essentially as expressed in the following paragraph.

The first step in the polymerization of olefins by acids is the addition of a hydrogen ion (a proton) to the extra electron pair

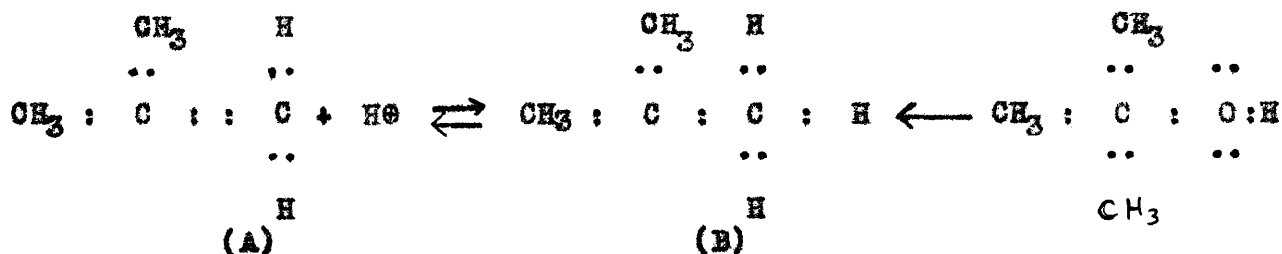




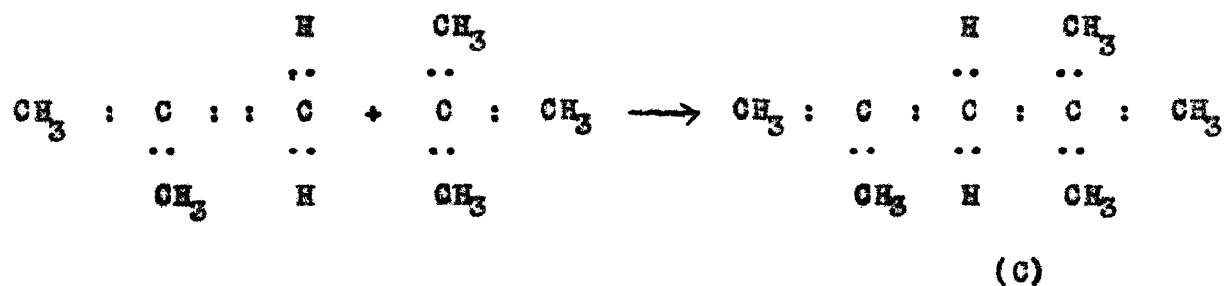
this leaves one of the carbons as a positively charged atom, which can then undergo the characteristic changes of positively charged atoms, namely:

1. Union with a negative ion.
2. Reversal of the process, to give the same, or a new olefin.
3. Rearrangement of the carbon skeleton, followed by loss of a proton, to give a new olefin.
4. Polymerisation. Polymerisation involves the addition of the positive organic fragment to another molecule of olefin, in the same way that the positive proton added to the first molecule of olefin. The result is a larger positive fragment, which can undergo the changes indicated.

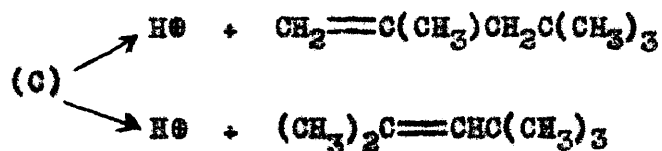
This theory has been used to explain the rearrangements involved in the formation of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 by the action of sulfuric acid on isobutyl alcohol. The addition of a hydrogen ion to isobutylene gives a positively charged tert.-butyl group. This same product is obtained by treating tert.-butyl alcohol with acids:



In the same way that a positive hydrogen ion adds, the positive tert.-butyl group (B) can add to isobutylene to give the intermediate (C).



The product (C) is positively charged. The carbon atom that shares but six electrons can attract a pair of electrons from one of the adjacent methyl groups, or from the methylene group, thus liberating a proton and forming a double bond.



Whitmore has applied this theory to the polymerizations of the isoenylenes. The most probable products are said to be 3,5,5-trimethylheptene-2, 3,5,5-trimethylheptene-3, 3,3,4,4-tetramethylheptene-1, 3,3,4,4-tetramethylheptene-2 and 2-ethyl-4,4-dimethylheptene-1. Of these five, the first is the only one that was found in this investigation, and it is improbable that there are more than two decenes, namely, 3,5,5-trimethylheptene-3 and 3,4,5,5-tetramethylheptene-2, in the diamylene mixture investigated. These two seem to be present in about equal quantities, and are present in equal quantities in the decene mixture obtained by the action of sulfuric acid on methylisopropylcarbinol. This mixture, also, seems to contain no other decenes.

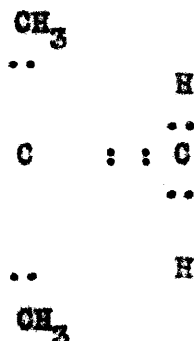
The author appreciates the utility of the mechanism proposed by Whitmore, since it provides a single mechanism for many anomalous transformations that are apparently of very different types. However, its chief virtue becomes its most serious fault, in that the characteristic changes of the postulated positively charged ion may occur in so many different ways. In view of these considerations, a simpler mechanism is here offered to explain the formation of the two decenes of diamylene. The mechanism is based on some of the principles expressed by Whitmore, and also utilizes the relative electronegativity, or attraction for electrons, of various groups, as defined and evaluated by Kharasch, and his associates 46, 47.

Kharasch views the olefinic bond as consisting of two

pairs of shared electrons, as may be typified by ethylene

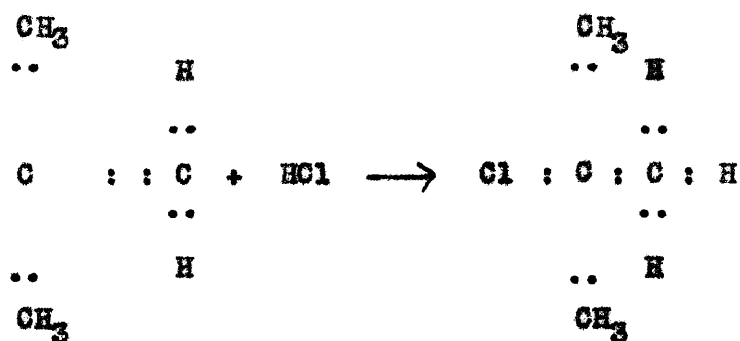


in which the two pairs of shared electrons are symmetrically located, with respect to the carbon atoms, because the groups attached to these atoms are equally electronegative. However, in unsymmetrical dimethylethylene, the methyl groups are more electronegative than the hydrogen atoms, and, consequently, the two pairs of shared electrons constituting the double bond are displaced toward the carbon holding the hydrogens

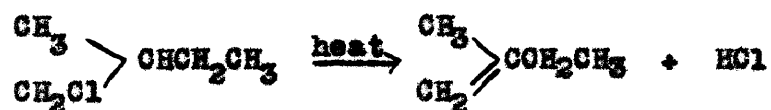
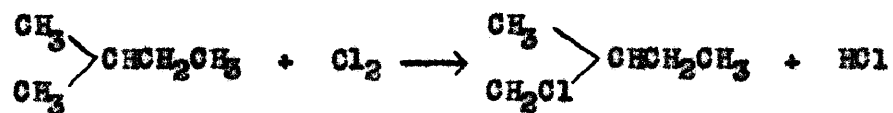


This is evidenced in the mode of addition of HCl to olefins.

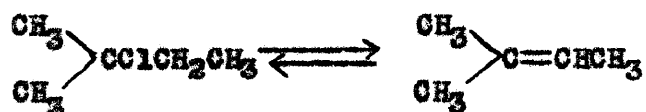
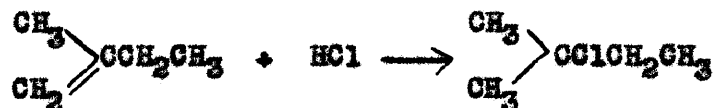
In this instance, the chlorine ion adds to the carbon holding the methyl groups, and the hydrogen to the carbon holding the hydrogens,



Ayres<sup>2</sup> has shown that 2-methylbutene-1 is formed in the chlorination of isopentane in the following way:

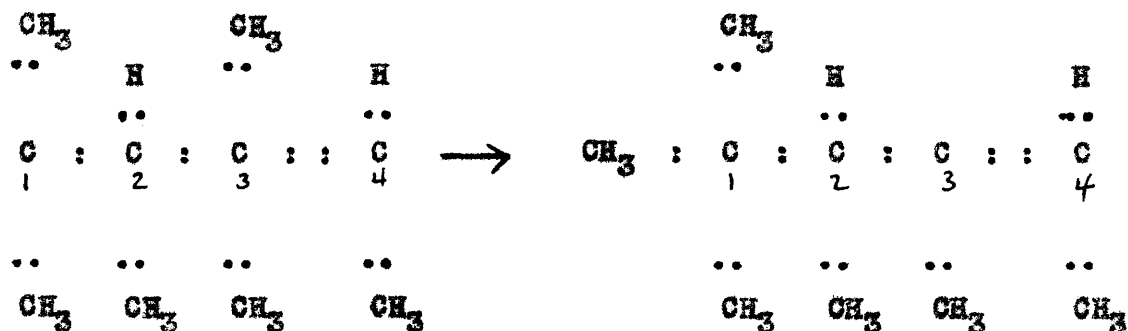


Trimethylethylene is formed from this by addition and loss of HCl.



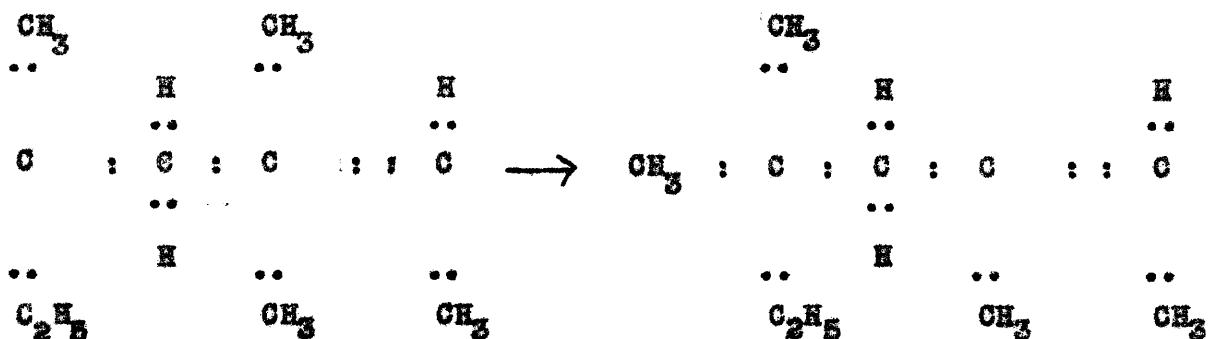
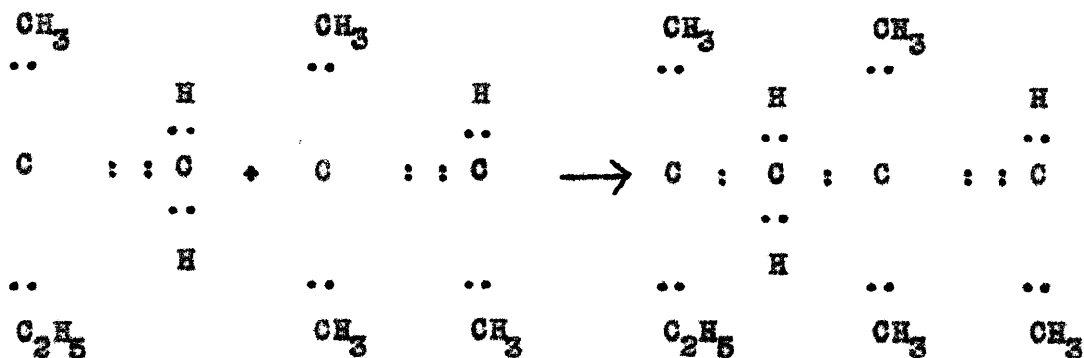


It will be noted that this mode of addition is in accord with the electronic arrangement of the trimethylethylene molecule. This molecule is unstable because carbon atom 1 shares but 6 electrons, and carbon atom 3 shares 10 electrons. Transfer of 2 electrons from carbon 3 to carbon 1 and the consequent shift of the methyl group that shared this pair of electrons, results in the establishment of a true olefinic bond between carbons 3 and 4.



This will be recognized as 3,4,5,5-tetramethylhexene-2 when written in the more conventional manner  $(\text{CH}_3)_3\text{CCH}=\text{CHCH}_3$ .

In a similar fashion, addition of a molecule of trimethylethylene to one of 2-methylbutene-2, followed by the rearrangement of a methyl group, yields the other decene found in diamylene, namely 3,5,5-trimethylheptene-2.

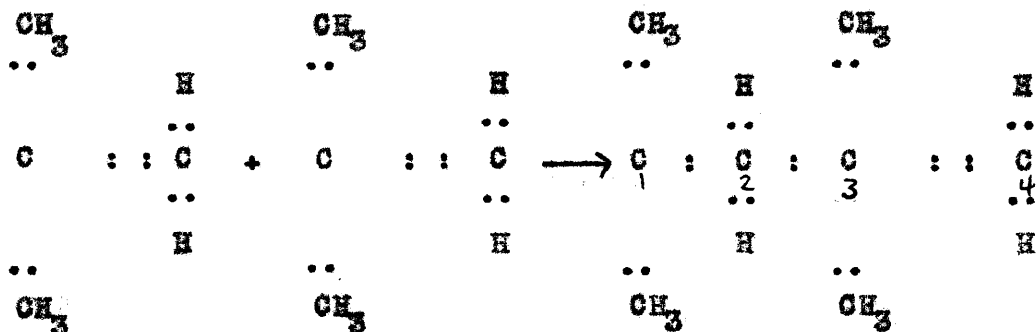


This last formula may be written  $\text{C}_2\text{H}_5\text{O}(\text{CH}_3)_2\text{CH}_2\text{CCH}_3=\text{CHCH}_3$ ; in this guise it will be recognized as 3,5,5-trimethylheptene-2.

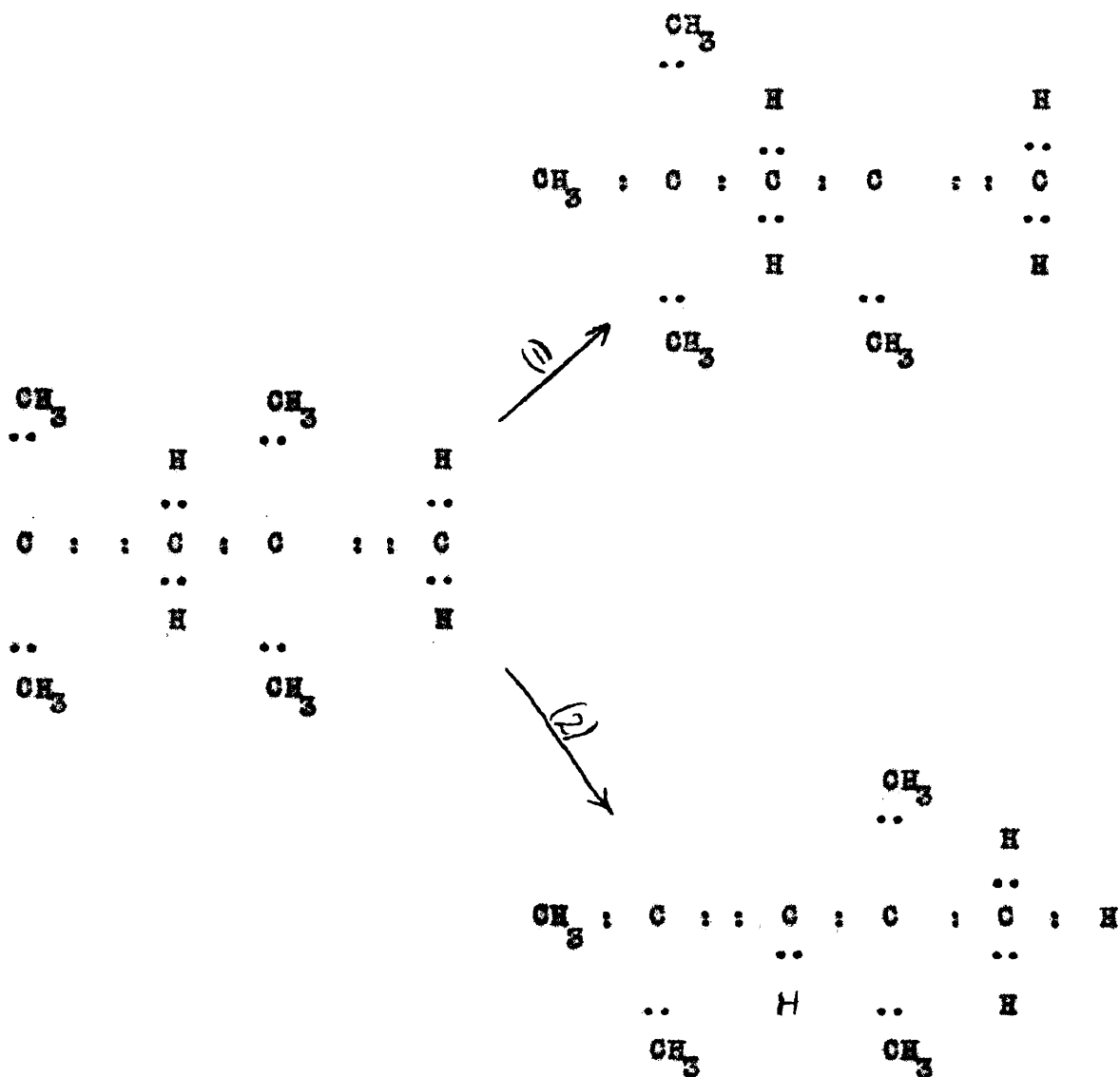
In support of this mechanism, it may be pointed out that it also offers an explanation of the experimental observation that vinyl chloride, trimethylethylene and unsymmetrical methylethylene all polymerize more readily than ethylene. In the light of this mechanism, this is due to the polarity established in the molecule, due to the replacement of hydrogen by the more electronegative methyl or ethyl groups or by chlorine.



The mechanism formulated above also explains the formation of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 from isobutylene, if one assumes the rearrangement of a proton, as well as a methyl group.



This may undergo rearrangement in one of two ways, (1) by completing the octet of carbon 1 by transfer of an electron pair from carbon 3, which <sup>ten</sup> shares electrons, followed by rearrangement of a methyl group, giving 3,4,4-trimethylpentene-1, or (2) by rearrangement of a proton, and the formation of the ethylenic bond at the other end of the molecule.



Although the latter is not very probable, the mechanism becomes more probable when it is remembered that this latter product, 2,4,4-trimethylpentane-3 constitutes but 20% of the diisobutylene mixture

### CONCLUSION

Two isomeric decenes have been obtained by fractionation of diisylene, obtained as a by-product in the chlorination of the pentanes. The decenes were shown to be 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2, by ozonolysis of the decene fractions. These two isomers are present in approximately equal amounts.

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