THE ACTION OF SULFURIC ACID ON METHYL ISOPROPYL CARBINOL

By

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CONTENTS

HISTORICAL

It has been known for a long time that hydrocarbons may be prepared by the action of sulfuric acid on alcohols and olefins. The mechanism of such polymerizations has been discussed and the conditions for condensation studied. Very little research has been carried out to establish the identity of the products obtained by polymerization of alcohols and olefins with sulfuric acid.

Wischnegradsky[1] condensed isoamylenes to diamylenes with concentrated sulfuric acid and obtained a polymer boiling from 154 to 156 degrees. From fifty-five grams of isoamylene he obtained forty grams of diamylene. On oxidation acetic acid, carbon dioxide and oxydiamylene were obtained.

Schneider[2] polymerized amylene (b.p. 35-37) to diamylene with diluted sulfuric acid (2 volumes of acid to 1 volume of water). Carbon dioxide, acetic acid, and oxydiamylene were formed on oxidation of the polymer.

By treating trimethyl carbinol with sulfuric acid Butlerow[3] obtained isobutylene which dissolved and polymerized to diisobutylene. One hundred parts of alcohol yielded sixty-five parts of diamylene.

1. Wischnegradsky, Ber., 8, 434. (1875)
2. Schneider, Ann., 157, 207. (1871)
3. Butlerow, Ann., 189, 75. (1878)

Konowalow[4] polymerized isobutyl alcohol with diluted sulfuric acid (4 parts acid to 1 part of water) and a little talc. From one hundred grams of isobutyl alcohol he obtained forty-three grams of polymer boiling from 104 to 178 degrees.

Kondakow[5] prepared octenes by treating isobutylene with sulfuric acid.

Nef[6] reported that isobutyl, tertiary butyl, and secondary butyl alcohols dissolved in four times their volume of concentrated sulfuric acid at zero degrees. After a short time an oil separated boiling from 150 to 400 degrees. Complete separation was obtained in twenty-four hours.

Michael and Brunel[7] found that trimethyl ethylene dissolved in concentrated sulfuric acid at zero degrees and polymerized on standing. By adding different amounts of water they varied the time for complete solution from twelve minutes to forty hours. They also polymerized other amylenes and some hexenes.

Michael and Zeidler[8] polymerized isopropyl ethylene by mixing with five volumes of sulfuric acid (2 vol. conc. acid to 3/4 vol. of water).

Brooks and Humphrey[9] have shown that in the washing and purification of petroleum distillates with sulfuric acid,

4. Konowalow, Ber., <u>13</u>, 2395. (1880)
5. Kondakow, J. Prakt. Chemie, <u>54</u>, 442, (1896)
6. Nef, Ann., <u>318</u>, 26. (1901)
7. Michael and Brunel, Am. Chem. J., <u>41</u>, 118 (1909)
8. Michael and Zeid , Ann. <u>385</u>, 252 (1911)
9. Brooks and Humphrey, J. Am. Chem. Soc. <u>40</u>, 822 (1918)

polymerization of the unsaturated hydrocarbons occurs. They found the tendency to condense to increase with increasing molecular weight. In addition to polymers, secondary and tertiary alcohols and alkyl esters of sulfuric acid are formed. Both dimers and higher polymers result, the percent of each depending on the nature of the olefin, the amount and concentration of the acid, and the temperature. Thus 2-methyl butene 1 was dissolved in twice its volume of eighty-five percent sulfuric acid at 10 degrees and no polymerization occurred. When diluted with ice water a forty-five percent yield of tertiary alcohol was obtained. Tetra methyl ethylene (46.5 grams) when treated with eighty-five percent sulfuric acid (150 grams) at zero degrees and allowed to stand for one hour yielded more than fifty percent dipolymer. When one hundred percent sulfuric acid was employed on hexenes at minus ten degrees, seventy-two grams of hexenes gave sixty-two grams of polymer. Condensation in this case went further than the dipolymer, for a small portion of the product was a viscous oil. Also considerable oxidation occurred as twelve percent tarry matter was left and evolution of sulfur dioxide was noticed.

Brooks and Humphrey state that the dipolymers contain one double bond. No ring formation was observed. They did not attempt to identify the polymers.

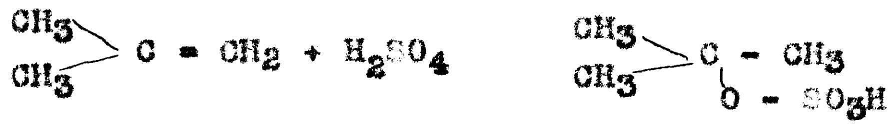
Later investigations by Morrell[10] have shown the loss due

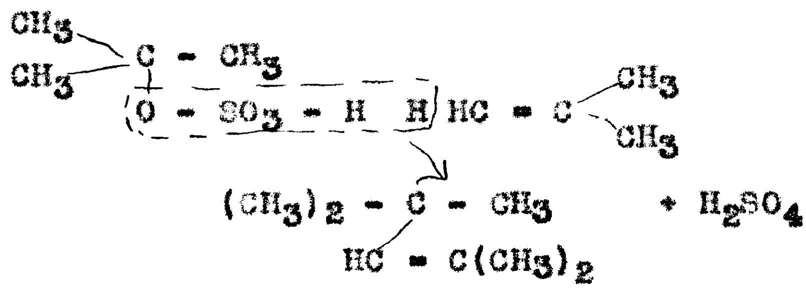
10. Jacque C. Morrell, Ind. and Engr. Chem., __19__, 794 (1927)

to polymerization in the purification of cracked distillates in sulfuric acid refining varies from a negative value to three and one-tenth percent. The amount of polymerization varies with different oils. The negative value obtained in certain cases is explained by condensation of low boiling hydrocarbons to form polymers boiling within the gasoline range. The quantity polymerized in this way was greater than the quantity of gasoline hydrocarbons condensed into heavier oils.

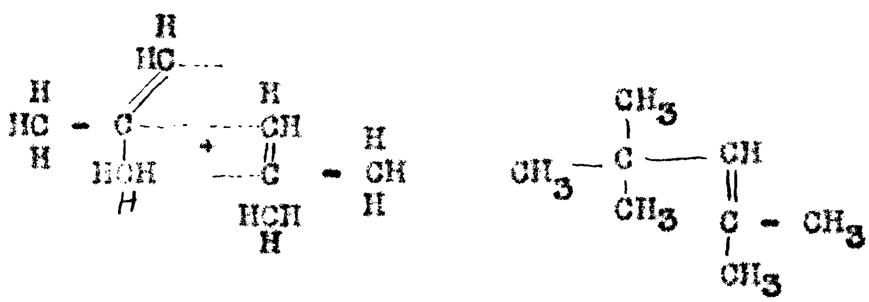
By increasing the amount of sulfuric acid on a given amount of distillate, the boiling point was increased showing an increase in polymerization. The same general effect was noted when the concentration of the acid was increased. The behavior of pure unsaturated hydrocarbons and the unsaturated hydrocarbons in cracked distillates toward sulfuric acid indicates that the increased boiling point is due not only to polymerization, but also to formation of neutral or dialkyl esters of sulfuric acid and subsequent decomposition of the neutral esters into higher boiling, tarry residue.

Morrell gives as one explanation for the mechanism of polymerization of unsaturated hydrocarbons by sulfuric acid, the formation at first of the acid ester or alkyl sulfuric acid by addition. This addition product subsequently reacts with another molecule of olefin to form the polymer. The sulfuric acid is liberated and theoretically may go through many cycles.

(1) 

(2) 

Thieles' theory of partial valence is also used by Morrell in an attempt to explain this polymerization. This theory postulates that double bond carbon atoms have a residual valence. The formation of diisobutylene may occur as follows:



Morrell also states that further assumption is made that the molecules contain a labile hydrogen atom which shifts from one molecule to the other, as shown, permitting polymerization.

In an investigation of the polymerization of amylenes Norris and Joubert[11] studied the structure of the polymer obtained, as well as the conditions under which polymerization took place and the mechanism of the reaction. They found trimethyl ethylene and unsymmetrical methyl-ethyl-ethylene to

11. Norris and Joubert, J.Am. Chem. Soc., 49, 873 (1927)

polymerize most readily. These amylenes have two radicals linked to an unsaturated carbon while the others have a hydrogen attached to each unsaturated carbon. Trimethyl ethylene was completely polymerized by seventy-five percent sulfuric acid in twenty minutes when heated. Equal molecular quantities of sulfuric acid and hydrocarbon were used and the product was mostly dipolymer. The temperature to which the mixture was heated was not given. Unsymmetrical methyl-ethyl-ethylene, when treated in similar way polymerized in twenty-five minutes, yielding mostly dipolymer. Isopropyl ethylene required six days for polymerization and yielded two-thirds dipolymer and one-third higher polymer. 1-methyl butene-1 gave no polymer in fourteen days and pentene-1 only a few drops in three days.

Norris and Joubert found polymerization with the amylenes takes place most readily when the acid ester is not formed. The formation of diamylenes results from the dehydration of the amyl alcohol in solution, or that formed as a result of hydrolysis of an alkyl sulfate. Norris and Joubert explain the dehydration of tertiary amyl alcohol by the following equation:

$$\begin{array}{l} C_2H_5(CH_3)_2C\,\boxed{OH + H}\,C\;\;CH_3\;\;C(CH_3)_2 \rightarrow C_2H_5(CH_3)_2C(CH_3)=C(CH_3)_2+2H_2O \\ \qquad\qquad\qquad\qquad\;\;\boxed{H \qquad OH} \end{array}$$

In support of this theory of the mechanism of polymerization the authors have given the following evidence:

1. It is in accord with the reactivity of the hydroxyl group on a tertiary carbon and of hydrogen on a CH_2 group attached

to a tertiary carbon.

(2) The dipolymer on oxidation did not yield aldehyde. Therefore no hydrogen is present on the unsaturated carbon.

(3) The diamylenes yielded ketones upon oxidation.

(4) The diamylenes decolorized a solution of bromine in carbon tetrachloride, which showed the presence of a double bond.

Norris and Joubert state that other methods of condensation than that given above would lead to compounds containing a hydrogen atom in combination with an unsaturated carbon atom.

The authors attempted to establish the constitution of the dipolymers obtained from trimethyl ethylene and isopropyl ethylene. The decene from trimethyl ethylene reacted very slowly with aqueous potassium permanganate. Potassium dichromate and sulfuric acid, hot or cold, also reacted very slowly. The ozonide was prepared and decomposed. Acetic acid, formic acid, and acetone were identified in the decomposition products. The presence of an acid of formula $C_6H_{12}O_2$ and ketones of high molecular weight was shown. The structure of the acid, $C_6H_{12}O_2$ was not established and the high molecular weight ketones were not identified.

Edgar[12] has prepared a new octane by polymerizing tertiary butyl alcohol with sulfuric acid and hydrogenating

12. Graham Edgar, J. Ind. and Engr. Chem. **19**, No.1, 145,(1927)

the octene. The quantity of octene resulting from polymerization was seventy-five percent of the calculated. The octene was hydrogenated over nickel catalyst and the yield of octane was ninety-seven percent of the theoretical.

The new octane has the structural formula

$$\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix} > C - CH_2 - CH \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

No proof of the constitution of this octane is given, it being evident that no other structure was possible regardless of the mechanism of the polymerization unless some rearrangement occurred. The elimination of a molecule of water by two alcohol molecules, and the loss of a second molecule of water by the tertiary alcohol formed would account for the octene.

$$(CH_3)_3-C-OH + H-\overset{H}{\underset{H}{C}}-C\begin{matrix} CH_3 \\ CH_3 \\ OH \end{matrix} \qquad (CH_3)_3C-CH=C(CH_3)_2$$

If isobutylene were first formed and reacted with the sulfuric acid to form the acid ester, subsequent splitting out of sulfuric acid and polymerization of the butene would give the same octene. Equations for this particular reaction have been given above.

In an investigation on the rearrangement and decomposition of amylenes Norris and Reuter[13] report that isopropyl ethylene rearranged to trimethyl ethylene when treated with

13. Norris and Reuter, J. Am. Chem. Soc., 49, 2624 (1927)

sixty percent sulfuric acid. One hundred cubic centimeters of carefully purified isopropyl ethylene was treated with an equal volume of sixty percent sulfuric acid for one hour. Three cubic centimeters of a tertiary alcohol was found in the products. The alcohol was formed from trimethyl ethylene which was present due to some rearrangement.

A small amount of polymer was also formed but no attempt was made to identify it.

Ormandy and Craven[14] have found that an excess of ninety-eight percent sulfuric acid on alcohols and olefins containing three or more carbon atoms will form polymers which are saturated hydrocarbons together with some highly unsaturated hydrocarbons. They found that open chain olefins yield open chain paraffins, while cycle olefins yield cyclic paraffins.

14. Ormandy and Craven, J, Inst. Petroleum Tech., 13 844 (1927)
J. Soc. Chem. Ind., 47, 317, 20T (1928)

EXPERIMENTAL PART

Introduction.

The purpose of this research was to study the behavior of methyl isopropyl carbinol on treatment with sulfuric acid and to investigate the properties of one of the simpler hydrocarbons formed in the reaction. The number of isomeric decanes is large and very few of them have been prepared and identified. Since it was anticipated that a decene would be formed in the above reaction, this process offered an easy means of synthesizing through the decene a highly branched decane. Furthermore, it should be possible to use a similar reaction in the preparation of like substances. First, however, the exact identity of the substances formed must be known beyond all reasonable doubt.

Methyl isopropyl carbinol or secondary isoamyl alcohol yields trimethyl ethylene readily and it has been shown that this amylene does not rearrange in sulfuric acid solution[13]. The hydrocarbon obtained by treating methyl isopropyl carbinol with sulfuric acid should therefore contain few, if any, isomeric decenes.

Methyl isopropyl carbinol was not available at the time the problem was undertaken and was prepared from isopropyl bromide and acetaldehyde by means of the Grignard reaction. The

13. Norris, loc. cit.

details of this preparation are given with the experimental data.

The alcohol was treated with sulfuric acid, specific gravity 1.67, and heated for twenty minutes at eighty degrees with vigorous stirring. The yield from this reaction of substance of the emperical formula $C_{10}H_{20}$ varied from sixty-five to seventy-five percent. This particular strength acid and temperature were used because a number of experiments proved that under these conditions the yield of the hydrocarbon $C_{10}H_{20}$ was highest. Acid of higher concentration gave a greater percent of higher boiling substances and acid of lower concentration yielded much trimethyl ethylene. Higher and lower temperatures affected the yield of the decene in a like manner. Treatment of the alcohol with sulfuric acid at room temperature over a long period was not studied. Norris[11] has shown that sulfuric acid, specific gravity 1.5, polymerizes trimethyl ethylene in six days at room temperature and yields a dipolymer only.

The polymer obtained was very carefully fractionated. It was analyzed and its molecular weight determined. The density and refractive index of the substance were measured and the molecular refractivity calculated by means of the Lorentz and Lorenz formula. The values obtained from the analysis and the molecular weight determinations and the molecular refractivity

11. Norris, loc. cit.

agreed well with those calculated for a decene of empirical formula $C_{10}H_{20}$.

The decene on treatment with acid potassium permanganate yielded acetone and a very small amount of a ketone. The semicarbazone of this ketone melted at 138 degrees. Meerwein[15] found that the semicarbazone of $(CH_3)_2-\underset{C_2H_5}{C}-COCH_3$ melts at 136 - 138 degrees, and although none of this material was available for the purpose of making the semicarbazone and taking a mixed melting point, it seems reasonably certain that the small amount of substance isolated together with much unchanged decene was the above ketone.

Attempts were made to oxidize the decene with potassium permanganate in acetone but were unsuccessful, in that no oxidation products could be identified. Aqueous potassium permanganate yielded acetone, but no other product was isolated. The decene was very difficultly oxidized in neutral potassium permanganate solution. The decene was then treated with ozone in carbon tetrachloride and the products of ozonization were studied. Formic acid and acetic acid were obtained in about equal quantities and identified. There was also obtained a ketone which was isolated by repeated fractional distillations. About one-sixth of the original material was obtained as acid and ketone.

An analysis yielded results in excellent agreement with the formula $C_7H_{14}O$. Molecular refraction calculated for such a

15. Meerwein, Ann. __419__, 173.

ketone checked with the observed molecular refraction. When treated with sodium hydroxide and iodine, iodoform was produced indicating a methyl ketone. The ketone formed a semicarbazone which melted at 158 degrees. This indicates different splittings of the decene when treated with acid permanganate and with ozone, or the presence of an isomer in the starting material. Since, however, the decene which was ozonized boiled over a range of one degree, we assume that it represents essentially one substance, or possibly a mixture of isomers of very closely related structure.

A portion of the ketone was treated with sodium hydroxide and bromine. The products identified were carbon tetrabromide and bromoform. An acid was also formed, but on account of its small quantity it was not analyzed. A toluide was made from the acid and para-toloudine. The toluide melted at 168 degrees.

It was thought the ketone might possibly be $(CH_3)_2CH-\underset{CH_3}{CH}-COCH_3$. This ketone was prepared and the melting point of its semicarbazone found to be 111 degrees.

The liquid decene was hydrogenated by means of platinum catalyst[16] and the product analyzed. The analysis checked for $C_{10}H_{22}$. Density and refractive index of the substance were measured and the molecular refractivity determined. This value checked with the calculated molecular refractivity of a decane $C_{10}H_{22}$.

16. Adams and Shriner, J. Amer. Chem. Soc. 45, 2171 (1923) Organic Syn. VIII, 92.

EXPERIMENTAL DATA

Preparation of Isopropyl Bromide. One mole of isopropyl alcohol (90 percent) and three moles of aqueous hydrobromic acid, specific gravity 1.49, were slowly distilled. In some cases more than the calculated amount of hydrobromic acid was employed. The bromide was transferred to a separatory funnel and washed with water, dilute sodium bicarbonate solution and water. The bromide formed was dried over sodium sulfate and when dry was fractionated through a twelve inch bead column and collected in a flask provided with a calcium chloride tube. B.P. 59-60 degree.

TABLE NO. I

Grams of Isopropyl Alcohol	Grams of HBr, Sp.Gr. 1.49	Grams of Isopropyl Bromide	Percent Yield
120	1200	134	60.4
360	2700	497	74.8
120	960	156	70.4
264	1800	372	76.2

Isopropyl bromide was also prepared by saturating isopropyl alcohol (90 percent) with dry hydrogen bromide. The flask containing the alcohol was closed with a two-hole rubber stopper. Through one hole a delivery tube extended almost to the bottom of the flask and a calcium chloride tube was placed in the second hole. The flask was kept cold in an ice and salt bath and hydrogen bromide bubbled in. When saturated, the flask was stoppered and allowed to come to room temperature slowly. The bromide was separated in a funnel and the water-alcohol-hydrobromic acid solution cooled and again saturated with dry hydrogen bromide. This mixture was treated in the same way as the first portion. The bromide was washed with water, dilute sodium bicarbonate solution and water. It was dried over sodium sulfate and carefully fractionated.

TABLE NO. II

Grams of Isopropyl Alcohol	Grams of Isopropyl Bromide	Theoretical Yield	Percent Yield
900	1390	1660.5	83.7
780	1200	1439.1	83.4
900	1220	1660.5	73.4

Preparation of Methyl Isopropyl Carbinol. 123 grams of dry magnesium turnings were put in a three neck, three liter flask, provided with a mercury sealed mechanical stirrer and a reflux condenser closed with a calcium chloride tube. 500 cc. of sodium dried ether were then added and 500 grams of dry isopropyl bromide slowly run in through a dropping funnel. Care was taken to have all parts of the apparatus thoroughly dry. The magnesium was dried in a vacuum dessicator, the ether over bright sodium wire, and the isopropyl bromide over sodium sulfate. When about ten or fifteen cubic centimeters of bromide had been added, the reaction started without the aid of iodine or a water bath. Efficient stirring and cooling were maintained at all times throughout the experiment. Running water was used to cool the flask during the preparation of the Grignard reagent. When all of the bromide had been added, a water bath was placed under the flask and the contents gently refluxed for forty-five minutes.

The flask was then cooled by an ice and salt bath kept at minus five degrees and 143 grams of acetaldehyde were introduced. The low boiling point of acetaldehyde made it convenient to add it to the Grignard reagent by distillation. The dropping funnel was removed and a delivery tube introduced extending downward into the flask below the surface of the ether solution. The acetaldehyde was caused to bubble into the mixture by gentle warming of its container. Adding the acetaldehyde in the vapor state resulted in more efficient mixing. This was particularly desirable toward the end of the reaction and no doubt increased the yield.

When all of the acetaldehyde had been added, the product was decomposed by pouring over cracked ice, care being taken to keep the solution cold. The magnesium hydroxide was decomposed with hydrochloric acid. The neutral solution was extracted with ether four times, and the ether extract dried over sodium sulfate and distilled. The methyl isopropyl carbinol was dried over sodium sulfate and redistilled. It boiled at 110.5 degrees at 760 mm. Yield 200 grams. The refractive index was taken by means of an Abbe refractometer and was found to be 1.4095 at 20 degrees.

The alcohol was analyzed for carbon and hydrogen. Substance, 0.1027: CO_2, 0.2554; H_2O, 0.1265. Calculated for $C_5H_{12}O$: C, 68.1; H. 13.7; Found: C, 67.8; H, 13.7 Substance, 0.1134: CO_2, 0.2821; H_2O, 0.1404. Found: C, 67.9; H, 13.75.

Table number three shows the quantities of materials used in several experiments and the yields obtained. The theoretical yields in the first four experiments are based on the amount of acetaldehyde used since fewer moles of acetaldehyde than isopropyl bromide were taken. In the last experiment the percent yield is calculated on the basis of the moles of isopropyl bromide used. Approximately a one-fourth excess of magnesium was used in each experiment in order to increase the yield of Grignard reagent.

TABLE NO. III

Magnesium		Acetaldehyde		Isopropyl Bromide		Yield Theoretical	Yield Obtained	Per Cent
Gms.	Moles:	Gms.	Moles:	Gms.	Moles	: Gms.	Gms.	
123	5	145	3.25	500	4	286	200	70
318	13.8	400	9.09	1340	10.9	800	590	73.7
292	12.	400	9.09	1200	9.75	800	502	60.3
290	11.9	400	9.09	1190	9.67	800	520	65.
275	11.3	375	8.5	1000	8.13	727	475	65.3

Reaction of Sulfuric Acid on Methyl Isopropyl Carbinol.

10 gram portions of methyl isopropyl carbinol were added to 1.7 molecular equivalents of sulfuric acid under various conditions of concentration of acid, temperature and time. The reactions were carried out in a flask provided with a mercury sealed stirrer and a reflux condenser. At the end of each condensation, the products were poured into cold water and extracted with ether. The ether extract was washed with a dilute sodium bicarbonate solution and water, dried, and distilled.

Table four shows the results of these experiments.

TABLE NO IV

Grams of Alcohol	H_2SO_4 Sp.Gr.	Gms.	Temp. when Mixed	Temp. Heated	Time Heated Minutes	Grams $C_{10}H_{20}$	Percent $C_{10}H_{20}$	Grams higher Polymer
10	1.67	26	Room	80	20	6.0	74	
15	1.67	39	Room	100	30	7.5	62.5	
15	1.67	39	Room	80	40	7.0	60.	
10	1.67	26	Room	80	10	4.0	50.	
10	1.67	26	Room	100	10	3.7	46.	
10	1.67	26	Room	60	20	3.5	43.7	
10	1.67	26	50	80	20	5.5	68.	
10	1.67	26	50	8	20	5.0	62.	
10	1.77	26	50	80	20	5.0	62	2
10	1.77	26	35	50	20	5.0	62	2
10	1.77	26	Room	40	20	5.0	62	2
10	1.72	26	Room	40	20	0.0		
10	1.72	26	50	80	20	5.0	62	1
10	1.61	31	50	80	20	5.0	62	
10	1.67	39	50	80	20	5.5	68	
30	1.77	78	20	50	20	17.5	72	5
50	1.77	130	20	50	20	26.0	64	10

116.?

<u>Preparation of $C_{10}H_{20}$.</u> Methyl isopropyl carbinol was added to one and one-half times the molecular equivalent of sulfuric acid, specific gravity 1.67, in a three neck flask provided with a mercury sealed stirrer and a reflux condenser. The alcohol was introduced below the surface of the acid and the solution vigorously stirred. The temperature was raised to 80 degrees and held there for twenty-minutes. Some refluxing occurred. At the end of twenty minutes the flask was cooled and contents poured into ice cold water. The layer of hydrocarbon was separated and washed with water, dilute sodium bicarbonate solution, and water again and dried over calcium chloride. The water layer was extracted three times with ether. The ether extract was washed with dilute sodium bicarbonate and water and dried over calcium chloride. The ether was boiled off and the residue added to the hydrocarbon. This was carefully fractionated and redistilled from sodium. B.P. 155.8 degrees at 762.8 mm; d, $\frac{19.2^{\circ}}{4^{\circ}}$, 0.7715; N_d 20, 1.43576. Analysis: Substance, 0.1443; CO_2, 0.4518; H_2O, 0.1880. Calculated for $C_{10}H_{20}$; C, 85.62; H, 14.38. Found: C, 85.39; H, 14.58. Substance, 0.1339: CO_2, 0.4184; H_2O, 0.1728. Found: C, 85.2; H, 14.45.

TABLE NO.V

Grams of Methyl Isopropyl Carbinol	Grams of H_2SO_4 Sp.Gr. 1.67	Grams of $C_{10}H_{20}$	Percent Yield
62	140	28	56
65	150	38	72
50	130	30	74
88	230	40	62
65	150	35	67
50	130	31	75

Molecular Weight of Decene.

The molecular weight of the decene was determined by the cryoscopic method with a Beckman apparatus. The benzene was distilled from sodium. Small portions of decene were weighed in small sealed glass bulbs and the sealed bulbs dropped into the benzene and crushed with the stirrer. The results are given below:

TABLE NO. V (a)

Grams of Benzene	Grams of Decene	F.P. Lowering Degrees	Calculated Mol. Weight
21.837	0.2367	0.391	141.4
21.837	0.3361	0.540	140.7
21.837	0.4493	0.746	141.2
21.837	0.5828	0.991	137.9

Oxidation of Decene with Potassium Permanganate. 5 grams of decene and 15 grams of potassium permanganate were shaken together. The potassium permanganate was added in small portions and the flask kept cool in ice water. The odor of acetone was noticed. After the potassium permanganate was reduced the mixture was distilled and the first portion of water distillate, about 5 cc., collected separately. To this was added some para-nitrophenyl-hydrazine and a few drops of dilute hydrochloric acid to bring about solution. The solution was filtered and made alkaline with sodium acetate. Bright yellow crystals of para-nitrophenyl hydrazone acetone separated, and were filtered and re-crystallized from alcohol. Melting point, 144 degrees. A sample of the para-nitrophenyl hydrazone acetone was prepared from pure acetone. Melting point 145 degrees. Mixed melting point 144 degrees.

35 grams of decene were treated with potassium permanganate acidified with sulfuric acid. The potassium permanganate was added in small portions until 105 grams had been introduced. Carbon dioxide was evolved and oxidation was rapid. The colorless solution was distilled and the oil separated from the water layer. The aqueous solution was extracted with ether and the ether extract dried and concentrated. The residue was heated with para-tolouidine and a toluide, melting point 143 degrees, obtained.

3 cc. of the oil were treated with 3 grams of

semicarbazid sulfate in water and 3.4 grams of potassium acetate in alcohol. About 100 cc. of water were added and on standing over night a very small amount of semicarbazone separated. It was filtered off, dried, and re-crystallized from dry ether. Melting point 138 degrees. The greater portion of the oil did not react with the semicarbazid sulfate and was evidently unchanged decene.

<u>Preparation of Para-nitrophenylhydrazine.</u> 20 grams of para-nitraniline were dissolved in 42 grams of hot concentrated hydrochloric acid (37 percent) and the solution poured over a little cracked ice in a beaker. The beaker was placed in an ice and salt bath. When ice cold the para-nitraniline was diazotized with 12 grams of sodium nitrite in 20 grams of water. The sodium nitrite solution was added slowly and with vigorous stirring. When the diazotization was complete the solution was quickly filtered, while ice cold. It was then neutralized with a saturated sodium carbonate solution and diluted to 200 cc. This solution was then added slowly to 100 cc of ice cold potassium sulfite solution, to which 20 grams of potassium carbonate had been previously added. The potassium sulfite solution was prepared by dissolving 20 grams of potassium hydroxide in 100 grams of water, saturating with sulfur dioxide, and neutralizing with potassium carbonate. Then 20 grams of potassium carbonate were added. The potassium salt was sucked dry on a Buchner funnel and added to 80 cc of concentrated hydrochloric acid (37 percent) and 80 cc. of water and the mixture warmed over a steam bath until a deep orange solution was obtained. The solution was then cooled and saturated sodium carbonate added until only slightly acid, care being taken to keep the solution cold. Sodium acetate was then added until the solution was neutral. Free, para-nitrophenylhydrazine separated and was filtered off. It was re-crystallized from alcohol twice. Orange red crystals.Melting point 156 degrees. Yield, 2 grams.

<u>Ozonization of Decene.</u> 5 cc. of decene and 10 cc. of carbon tetrachloride were placed in the ozonization tube and surrounded by an ice and salt bath at -7 degrees. Ozone in oxygen was slowly passed through the solution for two hours. At the end of this time the ozonized decene was pale yellow. The quantity of ozone being formed was then determined by passing the ozone and oxygen into a five percent solution of potassium iodide for five minutes, and titrating the liberated iodine with standard sodium thiosulfate.

The ozonized decene was placed in a flask, 25 cc. of water added, and the mixture refluxed for one hour to decompose the ozonide. Gas was evolved during the refluxing and was passed into water. The water did not give an aldehyde test with Schiff's Reagent. After refluxing for one hour, the mixture was cooled and titrated with standard sodium hydroxide. The water layer was separated, extracted three times with carbon tetrachloride and the carbon tetrachloride solutions combined and dried over sodium sulfate.

This experiment was repeated a number of times, the carbon tetrachloride solutions combined and the water solutions combined.

The water solution, after titration was acidified and extracted with ether and the ether dried. The ether was distilled off and the residue fractionated in a small flask. The portion boiling below 100 degrees was acid, it dissolved in sodium hydroxide, reduced potassium permanganate and on boiling with mercuric chloride precipitated mercurous chloride. The higher boiling fraction was acid and it was gently boiled with para-tolouidine for an hour. The product was extracted with boiling alcohol and poured into 100 cc. of warm water. The water solution was rapidly concentrated to 15 cc. and filtered hot. A toluide separated on cooling, and further concentration yielded more toluide. It was re-crystallized twice from boiling water. Melting point, 146 degrees, and is therefore the toluide of acetic acid. These reactions showed the presence of formic acid and acetic acid.

The dry carbon tetrachloride solution was carefully fractionated in a specially built fractioning column. A fraction boiling at 42.1 to 42.4 degrees at 17 mm. was obtained.

d $\frac{19.2^{\circ}}{4^{\circ}}$, 0.8346; N_d^{20}, 1.41980.

The substance was analyzed for carbon and hydrogen.

[illegible] 7 14 [illegible]: C, 73.61; H, 12.36. Found: C, 73.64; H, 12.39.

Substance, 0.1859: CO_2, 4985; H_2O, 0.2001. Found C, 73.93;

1 7

Substance, 0.1859: CO_2, 4985; H_2O, 0.2001. Found C, 73.93;

H, 12.18.

Table VI shows the results of a number of ozonizations of decene. In each experiment 5 cc. of decene in 10 cc. of dry carbon tetrachloride were used and ozone passed through the solution for two hours. Assuming one double bond in $C_{10}H_{20}$, the calculated amount of ozone required is 1.322 grams. Because of the apparent stability of the decane toward ozone at least twice the calculated amount of ozone was used. To be certain that this was the case, the amount of ozone being formed was determined at the end of each ozonization.

TABLE NO. VI

Flowmeter Reading	Liters per hour	cc. of $Na_2S_2O_3$ 0.2978N	Grams of O_3 per hour	Percent of O_3 Volume	cc. of NaOH 0.5952N
4.2	13.2	12.1	1.04	4.1	18.4
3.8	13.0	14.8	1.26	4.7	16.2
4.2	13.2	18.0	1.54	5.8	17.6
4.2	13.2	15.2	1.30	4.9	15.5
4.2	13.2	18.4	1.57	5.9	15.6
4.0	13.1	17.5	1.50	5.7	16.1
4.0	13.1	17.5	1.50	5.7	17.9
4.2	13.2	18.1	1.55	5.9	19.0
4.2	13.2	18.4	1.57	6.7	16.3
4.0	13.1	17.2	1.47	5.6	16.0
4.0	13.1	17.1	1.46	5.6	17.8
4.0	13.1	16.5	1.41	5.3	18.3
4.2	13.2	18.4	1.57	5.9	17.4
4.0	13.1	17.8	1.52	5.8	17.8
4.0	13.1	17.5	1.50	5.7	16.1
4.2	13.2	18.1	1.55	5.9	16.9
4.2	13.2	15.8	1.35	5.1	15.6
4.2	13.2	16.1	1.38	5.2	17.8
4.0	13.1	16.1	1.38	5.2	15.6
4.2	13.2	16.2	1.39	5.3	15.6
4.2	13.2	18.2	1.55	5.9	17.2
4.0	13.1	17.8	1.52	5.8	16.2
4.0	13.1	17.7	1.51	5.7	16.7

<u>Determination of the Relative Amounts of Acetic Acid and Formic Acid Formed in Ozonization of Decene.</u> 5 cc. of decene in 10 cc. of dry carbon tetrachloride were ozonized at zero degrees for two hours. The flowmeter reading was 4.2. At the end of this time the solution was added to 25 cc. of water and refluxed for one hour. The total amount of acid formed on decomposition of the ozonide was then determined by titrating with standard sodium hydroxide. The carbon tetrachloride was then separated and the water layer extracted with carbon tetrachloride three times. The neutral water solution was then titrated with standard potassium permanganate.

Approximately one tenth normal potassium permanganate was prepared and standardized with weighed oxalic acid. The normality was found to be 0.1053. Since formic acid reduces potassium permanganate slowly in the cold, and the acid is too volatile to titrate hot, the amount of formic acid was determined by titrating sodium formate. Potassium permanganate is rapidly reduded by sodium formate in the cold. Manganese dioxide was formed and the normality of the potassium permanganate was only three-fifths of the value determined with oxalic acid. Its normality was therefore 0.0632.

The formation of manganese dioxide made the end point of the potassium permanganate difficult to detect. The potassium permanganate was added until a pink color was noticed. The quantities of potassium permanganate given in

Table VII are therefore high and this no doubt accounts for the higher concentration of formic acid. At least it is evident that formic acid and acetic acid are formed in about equal molecular quantities.

A sample of carbon tetrachloride was ozonized for two hours, refluxed with water for one hour, and titrated with standard sodium hydroxide. Two drops of sodium hydroxide produced a deep pink coloration with phenolthalein, showing that no acid is formed by the action of ozone on the carbon tetrachloride under the conditions of the experiment.

TABLE NO. VII

Sample:	cc. : CCl_4	cc. Decene	:cc. NaOH 0.6329N	:cc. $KMnO_4$ 0.0632N	:Moles Acetic Acid	:Moles Formic Acid
1	10		2 drops			
2	10	5	20.4	103.6	0.0063	0.0065
3	10	5	19.8	105.0	0.0059	0.0066
4	10	5	19.4	101.8	0.0058	0.0064

Oxidation of $C_7H_{14}O$ with Iodine and Bromine in Alkaline Solution. 3 drops of substance $C_7H_{14}O$ were added to 1 cc. of ten percent sodium hydroxide and 15 cc. of iodine solution (1 grsm I_2 + 5 grams KI in 15 cc. water). The mixture was warmed to 60 degrees and vigorously shaken. The odor of iodoform was very noticeable. This indicated that the substance $C_7H_{14}O$ was a methyl ketone.

14 grams of sodium hydroxide were dissolved in 123 cc. of water and 21 grams of bromine added with constant stirring. The temperature was kept below 2 degrees. When all the bromine had been added and the temperature was -2 degrees, 5 grams of $C_7H_{14}O$ were slowly introduced. The temperature did not rise above 0 degrees during the introduction of the substance $C_7H_{14}O$. Stirring was continued for one hour at this temperature, and then for three hours at room temperature. The solution was pale yellow and was then warmed to 60 degrees and stirred at this temperature for one hour. At the end of this time all color had disappeared. The mixture was steam distilled. Carbon tetrabromide came over first and then bromoform. When all the bromoform had been distilled off, the solution was acidified with sulfuric acid and the steam distillation continued. The water distillate was extracted with ether, the ether extract dried, and distilled. About 2 cc. of an acid boiling from 185 - 190 degrees was obtained.

The acid was treated with phosphorous pentachloride and the acid chloride was treated with an ether solution of para-tolouidine. This ether solution was washed with hydrochloric acid, to remove any excess tolouidine, and then with sodium bicarbonate solution and water. It was dried and concentrated. White crystals of acid toluide separated. After recrystallization they melted at 168 degrees. This experiment gave further proof that $C_7H_{14}O$ was a methyl ketone. The melting point of the p-tolouide from the acid formed by oxidizing this ketone does not give us much additional information, as it does not correspond to any value to be found in the literature. The acid $(CH_3)_2\underset{\substack{|\\ C_2H_5}}{C} - COOH$ should be synthesized for the purpose of obtaining its p-toluide for a mixed melting point determination.

Semicarbazone of Ketone $C_7H_{14}O$. To a mixture of 3 grams of semicarbazide sulfate in 10 cc. of water and 3.4 grams of potassium acetate in alcohol, were added 2 grams of the ketone and more water until the total volume was 100 cc. A precipitate formed immediately and increased on standing over night. The semicarbazone was filtered off and sucked dry. An attempt was made to recrystallize it from petroleum ether, but it was insoluble. The semicarbazone was washed with petroleum ether and dried. M.P. 158.

Preparation of 2,3, Dimethyl Pentanone-4[17]

Methyl Acetoacetate. To 615 grams of methyl acetate in a three-neck flask provided with a mercury sealed mechanical stirrer and reflux condenser were added 63 grams of sodium. The sodium was finely divided by shaking while melted under hot xylene, and then placed under benzene. Care was taken to avoid adding benzene to the mixture, although about 1 cc. may have gotten in. When all of the sodium had dissolved, 50 percent acetic acid was slowly added until the solution was neutral. 500 cc. of saturated sodium chloride solution was then added and the mixture extracted with ether. The ether extract was dried and distilled in. 100 grams of methyl acetoacetate was obtained. B.P. 69, degrees, 22 mm. The low yield was probably due to the presence of much methyl alcohol present in the methyl acetate.

Methyl Acetacetic Methyl Ester. To 240 grams of absolute methyl alcohol in a three-neck flask provided with a mercury sealed mechanical stirrer and a reflux condenser, 19.3 grams of sodium were added. When all the sodium was in solution, 100 grams of methyl acetoacetate were added with stirring. The solution was warmed and 134 grams of methyl iodide[18] added slowly over a period of one hour.

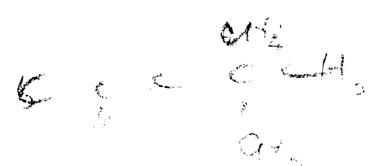
17. Willstaetter & Hatt - Ann., 418, 151
18. Prepared according a method by Adams, Kamm and Marvel, Univ. of Illinois Bulletin, 16, No. 43. (June 1919) Organic Chemical Reagents.

Refluxing was continued for another hour, when the solution was neutral to litmus. The alcohol was then distilled off, the temperature not rising above 65 degree. Considerable sodium iodide precipitated and was removed by filtering. The solution was transferred to a Claisen flask and distilled under vacuum. 85 grams of ester were obtained, boiling at 85 - 88 degrees at 37 mm.

Methyl Isopropyl Acetacetic Methyl Ester. 85 grams of the methyl ester of methyl acetoacetic acid were warmed on a steam bath with 120 grams of isopropyl iodide in a three-neck flask provided with a mercury sealed mechanical stirrer and reflux condenser. Into the solution was introduced 14.3 grams of sodium in methyl alcohol so slowly that the solution never gave a strongly alkaline reaction. 1 cc. was added every three minutes until about two-thirds of the sodium methylate had been introduced. Then 1 cc. was added every four minutes until about 10 cc. were left. This was added at the rate of 1 cc. every five minutes. The introduction of the sodium required about ten hours. The solution was gently refluxed all the time and the alkalinity tested every thirty minutes. When all of the sodium had been introduced refluxing was continued for twenty minutes. At the end of this time the solution was neutral. It was cooled, washed with 5 percent sodium hydroxide to remove any unchanged ester, and then with water. It was shaken with sodium sulfate and distilled in vacuum. B.P. 106 degrees at 33 mm. Yield, 36 grams.

<u>2, 3, Dimethyl Pentanone-4 Semicarbazone.</u> 36 grams of the methyl ester of methyl isopropyl acetacetic acid and 54 grams of constant boiling hydrobromic acid, specific gravity 1.49, with enough glacial acetic acid to bring about complete solution were gently refluxed for sixty-three hours. The mixture was then distilled and the ketone separated.

3 grams of semicarbazide sulfate in water were added to 3.4 grams of potassium acetate in alcohol and 2 grams of ketone introduced. The mixture was diluted with about 100 cc. of water and vigorously shaken. Semicarbazone precipitated and on standing over night more of the precipitate formed. The semicarbazone was separated, dried, and recrystallized from ether. M.P. 111 degrees.



Preparation of Isopropyl Iodide. Isopropyl iodide was prepared according to a method given by Adams, Kamm and Marvel[18] for the preparation of normal propyl iodide.

240 grams of redistilled isopropyl alcohol were dried over sodium sulfate. The alcohol was then placed in a one-liter round bottom flask and 36 grams of red phosphorus and 30 grams of white phosphorus were added. The white phosphorus was washed in a beaker of isopropyl alcohol before adding it to the dry alcohol. The flask was provided with a reflux condenser and was warmed over an oil bath. 300 grams of iodine were added over a period of thirty minutes by dropping small portions through the top of the condenser.

When all of the iodine had been added, the mixture was refluxed for ten minutes and then distilled, the temperature of the oil bath being about 130 degrees. The iodide was transferred to a separatory funnel and washed twice with water. It was then dried over sodium sulfate. Yield 317 grams. (81 percent). Some hydrogen iodide was evolved during the reaction. This indicated that the alcohol was not free from water and no doubt accounts for the low yield of halide.

18. Loc. cit.

Preparation of Decane. 40 grams of decene were hydrogenated[19] over .5 grams of platinum catalyst at room temperature. The quantity of hydrogen taken up was in the ratio of one mole of hydrogen for one mole of decene. This was determined by having calibrated the hydrogenation apparatus with a weighed sample of pure benzaldehyde in alcohol. The decane was filtered from the catalyst through a hardened filter on a Gooch crucible. It was washed with sulfuric acid, specific gravity 1.84, sodium bicarbonate solution, and water, and dried over calcium chloride. It was distilled from sodium. B.P. 155 - 156 degrees. $D\,\frac{19.2^{\circ}}{4^{\circ}}$, 0.7525. N_d^{20}, 1.42284.

The decane was analyzed for carbon and hydrogen. Substance, 0.2394: CO_2, 0.7450; H_2O, 0.3317. Calculated for $C_{10}H_{22}$: C, 84.40, H, 15.59. Found: C, 84.87; H, 15.50. Substance, 0.1394: CO_2, 0.4303, H_2O, 0.1917 Found: C, 84.19; H, 15.4.

19. The apparatus used for hydrogenation was purchased from the Standard Colorimeter Co., East Moline, Ill. It is described by Adams and Voorhees, Org. Syn. 8, 10.

Molecular Refraction of the Decene, Decane and Ketone.

In order to determine whether the physical properties of the decene, decane and ketone as determined corresponded with the empirical formulae, the molecular refractions of these substances were calculated from observed data by means of the Lorentz-Lorenz formula. The results of these calculations are given in the table below. The difference in each case is so small as to leave no doubt concerning the empirical formulae.

TABLE NO. VIII

	Density	Refractive Index	Molecular Refraction From Observed Data	Molecular Refraction From Empirical Formula	Difference
$C_{10}H_{20}$	0.7715	1.43576	47.47	47.74	0.27
$C_{10}H_{22}$	0.7725	1.42284	47.983	48.130	0.15
$C_7H_{14}O$	0.8346	1.41980	34.578	34.508	0.07

APPARATUS

The Ozonizer and Ozonization Apparatus.

The ozonizer used was a modified form of a laboratory ozonizer described in the literature by Smith[20]. Availability of materials and ease in operation were responsible for a few changes.

A ten gallon zinc ice cream can, 54 cm. high and 30 cm. in diameter, was used in place of a battery jar. Rubber stoppers, so cut that no weight was borne by the inlet tubes, were used as bases for the Berthelot tubes. The stoppers were set in warm asphalt and were firmly held in place when the asphalt had cooled.

The Berthelot tubes were made as described by Smith, except the central core was omitted. In place of this core, the Berthelot tubes were filled with distilled water within 4 cm. of the top and wires extended below the surface of the water. The zinc can also contained water within 4 cm. of the top, but cooling coils were omitted.

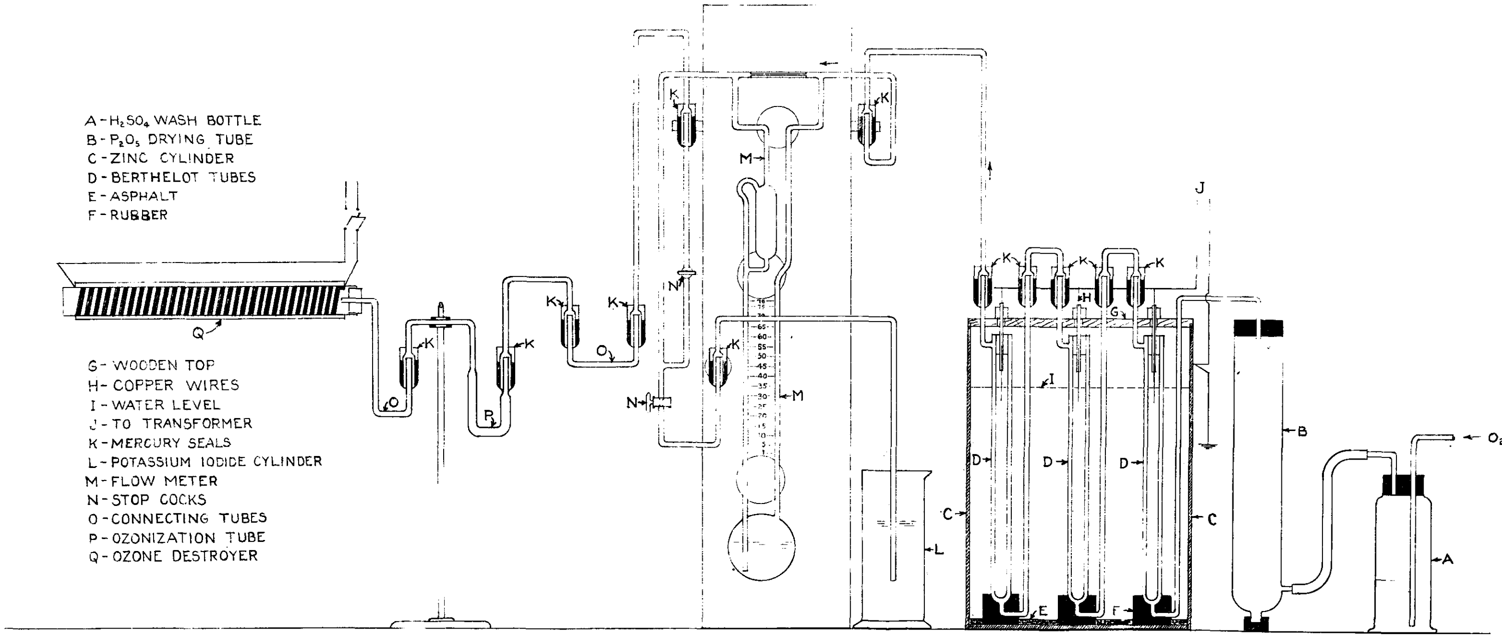
The ozonizer was connected with a flowmeter by mercury sealed cups. Two stopcocks were sealed to the exit tube of the flowmeter which permitted the ozone to be passed into the substance in the ozonizing tube or into the potassium iodide solution.

20. Smith, J. Amer. Chem. Soc., 47, 1844 (1925)

It was found convenient to employ a U tube provided with cups for mercury seals as a container for the samples to be ozonized. This type of tube could easily be cleaned and dried and could be easily kept at zero degrees.

Ozone which did not react with the sample was destroyed by passing through a glass tube 98 cm. long and heated to about 250 degrees. This tube was prepared by taking an ordinary combustion tube and wrapping it with one thickness of asbestos paper saturated with sodium silicate. 40 feet of Chromel-A ribbon, 1/8 of an inch wide and 0.01 of an inch thick, having a resistance of 0.424 ohms per foot, was tightly wrapped around the asbestos. Then the ribbon was tightly wrapped with three thicknesses of asbestos paper, saturated with sodium silicate. This provided sufficient insulation to give a temperature of about 300 degrees at the center of the tube. The terminals of the resistance ribbon were connected through a switch to a 110 volt line.

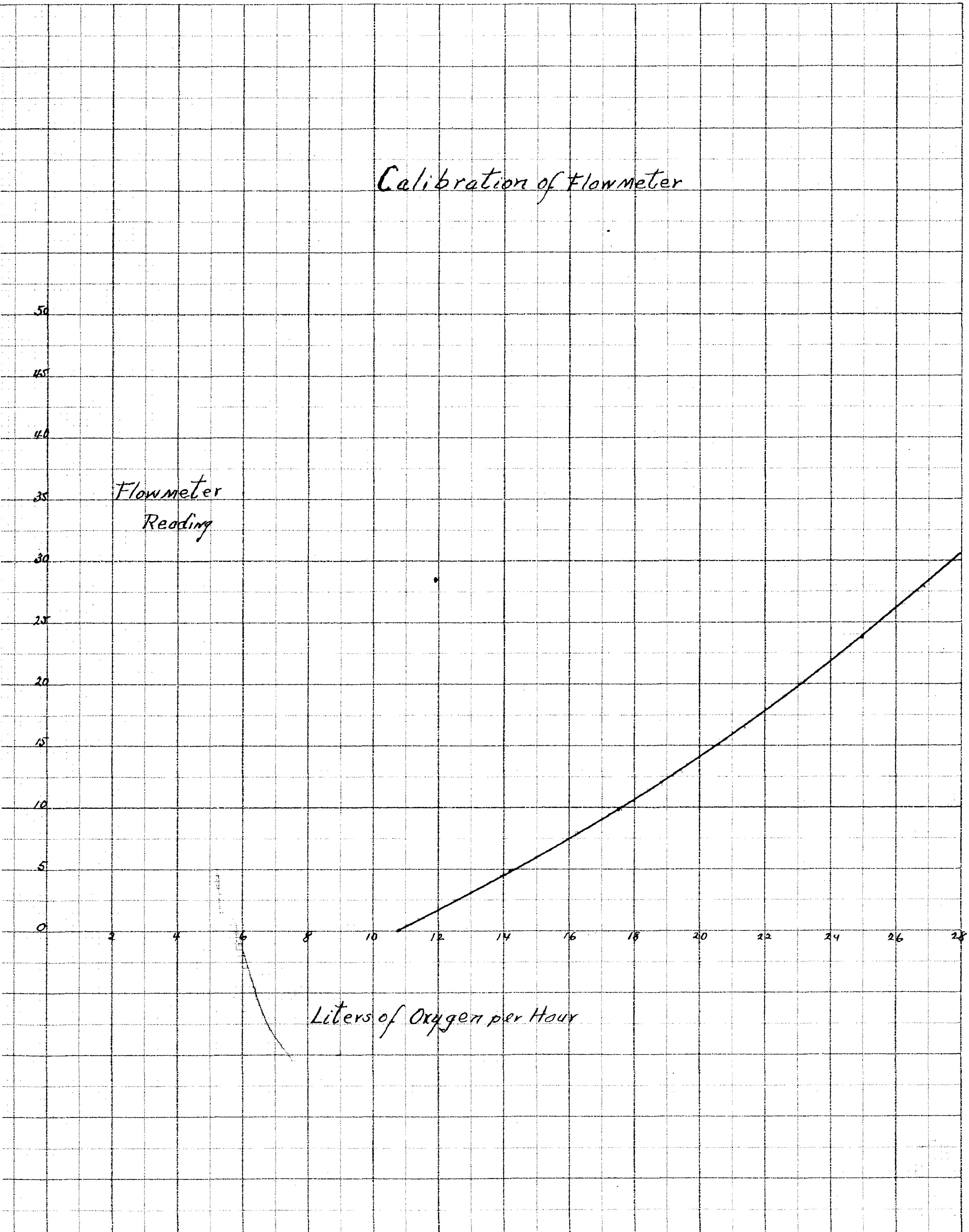
The transformer used operated upon a 110 volt and 60 cycle primary current. The voltage in the secondary was 10,000.


A - H_2SO_4 WASH BOTTLE
B - P_2O_5 DRYING TUBE
C - ZINC CYLINDER
D - BERTHELOT TUBES
E - ASPHALT
F - RUBBER
G - WOODEN TOP
H - COPPER WIRES
I - WATER LEVEL
J - TO TRANSFORMER
K - MERCURY SEALS
L - POTASSIUM IODIDE CYLINDER
M - FLOW METER
N - STOP COCKS
O - CONNECTING TUBES
P - OZONIZATION TUBE
Q - OZONE DESTROYER
O_2

<u>Calibration of Flowmeter.</u> In order to determine the volume of oxygen passing through the ozonizer, a flowmeter was sealed into the system and connected to the exit tube of the ozonizer. The flowmeter was equipped with a millimeter scale and the volume of oxygen passing through the system at different readings determined. This was accomplished by inverting a two liter volumetric flask in a trough of water and allowing the oxygen to pass through ozonizer and flowmeter and displace the water. The temperature of the water, the temperature of the oxygen, the barometric pressure, the flowmeter reading and time required to displace two liters of water were recorded. When the corrected volumes were obtained for several readings a curve was plotted which made it possible to determine the volume of oxygen and ozone passing through at any scale reading.

TABLE NO. IX

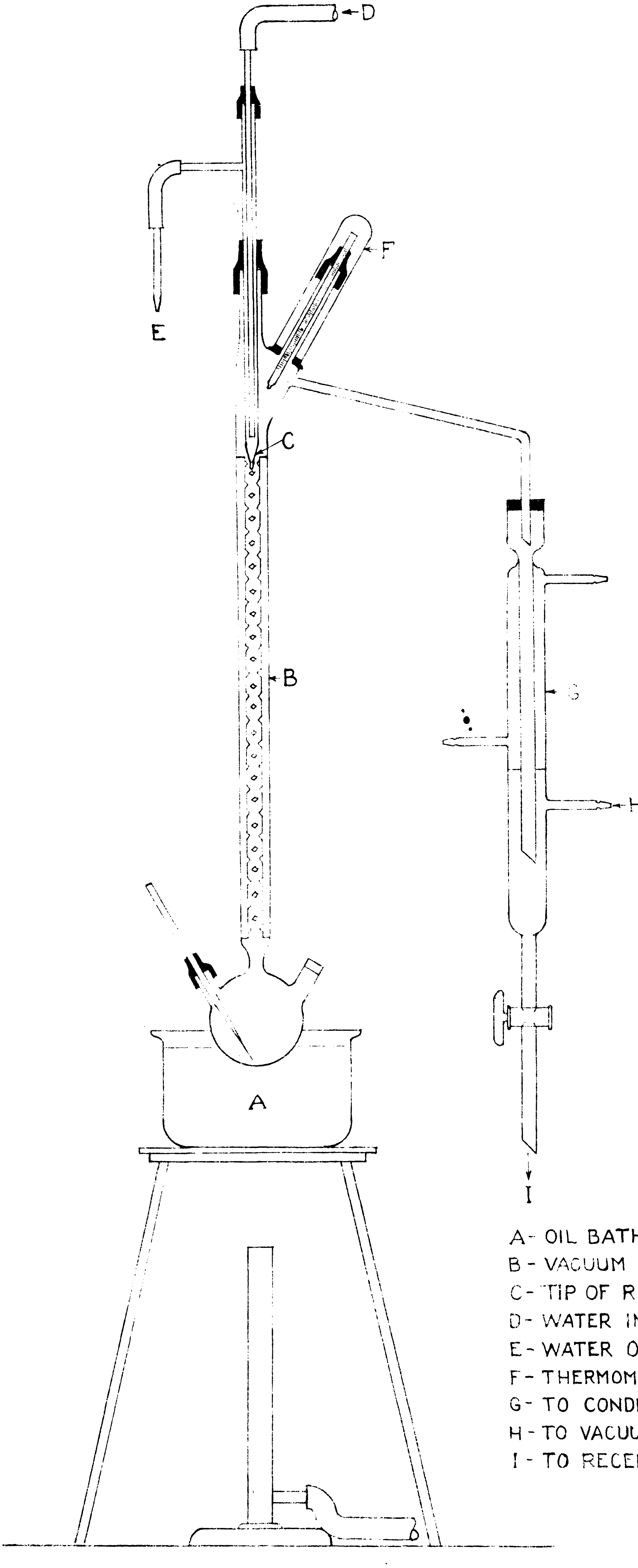
Flowmeter Reading	Temperature of Oxygen	Barometric Pressure	Time (Minutes)	Corrected Vol. O_2 cc.	Liters O_2 per hour
0	23	762.8	9.95	1787.2	10.78
5.0 4.8	23.5	762.8	7.58	1790.2	14.17
9.8 9.6	23	762.8	6.16	1795.0	17.48
24.0 23.8	23.5	762.8	4.32	1791.1	24.90


Calibration of Flowmeter
Flowmeter
Reading
50
45
40
35
30
25
20
15
10
5
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Liters of Oxygen per Hour

Fractional Distillation Apparatus.

The fractional distillation apparatus used in the purification of the ketone was a modification of one described by Cooper and Fasce[21]. It was especially designed for the fractionation of small quantities of liquids in vacuo, although it could be used for fractionating liquids under atmospheric pressure. The accompanying figure shows the apparatus in some detail.

21. Cooper and Fasce, Ind. and Eng. Chem, 20, 420 (1928)



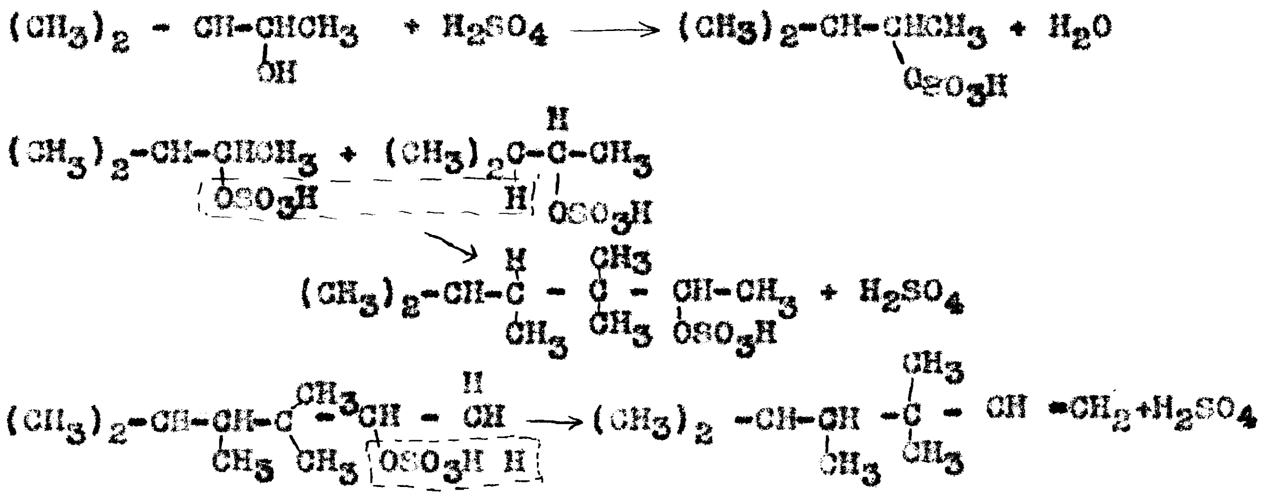
A- OIL BATH
B - VACUUM JACKET
C - TIP OF REFLUX CONDENSER
D - WATER INLET
E - WATER OUTLET
F - THERMOMETER JACKET
G - TO CONDENSER
H - TO VACUUM PUMP
I - TO RECEIVER

DISCUSSION

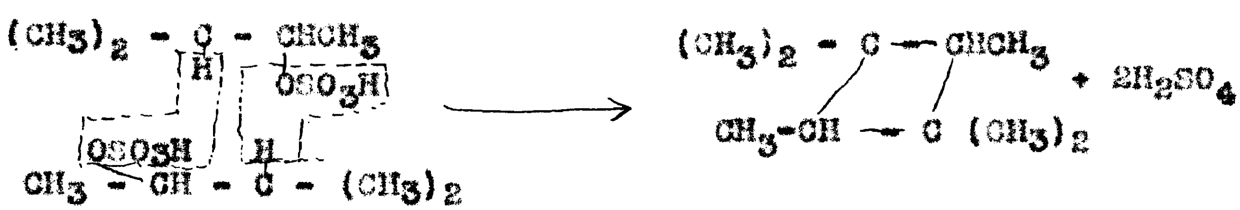
The constitution of the decene has not been fully established. A consideration of the mechanism of the reaction of methyl isopropyl carbinol with sulfuric acid would be of service in considering the different possible structures of this decene.

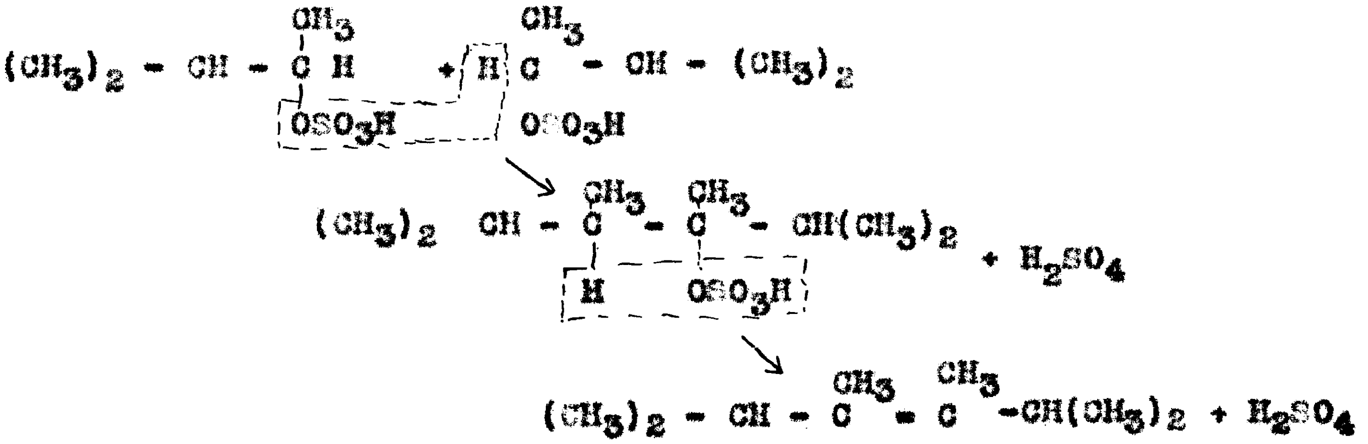
Sulfuric acid may have first added to the alcohol to form the acid ester. Assuming this to be the case, condensation of two molecules of ester to form the decene may have occurred in any one of the ways shown below:

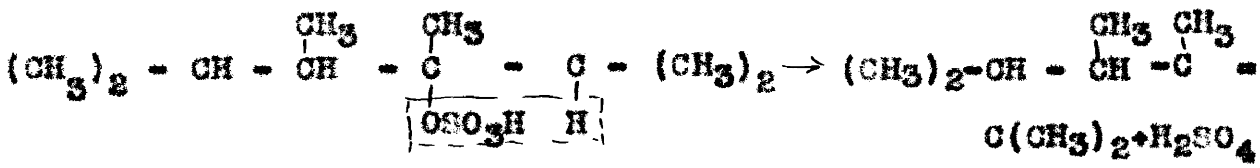
(1)

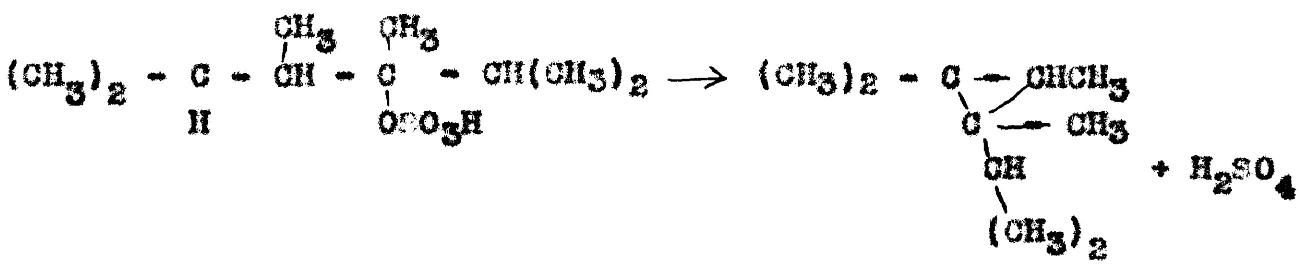


(2)



(3) 

(4) 

(5) 

Trimethylethylene might have been first formed, and then the addition of sulfuric acid have taken place. The formation of decene could have occurred in one of the following ways:

(6) $$(CH_3)_2 - \underset{\boxed{H}}{C} - \underset{\boxed{OH}}{CH} - CH_3 \xrightarrow{H_2SO_4} (CH_3)_2 - C = CHCH_3 + H_2O$$

$$(CH_3)_2 - C = CHCH_3 + H_2SO_4 \longrightarrow (CH_3)_2 - \underset{OSO_3H}{C} - CH_2CH_3$$

$$(CH_3)_2 - \underset{\boxed{OSO_3H}}{C} - CH_2CH_3 + CH_3 - \underset{\boxed{H}}{CH} - \underset{OSO_3H}{C} - (CH_3)_2$$

$$\longrightarrow (CH_3)_2 - \underset{C_2H_5}{C} - \overset{CH_3}{\underset{\boxed{H}}{C}} - \underset{\boxed{OSO_3H}}{C} - (CH_3)_2 + H_2SO_4$$

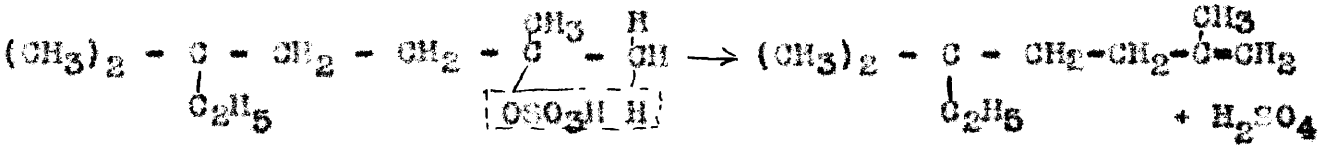
$$\longrightarrow (CH_3)_2 - \underset{C_2H_5}{C} - \underset{CH_3}{C} = C(CH_3)_2 + H_2SO_4$$

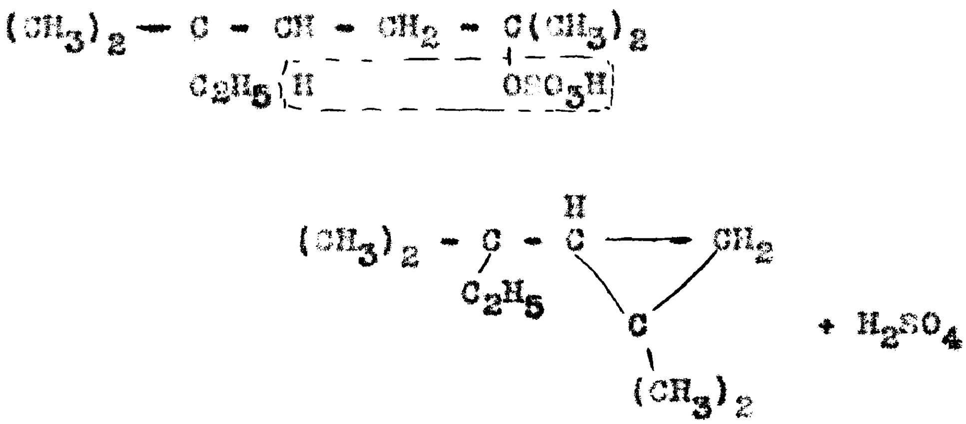
(7) $$(CH_3)_2 - \underset{C_2H_5}{C} - \underset{CH_3}{CH} - \overset{CH_3}{\underset{\boxed{OSO_3H}}{C}} - \overset{H}{\underset{\boxed{H}}{CH}} \longrightarrow (CH_3)_2 - \underset{C_2H_5}{C} - \underset{CH_3}{CH} - \overset{CH_3}{C} = CH_2 + H_2SO_4$$

(8) $$(CH_3)_2 - \underset{C_2H_5}{C} - \boxed{OSO_3H + H} - \overset{H}{\underset{H}{C}} - CH_2 - \underset{OSO_3H}{C} - (CH_3)_2$$

$$\longrightarrow (CH_3)_2 - \underset{C_2H_5}{C} - CH_2 - \underset{\boxed{H}}{CH} - \underset{\boxed{OSO_3H}}{C} - (CH_3)_2 + H_2SO_4$$

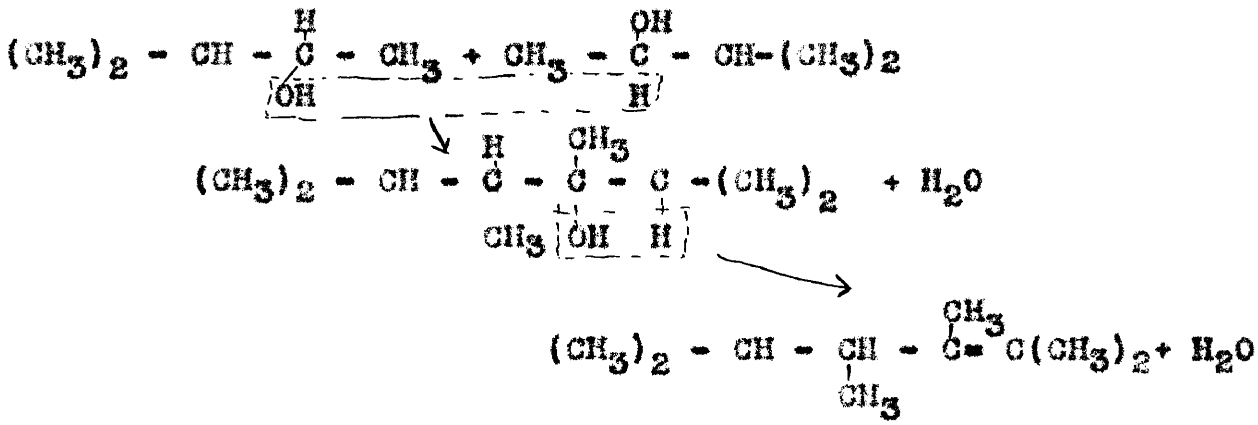
$$\longrightarrow (CH_3)_2 - \underset{C_2H_5}{C} - CH_2 - CH = C - (CH_3)_2 + H_2SO_4$$

(9) 

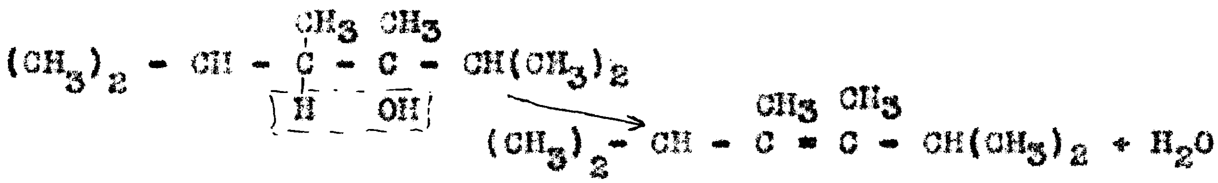
(10) 

According to Norris[22] condensation may have occurred by one molecule of alcohol condensing with a second as the result of the elimination of an hydroxyl group from one and a hydrogen atom from the other. The tertiary alcohol formed in this way loses a second molecule of water. This type of reaction is considered in the following equations:

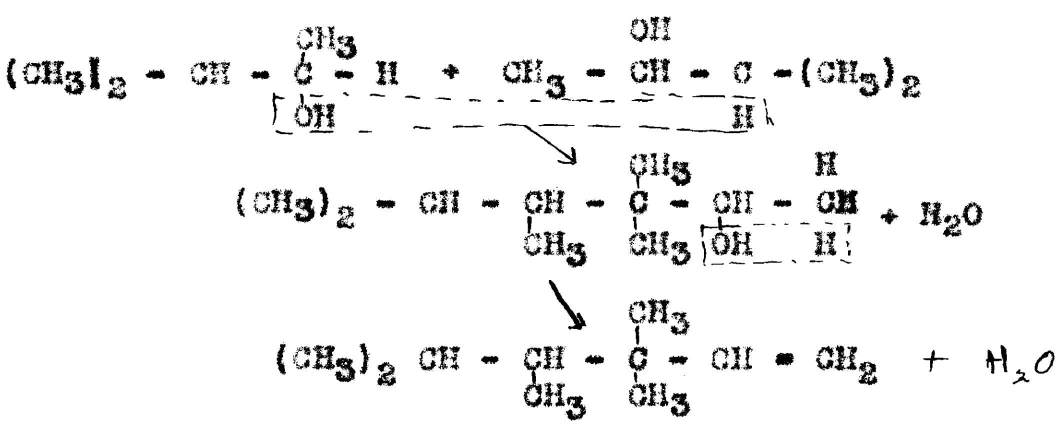
(11)



(12)

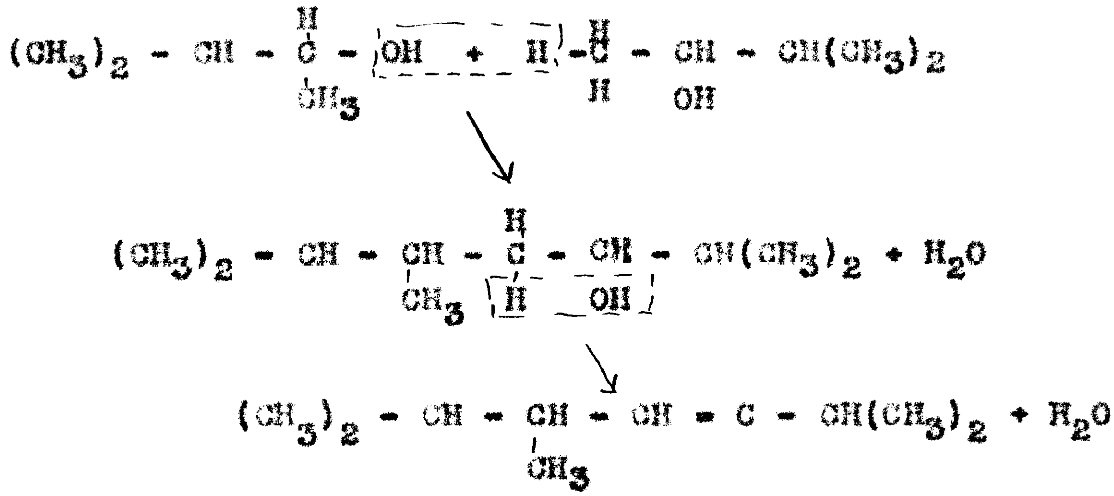


(13)

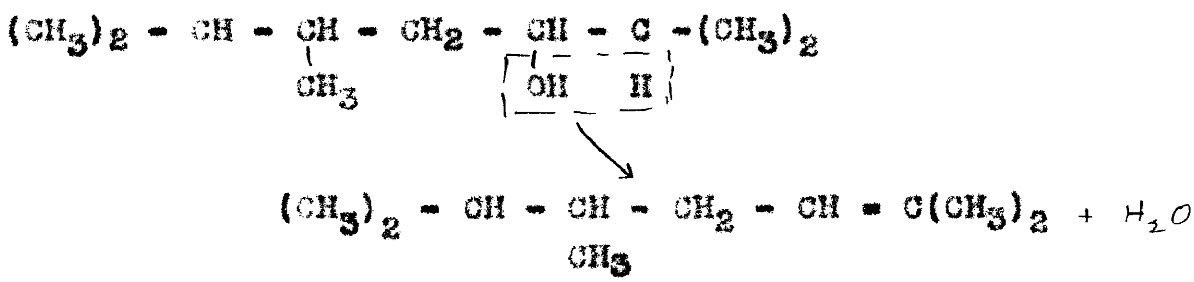


22. Norris and Joubert, Loc. cit.

(14)



(15)



An examination of these reactions in the light of the experimental data results in the elimination of all but two.

On oxidation and ozonization of the decene, no test for aldehyde was obtained. Therefore, all the reactions giving a decene with hydrogen on a carbon holding a double bond must be eliminated. These are reactions number (1), (7), (8), (9), (13), (14) and (15).

The molecular refraction calculated from observed data checked with the molecular refraction calculated for $C_{10}H_{20}$ having a double bond. The polymerization could not, then, have taken place according to reactions number (2), (5) or (10).

On ozonization of the decene, a ketone of seven carbon atoms was obtained. Reactions number (3), and (12) are therefore eliminated.

This leaves reactions number (4), (6) and (11) to be considered, and the same decene is formed in (4) and (11). It is evident that the decene obtained must be either $(CH_3)_2-CH-\underset{CH_3}{CH}-\underset{CH_3}{C}=C(CH_3)_2$ or $(CH_3)_2-\underset{C_2H_5}{C}-\underset{CH_3}{C}=C(CH_3)_2$. Upon treatment with potassium permanganate or ozone ketones would be formed having the formulae $(CH_3)_2-\underset{C_2H_5}{C}-COCH_3$ and $(CH_3)_2-CH-\underset{CH_3}{CH}-COCH_3$. The former ketone was obtained and identified by the melting point of its semicarbazone. Therefore, the decene $(CH_3)_2-\underset{C_2H_5}{C}-\underset{CH_3}{C}=C(CH_3)_2$ must have been formed. The behavior of the decene toward ozone cannot be fully explained. It seems evident, however, that either rearrangement occurred or that an isomeric decene was present.

The other possible ketone, $(CH_3)_2CH-\underset{CH_3}{CH}-COCH_3$ was proved to be absent by the preparation of this substance and its semicarbazone which did not correspond with the properties of the semicarbazone made from the ketone obtained by ozonization.

Edgar and Calingaert[23] have shown that certain definite relationships exist between the structure and

23. Edgar and Calingaert, J. Amer. Chem. Soc. <u>51</u>,1540 (1929)

physical properties of isomeric paraffins. Thus a methyl group in the 2-position decreases the specific gravity and refractive index below that of the normal hydrocarbon while a methyl group in the 3-position increases these properties above that of the normal hydrocarbon. When two groups are adjacent the values of the various functions are always quite high relative to the normal.

hydrogenation of the decene must be either,

$$\begin{array}{lllllllllllllllllll} & & CH_3 & & & & & & & & & & & & & & & & \\ 1\ CH_3 & - & C & - & CH & - & C & - & CH_3 & \text{or} & CH_3 & - & CH & - & CH & - & CH & - & C - CH \\ & & C_2H_5 & & CH_3 & & CH_3 & & & & & & CH_3 & & CH_3 & & CH_3 & & CH_3 \\ CH_3 & - & C & - & CH & - & C & - & CH_3 & \text{or} & CH_3 & - & CH & - & CH & - & CH & - & C - CH_3 \quad \text{or} \\ & & C_2H_5 & & CH_3 & & CH_3 & & & & & & CH_3 & & CH_3 & & CH_3 & & CH_3 \end{array}$$

a mixture of both. Either of these decanes should have a greater density and higher index of refraction than normal decane.

The decane prepared has higher values for these functions than normal decane.

SUMMARY

1. A decene (or a mixture of isomeric decenes) has been prepared by the treatment of methyl isopropyl carbinol with sulfuric acid.

2. The presence of 2,3,4 trimethyl, 4-ethyl pentene-2 has been established.

3. The decane (or the mixture of isomeric decanes) derived from the decene has been prepared by hydrogenation.

4. A pure ketone $C_7H_{14}O$ has been obtained by ozonization of the unsaturated hydrocarbon and its semicarbazone prepared.

5. The ketone $C_7H_{14}O$ has been shown to be a methyl ketone, and has been oxidized with bromine in alkaline solution to an acid.

6. The p-toluide has been prepared from this above mentioned acid, but more work is necessary to determine its identity.

7. The ketone has been shown not to be 2,3 dimethyl pentanont-4, and the decene cannot therefore be 2,3,4,5 tetramethyl hexene-2, one of the two possibilities according to our theoretical considerations and experimental work.