

**A STUDY OF THE ACTION OF SULPHURIC ACID
ON SECONDARY BUTYL ALCOHOL**

BY

FLETCHER P. VEITCH, JR.

*Clem
LD
3231
.M70d
Veitch,
F.P.
Folio*

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of the requirements for the degree of
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HISTORICAL

The object of this investigation was to determine whether dipolymers of butene-2 could be produced by the action of sulphuric acid on secondary butyl alcohol, and if so to establish the structure of the polymer or polymers thus produced so as to accumulate more evidence as to the mechanism of the polymerization of olefins. Under the conditions employed, approximately sixteen per cent of the secondary butyl alcohol was converted to a dimer, (3,4,dimethylhexene-2) and eighteen per cent to di-secondary butyl ether.

Cooke¹, Wheeler², and Kline³, working in this laboratory, have investigated the structures of the dimers formed by the action of seventy-five (75) per cent sulphuric acid on methyl isopropyl carbinol. Rose⁴, also of this laboratory, has investigated the constituents of diamylene, a by-product formed in the chlorination of the pentane fraction of petroleum, by polymerization of the amylenes.

During the past three years, Whitmore⁵⁻²⁰ and his students have investigated the structures of a number of olefins resulting from the dehydration of alcohols, and have proposed a mechanism to explain the polymerization

of olefins. This mechanism will be discussed in detail later in this paper.

Ipatjew and Sdzitowecy²¹ found that upon passing the vapors of secondary butyl alcohol through a copper tube filled with zinc chloride and heated to 450°C., there was obtained butylene, isobutylene, methyl ethyl ketone and a liquid unsaturated hydrocarbon which they did not identify. Upon passing secondary butyl alcohol over reduced copper at 160 - 300°C. they obtained methyl ethyl ketone and water. When nickel was substituted for the copper, water and hydrocarbons which they did not identify, were produced instead of methyl ethyl ketone.

Marcel and Guerbet²² found that upon heating secondary butyl alcohol and its sodium derivative at 200°C. polymerisation occurred with the formation of a dissecondary butyl alcohol. The authors assigned the structure of 3-methylheptanol-5 to the dimer so produced on the evidence that oxidation of the alcohol yielded a ketone which did not form an addition product with sodium bisulfite. This ketone upon oxidation yielded a mixture of acids which were separated by fractional distillation. From determinations of the per cent of barium in the barium salts of these acids the authors claimed the presence of acetic, hexanoic, propionic, and methyl ethyl acetic acids. According to these authors the formation of these acids is

accounted for by the structure assigned to the ketone.

R. V. Wheeler and W. L. Wood²³ investigating the thermal decomposition of normal olefins found that heating alpha and beta butene together in a quartz tube at 600°C. gave rise to the formation of cyclohexene and methyl-cyclohexene. Benzene and toluene were also found present in small amounts as was methyl-cyclohexadiene and cyclohexadiene.

C. B. Heisig²⁴ has found that butene-2 as well as certain other olefins is polymerized by the action of Radon. The amount of polymer obtained was small, however, and no attempt was made to investigate the nature of the compounds produced.

L. F. Marek and H. K. Flege²⁵ noted the production of about five (5) per cent of polymer in their experiments upon the "Catalytic Vapor-Phase Hydration of Butene-2 Under High Pressures". Cuprous chloride, thorium, and cupric phosphate, were used as catalysts at temperatures from 427 to 538°C and pressures of 3000 to 5000 pounds per square inch. The nature of the polymer was not investigated.

C. G. Coffin, H. S. Sutherland, and O. Maass²⁶ investigating the action of hydrochloric acid upon the three butenes, found that in the case of butene-1 and butene-2, polymers were produced as well as the expected butyl chlorides. Molecular weight determinations, boiling

points and halogen analyses indicated that these polymers were octyl chlorides. The structure 3-methyl-4-chloromethylhexane is suggested for the polymer from butene-1 because it was observed to decompose readily to an octene and HCl. The octene thus formed was assigned the structure 2-ethyl 3-methyl pentene-1. The polymer from butene-2 is assigned the structure of a 3,4,dimethyl 2-chloro hexane. This compound is supposed to result from the action of hydrochloric acid upon 3,4,dimethyl hexene-1. No proof that these are the structures of the polymers is advanced by the authors.

DISCUSSION

Several theories have been advanced to explain the polymerization of olefins. Chief among these are the theories of Berthelot²⁷, McCubbin and Adkins²⁸, Norrell²⁹, Norris and Joubert³⁰, Hunter and Yohe³¹, and Whitmore and co-workers.^{18,19} These theories have been summarized and discussed by Rose⁴, and with the exception of that of Whitmore et. al. will not be discussed here.

The theory of Whitmore will be outlined here because it seems to be the most generally applicable of the mechanisms advanced. The following assumptions form 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 shared an electron pair with the electronegative group is thus left with only a sextet of electrons.

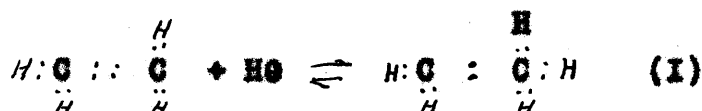
4. This deficiency of two electrons may induce a

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 application of the theory to the polymerization of olefins makes necessary the introduction of further assumptions; essentially as follows.

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

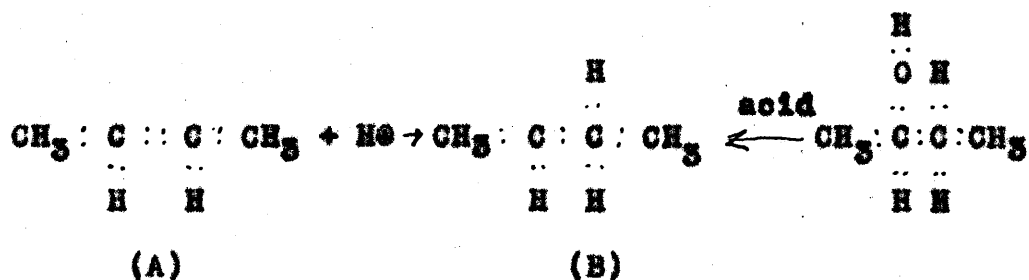


This leaves one of the carbons as a positively charged atom, capable of undergoing the reactions of a positively charged atom, namely:

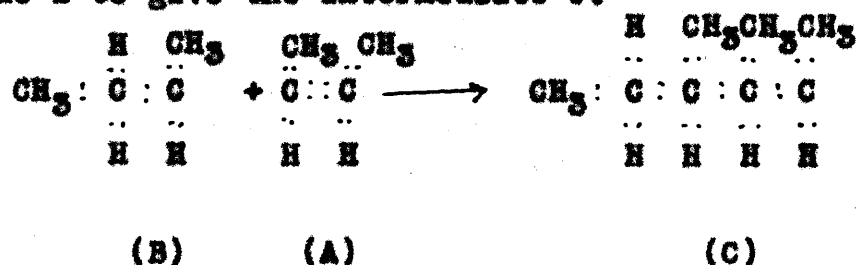
1. Union with a negative ion.
2. Reversal of the process as indicated in reaction 1, to give the same or a new olefin.
3. Rearrangement of the carbon skeleton, followed by the loss of a proton, to give a new olefin.
4. Polymerization. This involves the addition of the positive organic fragment to another molecule of olefin in the same manner that the positive proton added to the first molecule of olefin.

A larger positive fragment results which may undergo the above changes.

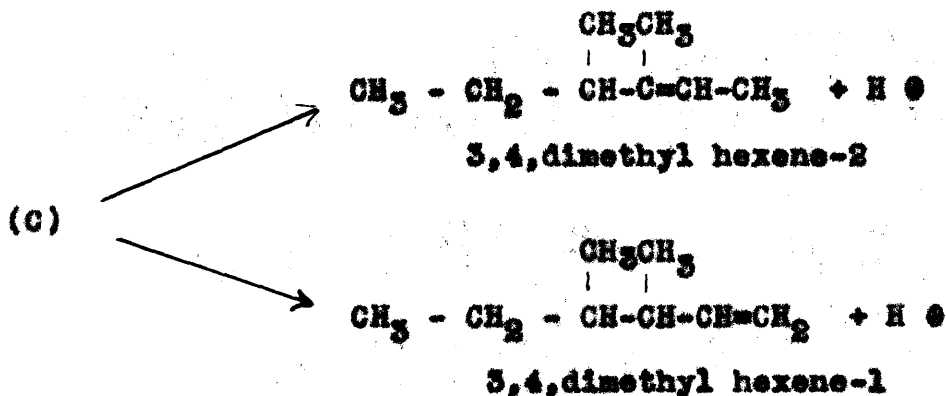
According to this mechanism the polymerization of butene-2 would proceed in the following manner. The addition of a hydrogen ion to butene-2 gives a positively charged secondary butyl group. This same product is obtained by treating secondary butyl alcohol with acid.



The positive secondary butyl group, B can add to butene-2 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 the adjacent methyl group, or from the carbon holding a tertiary hydrogen, liberate a proton and establish a true olefinic linkage.



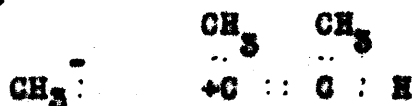
Since tertiary hydrogens are more liable than are the hydrogens of a methyl group, the rearrangement of (C) should take place mainly to form 3,4,dimethyl hexene-2. It is not unlikely though that the carbon in (C) which shared but six electrons might attract a pair of electrons from the adjacent methyl group thus giving rise to a small amount of 3,4,dimethyl hexene-1.

In this investigation, however, results seemed to indicate that 3,4, dimethyl hexene-2 is the only octene produced by the action of sulphuric acid on secondary butyl alcohol, under the conditions employed in this work.

A mechanism recently proposed by Kline^{3,52} to explain the polymerisation of olefins, utilizes the theory of electronegativity advanced by Kharasch⁵³. Kline views the formation of olefinic polymers as a sort of a chain reaction analogous to the polymerization of ethylene⁵⁴. Carothers⁵⁴ previously held this view, which is essentially that collision of an activated molecule of monomer with an

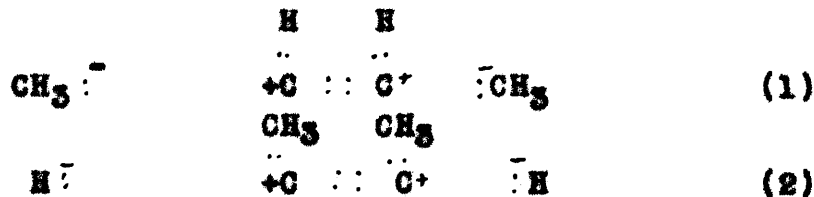
unactivated molecule of monomer results in the formation of an activated dimer which may then react with another unactivated molecule of monomer and so on. The activating energy may persist in the polymeric chain until it has grown to considerable length. The presence of a strongly electronegative group in the molecule is believed to produce rearranged products.

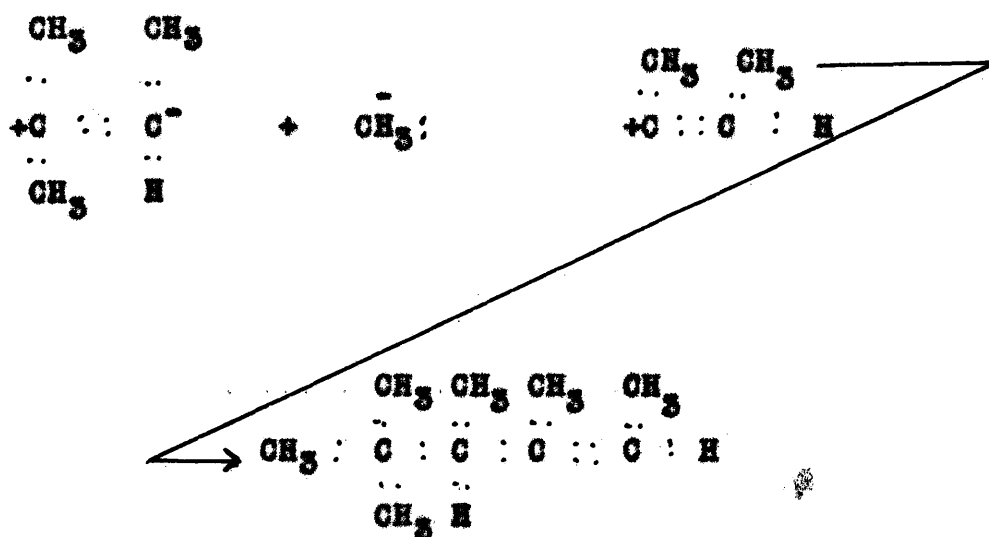
According to Kline, Trimethylethylene behaves as though it were activated, due to the relative electronegativity of the adjacent carbon atoms involved in the following manner,



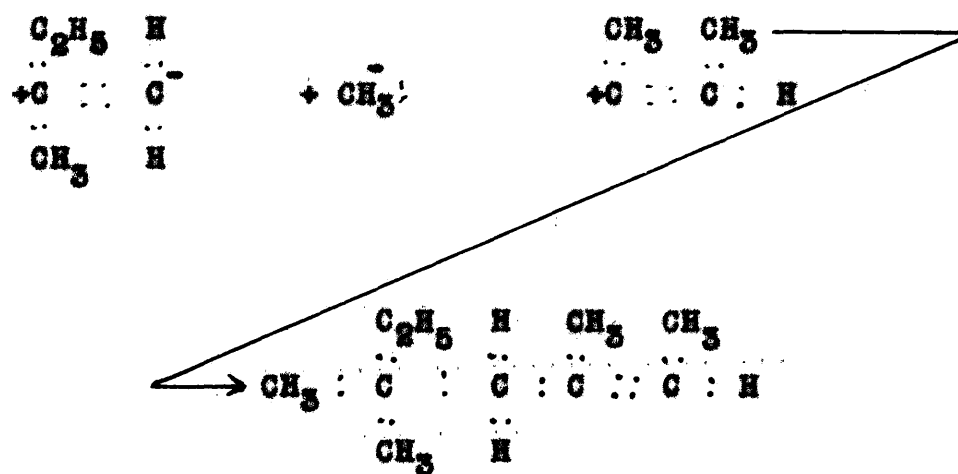
The addition of these two fragments to the double bond of trimethylethylene or of 1-methyl-1-ethylethylene, the two olefins formed by dehydration of methyl isopropyl carbinol, can then take place to form 3,4,5,5 tetramethylhexene-2 and 3,5,5 trimethyl-heptene-2. These two products have been shown to be produced by the action of sulphuric acid on methyl isopropyl carbinol.

Butene-2 according to this mechanism should activate as in (1) rather than as in (2).



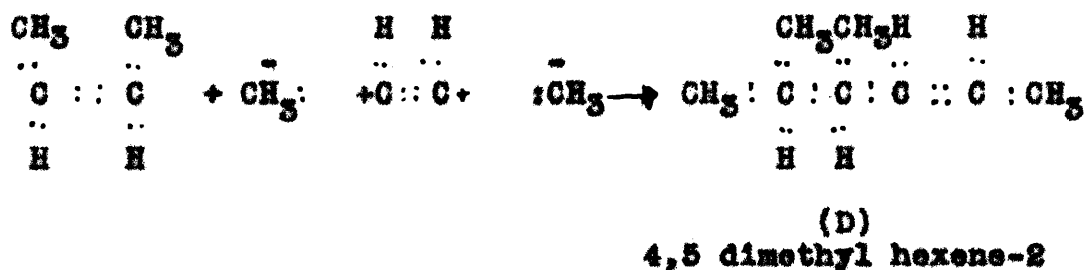


3,4,5,5-tetramethyl Hexene-2



3,5,5-trimethyl heptene-2

Activation as in (1) and subsequent addition of this fragment to unactivated butene-2 should lead to the formation of 4,5,dimethyl hexene-2. (D)



No formation of 4,5,dimethyl hexene-2 (D) was observed, in this investigation, by the action of sulphuric acid on secondary butyl alcohol. In order to account for the formation of 3,4, dimethyl hexene-2 found to result from the action of sulphuric acid on secondary butyl alcohol, the activation of butene-2 must take place as in (2). This, however, is inconsistent with the relative electronegativities of hydrogen and methyl.

EXPERIMENTAL

Effects of Conditions on Yield of Polymer from Secondary Butyl Alcohol

Cooke, Wheeler, and Kline (loc. cit.) working in this laboratory, have found that by treating methyl isopropyl carbinol with seventy-five (75) per cent sulphuric acid for twenty (20) minutes at 80°C., and atmospheric pressure, a mixture of dimers (decenes) is produced.

We have found that with secondary butyl alcohol these same conditions failed to produce any dimer (octene). Varying the concentration of the acid from 50 to 100 per cent, the time of the reaction from twenty (20) minutes to forty-eight (48) hours, and the temperature from 25 to 100°C. at atmospheric pressure yielded no appreciable quantities of octene. Concentrations of acid greater than ninety (90) per cent resulted in the formation of a quantity of high boiling material the components of which were not identified, but which probably consists of a mixture of higher polymers. The failure of the conditions employed by Cooke, Wheeler, and Kline to produce any octene was ascribed to the fact that at temperatures at which the

velocity of the reaction



becomes appreciable, the butene-2, formed by the dehydration of the secondary butyl alcohol, is driven from the reaction mixture as a gas before polymerization can take place.

The effect of keeping the butene-2 in contact with the acid by pressure was then investigated. 100 grams of secondary butyl alcohol were placed in a sealed tube with 176 grams of eighty-three (83) per cent sulphuric acid and heated at 80°C. for one hour. The oily layer which separated on top of the reaction mixture was separated, washed with sodium bicarbonate solution to remove acid, dried over anhydrous sodium sulfate, and distilled through a glass column, 10 mm. in diameter, and 25 cm. long, filled with glass beads. 10 grams of material, which from its distilling range 120-125°C. was thought to be dipolymer, was obtained. This is a yield of thirteen (13) per cent of the theory.

The effects of acid concentration, temperature, and time of reaction on the production of dimer in a closed system was further investigated with a view to increasing the yield. Since no suitable method was available to insure the mixing of the butene vapors with the sulphuric acid, dependence for the formation of the polymer was placed entirely

on time, temperature, and pressure to perform the desired reaction.

In this work an electrically heated, lead lined, steel pressure autoclave of about one gallon capacity, was used as a reaction vessel. The temperature of the reaction vessel was thermostatically controlled. The procedure followed was the same in all cases. Certain quantities of alcohol and acid were placed in the autoclave and heated at the designated temperature for the stated time. The autoclave was allowed to cool, opened, and the hydrocarbon layer syphoned off. The hydrocarbon layer was then washed with a saturated solution of sodium bicarbonate to remove acid, then with water and finally dried over anhydrous sodium sulfate and distilled through a short column (previously described). The results of this investigation are best summarized in Table I.

TABLE I
Effects of Conditions on Yield of Polymer from Secondary
Butyl Alcohol

Alcohol gms.	Conc. acid Wt. %	Acid used Gms.	Time hrs.	Temp. °C.	Distillate		Yield calc. as octene %
					B. P. 110-125 gms.	above 125 gms.	
200	85.5	200	1	98	21	5	14.0
200	78.5	200	1	105	19	25	9.5
200	78.5	200	1	98	10	5	6.6
200	78.5	200	1	92	18	15	9.0
200	75.0	200	1	80	17.5	72	28.0
400	75.0	1660	28	80	68.5	70	22.8
800	75.0	1660	48	80	188.0	100	36.0
800	75.0	1660	68	80	188.0	150	36.0

Of the conditions investigated, seventy-five (75) per cent acid at 80°C for forty-eight (48) hours gave the best yield of dipolymer. Under these conditions the formation of dimer is not very rapid. (16 per cent in 48 hours). The formation of higher polymers by polymerization of the dimer is much more rapid as evidenced by the fact that boiling the dimer in the presence of even a small amount of acid converts it to a mixture of higher polymers.

Purification and Fractionation of the Octene
Mixture

2.5 kilos of material distilling between 110 and 125°C. (a) were prepared from 6 kilos of secondary butyl alcohol. This product was refluxed over metallic sodium for fifty (50) hours to remove any alcohol present, and then distilled from the sodium through the column already described. 2 kilos of distillate (b) distilling between 116 and 125°C. were obtained. This distillate (b) was fractionated at the Bureau of Standards through the courtesy of Dr. S. T. Schicktans. The still used has been fully described by Schicktans³⁵. The results of this fractionation are given in Table II.

TABLE II

Fractionation of distillate (b)

Fraction #	Total volume cc.	Cottrell b.p. °C.	Barometric pressure inches of Hg	Refractive index n _D ²⁵
1	54	108.3	29.56	1.4068
2	109	109.9	29.56	1.4098
3	187	111.95	29.52	1.4113
4	240	112.95	29.46	1.4126
5	294	114.25	29.42	1.4142
6	352	114.55	29.46	1.4145
7	405	114.60	29.49	1.4152
8	460	115.5	29.47	1.4152
9	526	115.32	29.48	1.4155
10	582	115.5	29.48	1.4155
11	635	115.55	29.63	1.4156
12	694	115.7	29.63	1.4156
13	751	115.85	29.60	1.4155
14	825	116.65	29.56	1.4152
15	875	116.90	29.56	1.4142
16	946	118.10	29.58	1.4136
17	1007	120.05	29.65	1.4114
18	1067	120.00	29.65	1.4101
19	1141	120.60	29.67	1.4082
20	1199	121.05	29.76	1.4061
21	1257	121.40	29.83	1.4046
22	1331	121.50	29.86	1.4032
23	1385	121.65	29.92	1.4017
24	1422	122.0	29.98	1.3992
25	1485	122.1	29.98	1.3975
26	1551	122.2	30.04	1.3963
27	1607	122.2	30.00	1.3952
28	1667	122.3	29.91	1.3945
29	1722	122.35	29.86	1.3937
30	1776	122.45	29.84	1.3933
31	1829	122.5	29.79	1.3932
32	1879	122.55	29.77	1.3931
residue	2179	---	---	1.4118

Refractive Index

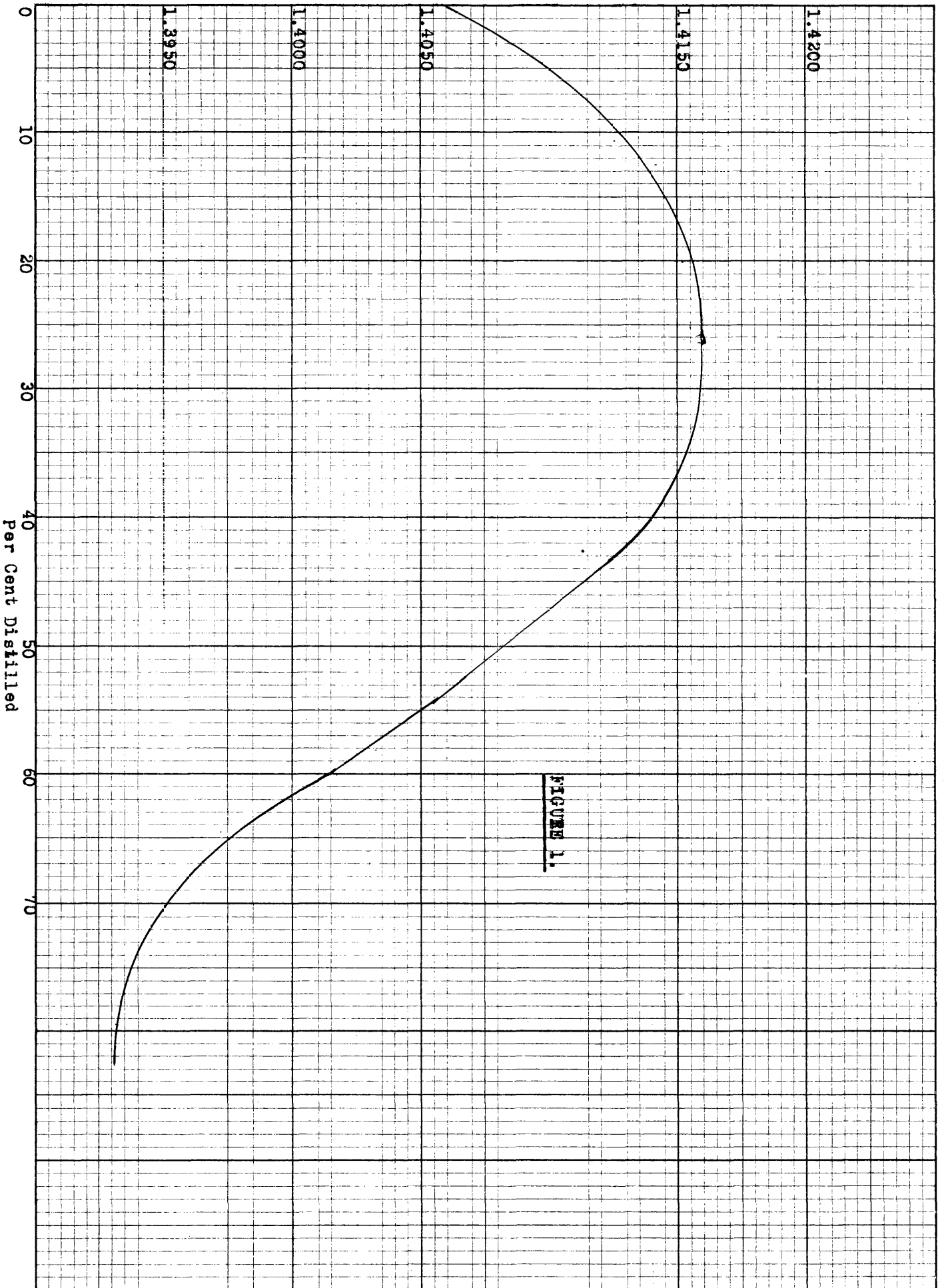


FIGURE 1.

Ozonolysis of Low Boiling Fractions of Distillate (b)

The curve resulting from plotting refractive index against per cent distilled is shown in Figure 1. This curve indicates that there are at least two substances present in distillate (b). Fractions 7-14, Table II, were combined, subjected to the action of ozonized oxygen and the fragments formed by the decomposition of the ozonide identified. The ozonizer used was the same as that used by Cooke, Wheeler, Kline and Rose (1906. cit.), and generated ozone at the rate of 0.0584 to 0.0415 mol per hour when oxygen was supplied at the rate of 16.5 liters per hour. The amount of ozone being generated was determined by passing the ozonized oxygen into five (5) per cent potassium iodide for five minutes, acidifying with hydrochloric acid and titrating the liberated iodine with standard thiosulfate.

Fractions 7 - 14, ⁴¹⁸419 cc (Table II) were ozonized in portions of fifty-six (56) grams each in 180 cc of ethyl acetate as solvent. The ozonization was carried out in a specially constructed flask having a bubbler tube sealed to the top. The flask was connected to the ozonizer by means of a mercury sealed cup, and was immersed in a mixture of carbon tetrachloride and chloroform maintained

at -15 to -25^o C. by means of solid carbon dioxide. The ozonized oxygen was bubbled through the solution for the time theoretically required as indicated by the ozone determination described above.

The Products of Ozonolysis

The ozonide was decomposed by the method of Whitmore and Church⁷ except that the solvent was not removed from the ozonide before decomposition. This procedure obviated the danger of explosive decomposition of the ozonide and gave satisfactory results.

The water layer from the decomposed ozonide gave a strong aldehyde reaction with Fehlin aldehyde reagent, but gave a negative test for formaldehyde with resorcinol. The aldehyde present was proved to be acetaldehyde by the formation of a p-nitro-phenyl hydrazone m.p. 125.5-126°C. (corr.) A mixed melting point of this derivative with the p-nitro phenyl hydrazone prepared from pure acetaldehyde showed no depression of the melting point. Further examination of the water layer failed to reveal the presence of appreciable quantities of any other substances.

The ethyl acetate layer gave a strong aldehyde reaction, which later developments showed to be due to acetaldehyde. No test for formaldehyde was obtained with resorcinol.

The ethyl acetate layer was dried over anhydrous sodium sulfate and the ethyl acetate removed from the products of decomposition of the ozonide by fractionating through a 20 inch Widmer column. The high boiling material (o)

left in the distilling flask (250 cc) was transferred to a specially constructed pyrex still pot which was sealed to a Fedbielniak¹⁴ column. The distillation was carried out at atmospheric pressure at the rate of 0.1 cc per minute. The results of the distillation are given in Table III.

TABLE III

Fractionation of Material (c)

Charge 250 cc

Fraction #	Total volume cc	Temp. °C (a)	Refractive index $n_{D^{25^{\circ}C}}$
1	10	79.0	1.3761
2	20	93.5	1.3797
3	30	110.0	1.3882
4	40	116.0	1.3929
5	49	116.0	1.3929
6	59	122.0	1.3941
7	69	123.5	1.3941
8	79	123.5	1.3946
9	89	125.0	1.3946
10	99	125.0	1.3949
11	109	125.0	1.3949
12	119	125.0	1.3956
13	129	125.0	1.3956
14	140	125.0	1.3956
15	150	126.0	1.3956
16	160	126.0	1.3956
17	170	126.0	1.3956
18	180	126.0	1.3956
19	190	128.5	1.3956
20	200	137.5	1.3969
21	210	170.5	1.4189
22	220	180.0	1.4194
23	224	189.0	1.4291
residue	5	---	----
Total	254		

(a) The temperature of the distilling vapors was determined by means of a triple junction copper-advance thermocouple placed in a re-entrant thermocouple well at the top of the column. At the rate of distillation used in this fractionation, temperature indications are inaccurate.

The refractive indices and also the distilling temperatures (keeping in mind the lack of exactness of these) remain fairly constant for fractions 4 to 11 (79 cc) and for fractions 12 to 19 (81 cc), indicating that in these fractions the distillate was fairly pure or was a fairly uniform mixture of two or more components.

Purification of Material (c)

Acetic acid was found to be present in all fractions of the distillate due to the oxidation of a small amount of acetaldehyde in the original charge. Accordingly fractions 1 to 11 (Table III) (109 cc.) were combined, refluxed with twenty (20) per cent sodium hydroxide for four and one-half (4½) hours, and the oily layer steam distilled from the alkaline solution. The oily layer of this steam distillate was separated, dried over anhydrous sodium sulfate and distilled through a short column (loc. cit.). The entire amount of liquid, 50 grams, distilled at 116° C. The material obtained by combining fractions 12 to 19 inclusive (Table III), washing with a saturated solution of sodium bicarbonate, then with a little water, drying over anhydrous sodium sulfate and distilling had the same

physical properties as the material obtained from fractions 1-11 inclusive. The total amount of material (d) obtained from fractions 1-19 (Table III) was 100 grams.

This material, (d), was found to have the following physical constants.

Cottrell boiling point; 116.2°C at 758 mm.;
Refractive index, n_D^{18} 1.4000; Density at 25°C . 0.812.

Identification of Material (d)

The material (d) gave no test with Fuchsian aldehyde reagent but did give a positive iodoform test by the method of Fuson³⁷, which establishes the material as a methyl ketone. Since acetaldehyde is the only other product of the decomposition of the ozonide, the original octene must have the structure $\text{R} - \text{C} = \text{CH} - \text{CH}_3$ and the ketone obtained must be a six carbon methyl ketone.

The physical properties of (d) agree more closely with those of methyl secondary butyl ketone than with those of the other three possible methyl ketones. This is shown in Table IV.

TABLE IV

Physical Properties of Methyl Butyl Ketones

Ketone	b.p. ^{°C.}	Density	Refractive index $n_{20}^{20°C}$
Methyl n-butyl	127.2	0.830 0 ^{°C.}	----
Methyl sec.-butyl	117.8	0.815 20 ^{°C.}	1.3990
Methyl iso-butyl	119.0	0.803 20 ^{°C.}	1.3959
Methyl tert.-butyl	106.0*	0.826 0 ^{°C.*}	-----

* Values from Beilstein. Other values from Int. Crit.Tables.

The methyl ketone, b.p. 116.2^{°C.} (d) obtained in this work yielded a 2,4, dinitrophenyl hydrazone¹⁶ melting at 71.2^{°C.} (corr.) Pure methyl secondary butyl ketone prepared by an acetoacetic ester synthesis yielded a 2,4, dinitrophenylhydrazone melting at 71.2^{°C.} (corr.) A mixed melting point of this derivative and the corresponding derivative prepared from the unknown methyl ketone (d) showed no depression, thus establishing the identity of (d) and methyl secondary butyl ketone.

Preparation of the 2,4,-dinitro-phenylhydrazones³⁸
of the Methyl Ketone (d), b.p. 116.2°C.

2.0 grams of 2,4, dinitro-phenylhydrazine and 1.5 grams of the methyl ketone (d) were placed together in a flask with 100 cc of ninety-five (95) per cent alcohol and heated to boiling on the steam bath. The mixture was allowed to cool for one minute, at the end of which time 2.0 cc of concentrated hydrochloric acid were added to the solution and the solution boiled for an additional two minutes. The crystals which separated out on cooling were filtered off and recrystallized from a little ninety-five (95) per cent alcohol. The yield was 2.0 grams (71.5% of theory) of material melting at 71.2°C. (corr.). Further recrystallizations of this derivative failed to raise the melting point.

Synthesis of Pure Methyl Secondary
Butyl Ketone

1. Preparation of ethyl acetoacetic ester³⁹ 750
grams of ethyl acetate and 50 grams of clean thinly sliced sodium were placed in a 2-l. round-bottom flask fitted with an efficient reflux condenser closed by a calcium chloride tube, and warmed on the steam bath until the

reaction started. Heating was then discontinued until the reaction had subsided, after which the mixture was again heated until all of the sodium had reacted.

The reaction mixture was poured slowly into a well shaken solution of 110 grams of ninety-eight (98) per cent sulphuric acid and 600 grams of water, which mixture had been cooled to 10°C. During the acidification the temperature was maintained below 25°C. by cooling in an ice bath when necessary.

After the acidification the two layers were separated and the ester layer subjected to distillation from a steam bath through a bead column one and one-half (1½) feet in length. The crude ester left in the distillation flask was removed, allowed to cool to room temperature, and washed with a saturated solution of sodium bicarbonate. The crude washed product was transferred to a Claisen flask with a fractionating side arm, and distilled under reduced pressure. 150 grams of ester boiling at 79°C at 18 mm. pressure was obtained.

2. Preparation of ethyl methyl acetoacetate. 400 cc. of absolute alcohol were placed in a three necked one liter round bottom flask fitted with an efficient mechanical stirrer, a reflux condenser closed by a calcium chloride tube, and a dropping funnel. The flask was arranged for

heating on a steam bath. 18 grams of clean thinly sliced metallic sodium were then added to the alcohol. When the sodium had all reacted, 110 grams of ethyl acetoacetate was added, the stirrer started and the solution heated to gentle boiling. 120 grams of methyl iodide was added to the boiling solution over a period of two hours. Refluxing and stirring were continued for eight hours after this addition.

The reaction mixture was removed from the flask and washed with sufficient water to remove the sodium iodide present. Alcohol and water were removed from the ester by distillation from a steam bath through a short column filled with glass beads. The crude product was transferred to a Claisen flask with fractionating side arm and distilled under reduced pressure. The yield of product boiling at 80 to 85°C. at 14 mm. pressure, was 71 grams.

3. Preparation of ethyl methyl ethyl acetoacetate.

This preparation was carried out in the same manner as described in the preparation of ethyl methyl acetoacetate. 11.5 grams of sodium were reacted with 250 cc. of absolute alcohol. To this was added 71 grams of ethyl methyl acetoacetate. The solution was brought to boiling and 54 grams of ethyl bromide was added to the boiling solution with stirring over a period of one and one-half hours. Stirring

and refluxing were continued for eight hours after the addition of the bromide. After removal of alcohol from the crude ester by distillation through a short column, the ester was distilled under reduced pressure in a Claisen flask with fractionating side arm. 20 grams of material boiling at 198°C. at 761 mm. pressure was obtained.

4. Preparation of methyl secondary butyl ketone.

20 grams of ethyl methyl ethyl acetoacetate was stirred at room temperature with 150 cc of five (5) per cent sodium hydroxide for four hours. The aqueous solution was then transferred to a flask fitted with a separatory funnel and a large bent glass tube leading to a condenser set for distillation. 15 cc of fifty (50) per cent sulphuric acid was then added slowly through the separatory funnel. When the evolution of carbon dioxide had ceased the mixture was steam distilled. The water layer of the steam distillate was steam distilled several times to recover as much of the ketone as possible. The combined ketone fraction was washed four times with one-third of its volume of concentrated calcium chloride solution, dried over anhydrous calcium chloride, filtered and distilled. 10 grams of methyl secondary butyl ketone boiling at 116.0°C. were obtained. The refractive index

of this material was n_D²⁵ 1.3998, and its density was 0.812 at 25°C.

Further proof of the identity of (d) and methyl secondary butyl ketone was obtained by subjecting (d) to a hypobromite oxidation. An acid was produced by this treatment, the physical properties of which and the melting point of the amide of which checked with the literature values given for dl-methyl ethyl acetic acid, the acid which should be produced by hypobromite oxidation of methyl secondary butyl ketone.

Hypobromite Oxidation of Methyl Ketone (d)

33.0 grams of sodium hydroxide and 280 cc of water were placed in a one liter flask equipped with an efficient mechanical stirrer, and the solution cooled to 0°C. in an ice-salt bath. To the well stirred solution were added 15.4 cc of bromine through a separatory funnel, at such a rate as to keep the temperature below 10°C. The solution was then cooled to 0°C. and 10 grams of the methyl ketone (d) were added through the separatory funnel, keeping the temperature below 10°C. After the solution was decolorised (one hour) it was stirred for three hours at room temperature. The flask was then fitted with a

condenser for distillation and heated to steam distill the bromoform and carbon tetrabromide. When these two substances had been distilled off, the mixture remaining in the distillation flask was allowed to cool to 50°C. and 40 cc of concentrated sulphuric acid was added through the separatory funnel. The flask was then heated until all of the insoluble material had distilled. The insoluble material in the steam distillate was separated and dried over calcium chloride. The dried material was distilled through a column 20 x 8 mm. filled with glass beads. 7 grams of an acid boiling point 178°C., refractive index n_{25}^{25} 1.4050; density 25°C 0.938, were obtained.

Preparation of the Amide of the Acid Resulting from Hypobromite Oxidation of the Methyl Ketone (d)

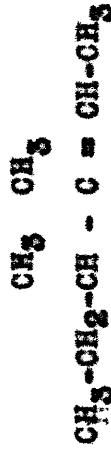
One gram of acid was refluxed with 2 grams of thionyl chloride for thirty minutes on a steam bath. The cooled residue was added slowly and with shaking to 5 cc of ammonium hydroxide maintained at 0°C. by an ice and salt bath. The crystals which were formed were filtered off and recrystallized from a little water. The crystals melted at 110.9°C. (corr.) and further crystallization failed to raise this melting point.

Preparation of the p-Phenylphenacyl Ester⁴² of the
Acid Resulting from Hypobromite Oxidation of the
Methyl Ketene (d)

0.5 gram of acid was treated with 5 cc of 1 normal sodium hydroxide and 10 cc of alcohol added to the solution. 1.375 grams of p-phenylphenacyl bromide were added to the mixture and the whole refluxed on a steam bath for one hour. The crystals which separated out on cooling were filtered off and recrystallized from a little alcohol.

The pure product had a melting point of 70.6°C. Further recrystallization failed to raise this melting point.

Since the fragments from the decomposition of the osonide have been shown to be acetaldehyde and methyl secondary butyl ketone, the octene present in the original material (b) must have the following structure.



3,4-dimethyl hexene-2

**Preliminary Examination of the Higher Boiling Component
of Distillate (b)**

56 grams of fraction 32 (Table I) dissolved in 180 cc of ethyl acetate were subjected to the action of ozonized oxygen as previously described. Ozone was passed at the rate of .04 mol. per hour, at which rate 12.5 hours would be required to ozonize 56 grams of octene. However, ozonization was complete at the end of one hour as indicated by the decomposition of the rubber outlet tube from the ozonization flask. This indicated that there was very little unsaturation present in this high boiling last fraction of the fractionated liquid (b). It was proposed to purify the saturated material thus indicated to be present in the fractions boiling at 121° and above by subjecting it to the action of ozonized oxygen, decomposing the ozonide and fractionating the mixture.

**Purification of the Higher Boiling Component
of Distillate (b)**

500 cc. of the mixed fractions 24-31 (Table I) inclusive were subjected to the action of ozone in the absence of any solvent until no more ozone was adsorbed.

This operation required 14 hours with ozone passing at the rate of .04 mol per hour. The ozonide was decomposed by the method of Whitmore and Church (loc.cit.). The insoluble layer (e) was separated, dried, and distilled through a Podbielniak type still. The results of this fractionation are given in Table V.

TABLE V

Fraction of Product (a)

Distillation rate, .1 cc per minute
Charge 435 cc.

Fraction #	Total volume cc	Temperature °C (a)	Refractive index N 25°C.
1	10	102	1.3891
2	20	105	1.3917
3	30	105.5	1.3917
4	40	108.5	1.3927
5	50	109.0	1.3927
6	61	112.0	1.3927
7	71	112.0	1.3927
8	83	112.0	1.3927
9	95	113.0	1.3928
10	106	113.0	1.3929
11	120	113.5	1.3929
12	130	113.5	1.3929
13	150	114.0	1.3929
14	200	114.0	1.3930
15	215	114.0	1.3930
16	255	114.0	1.3930
17	365	114.0	1.3930
18	425	114.0	1.3930
residue	10	---	---
Total	435		

(a) At the slow rate used in this distillation temperature indications are inaccurate.

A portion of fraction 17 (Table V) was refluxed over metallic sodium for six (6) hours and then distilled from the sodium. The refractive index of the material (f) obtained from this treatment was found to be 1.5931 at 25°C. The density was found to be 0.759 at 25°C. and the Cottrell b.p. 121.0 at 760.1 mm.

Identification of Pure Higher Boiling Component (f)
from Distillate (b)

Molecular weight determination by the lowering of the freezing point of thiophene free benzene showed the compound to have a molecular weight of approximately 186. Analysis of the compound showed it to contain 73.86 per cent carbon, 13.84 per cent hydrogen, and 12.30 per cent oxygen. The molecular formula calculated from the above results would be $C_8H_{18}O$. Since the compound did not react with ozone or metallic sodium it was concluded that the oxygen in the compound must be present in an ether linkage.

Since alcohols containing from one to five carbon atoms form ethers when heated with sulphuric acid, it seemed logical to suspect the oxygen containing compound to be a di-butyl ether, probably symmetrical di-secondary butyl ether. Examination of several physical constants of some

di-butyl ethers showed that the compound in question (f) might be either di-iso-butyl ether or di-secondary butyl ether. (see Table VI.)

TABLE VI

Physical Properties of Di-Butyl Ether

Ether	Density 20°C	Boiling Point °C.
Di-n-butyl	.769	140.9
Di-iso-butyl	.762	122.5
Di-sec.-butyl	.756	121.0
Unknown ether (f)	.759 at 25°C.	121.0

TABLE VII

Physical Properties of Butyl Bromide

Bromide	Refractive Index n _D 20°C.	Density at 20°C.	b.p. °C
n-butyl	1.4396	1.275	101.6
iso-butyl	1.4360	1.264	91.5
sec.-butyl	1.4344	1.261	91.5
tert-butyl	1.4280	1.222	73.3
Unknown bromide	1.4341	1.250 25°C	91.0

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Preparation of the 3,5, Di-Nitro Benzoate⁴⁸ of the Alcohol Resulting from Hydrolysis of the Ether

1 cc. of the material suspected of being di-secondary butyl ether (fraction 17, table V.) was mixed with 0.5 gram of 3,5, dinitro benzoyl chloride and 0.15 gram of anhydrous zinc chloride and refluxed for one hour. The product was leached with 10 cc of water and 10 cc of 1.5 normal sodium carbonate, warmed, filtered, and the precipitate washed with 10 cc of 1.5 normal sodium carbonate and a little water. The residue was extracted with hot carbon tetrachloride, the carbon tetrachloride evaporated off, and the residue recrystallized from a little ninety-five (95) per cent ethyl alcohol. 0.1 gram of material melting at 75.5°C. (corr.) was obtained. This dinitro benzoate was proved by a mixed M.P. determination to be identical with the 3,5 dinitro benzoate prepared from secondary butyl alcohol.

Hydrolysis of the Ether with Hydrobromic Acid

Forty grams of the material (fraction 17, Table V.) were saturated with hydrobromic acid and then heated under reflux for three hours. The product was washed with water, then with a saturated sodium bicarbonate solution, and finally with water. The washed liquid was then dried over anhydrous calcium chloride, filtered, and distilled through a short column (250 x 10 mm.) filled with glass beads. 68.5 grams of a bromide (g) (81.2 per cent of the theory for di-secondary butyl ether) boiling point 90-91°C at 756.6 mm., refractive index n_{25}^{25} 1.4341 and density d_{25}^{25} 1.250 were obtained.

The fact that the unknown ether (f) formed a 3,5,dinitrobenzoate, when treated with 3,5,dinitrobenzoyl chloride and anhydrous zinc chloride, that proved to be identical by a mixed melting point determination with the 3,5, dinitrobenzoate prepared from pure secondary butyl alcohol, and that upon splitting with hydrobromic acid this ether gave an eighty-one (81) per cent yield of a bromide whose physical properties check with the physical properties of secondary butyl bromide as given in the literature, is very good evidence that the ether in question is di-secondary butyl ether.

An attempt to prepare the 3,5, dinitrobenzoate of secondary butyl alcohol from the secondary butyl bromide (g) obtained by splitting the ether, and the silver salt of 3,5, dinitro benzoic acid was unsuccessful. Hydrobromic acid split out, and consequently no ester formation took place.

Another attempt to make a solid derivative of this bromide involved the use of potassium phthalimide. In this case also hydrobromic acid split out and no derivative was obtained.

An attempt to prepare di-secondary butyl ester by a Williamson's ether synthesis, using secondary butyl bromide and the sodium salt of secondary butyl alcohol was unsuccessful despite all precautions to avoid the presence of moisture and unreacted sodium, or sodium oxide in the reaction mixture.

Search for Presence of Other Unsaturation

To make sure that no unsaturated compounds, other than the one whose structure had been established, were present in the original mixture, 10 cc portions of fractions 1,4,17,20,23 (Table II) respectively were subjected to the action of ozonized oxygen. Low boiling petroleum ether, free from unsaturates, as shown by a test with tetranitromethane, was used as a solvent in these ozonolysis. The

ozonides were decomposed by the method already cited and the fragments characterized by the formation of suitable derivatives.

The procedure followed in the investigation of these fragments was briefly as follows. 10 cc of the material and 10 cc of low boiling petroleum were placed in a specially constructed ozonization tube having an inlet tube sealed in the bottom through which the ozone was bubbled into the solution. The ozonization tube was immersed in a solution of carbon tetrachloride and chloroform maintained at -15 to -25° C. by means of solid carbon dioxide. Ozone was passed into the solution until adsorption was complete as indicated by the breaking off of the rubber outlet tube. The ozonide was decomposed by the method of Whitmore and Church (loc.cit.) without the removal of the solvent. The steam distillate containing the decomposed ozonide and solvent was tested for the presence of aldehydes with Fuchsin reagent and for the presence of formaldehyde by the resorcinol test. Each of the fractions thus examined gave positive tests with Fuchsin reagent, due to the presence of acetaldehyde, but gave negative tests for formaldehyde. Acetaldehyde was characterized by the formation of a p-nitro phenylhydrazone, m.p. $125.5-126^{\circ}$ C. (corr.). The insoluble layer was separated

from the steam distillate, washed with a concentrated solution of sodium carbonate, then with water, and dried over anhydrous calcium chloride. The petroleum ether was then removed by distillation from a steam bath through a short column filled with glass beads. The residue in the distilling flask was examined for the presence of carbonyl compounds. Each of the fractions yielded a 2,4,-dinitrophenyl hydrazone. The 2,4,-dinitrophenyl hydrazones from these fractions all melted at $71.0 - 71.2^{\circ}\text{C}$. (corr.) and proved to be identical with the 2,4-dinitro phenyl hydrazone of methyl secondary butyl ketone by mixed melting point determinations. No evidence of any other carbonyl compounds in the decomposition products of the ozonides was noted.

ANALYTICAL DATA

The analytical data on the compounds prepared in this investigation can best be presented in tabular form. Duplicate analyses were run only on compounds not previously reported in the literature.

<u>Substance</u>	<u>Wt. of sample</u> <u>mg.</u>	<u>Wt. CO₂</u> <u>mg.</u>	<u>Wt. H₂O</u> <u>mg.</u>	<u>%C</u>	<u>%H</u>
2,4,dinitro-phenylhydrazone of methyl sec.-butyl ketone.	4.474 4.388	8.417 8.239	2.239 2.286	51.31 51.56	5.60 5.86
Theoretical composition of C ₁₂ H ₁₆ N ₄ O ₄					
Amide of methyl ethyl acetic acid	4.172	9.103	4.023	59.50	10.79
Theoretical composition of C ₈ H ₁₁ N O					
p-phenyl phenacyl ester of methyl ethyl acetic acid	4.846 3.741	13.641 10.560	3.005 2.285	76.76 76.98	6.93 6.83
Theoretical composition of C ₁₉ H ₂₀ O ₃					
Di-sec.-butyl ether (a)	5.228	14.159	6.465	73.86	13.84
Theoretical composition of C ₈ H ₁₈ O					
Methyl sec.-butyl ketone.	4.156	10.968	4.496	71.98	12.02
Theoretical composition of C ₆ H ₁₂ O					
3,5,dinitro benzoate of sec.-butyl alcohol	2.874	6.160	1.095	48.97	4.26
Theoretical composition of C ₁₁ H ₁₈ O ₆ N ₂					

(a) The author is indebted to Dr. J. R. Spies, of the Bureau of Entomology and Plant Quarantine, U.S. Department of Agriculture, for this analysis.

SUMMARY

1. Secondary butyl alcohol has been subjected without agitation in a closed system to the action of seventy-five (75) per cent sulphuric acid at 80°C. for forty-eight (48) hours.
2. This treatment resulted in the formation of 3,4, dimethyl hexene-2, and di-secondary butyl ether in approximately equal amounts together with other undetermined products.
3. The mechanism of the polymerization of olefins, postulated by Whitmore, accounts for the formation of 3,4, dimethyl hexene-2 from secondary butyl alcohol. There was no indication of the presence of a second substance, 3,4, dimethyl hexene-1, which might also be expected according to Whitmore's theory.

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ethyl

Butyl Ketone

I.C.T. Vol I
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Vol I
P. 202

ND^{200c}

Methyl Sec

Butyl "

Vol I
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Vol I
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" iso

butyl "

Vol I
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Vol I
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Methyl Tert

Beil. Band I Page 694

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tab. VI all values I.C.T. Vol I Page 204

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tab. VII

Densities B.P

I.C.T.

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ND^{200c}

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309

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Bromide

n-Butyl

sec butyl

iso butyl

tert butyl

Page 31

CH₃COOH

Physical constants of Methyl Ethyl itic acid

B.P. 174 } I.C.T. Vol I Page 192
D^{20°} .941 }

n_D^{20°} 1.4051 I.C.T. Vol I Page 276

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[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Diamylenes Produced from Methylisopropylcarbinol by Sulfuric Acid¹

BY NATHAN L. DRAKE, G. M. KLINE AND W. G. ROSE

Many investigators have studied the polymerization of amylenes, but to date no *conclusive* proof of the structure of any of the polymers has been offered.^{2,3,4,5,6,7}

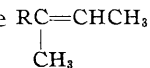
Previous work on the structures of the decenes produced by sulfuric acid from methylisopropylcarbinol has likewise been inconclusive.^{8,9}

The present paper advances evidence that 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2 result from the action of warm sulfuric acid on methylisopropylcarbinol. These substances are produced in approximately equal

quantities, and no evidence of the presence of other decenes has been found.

The formation of 3,5,5-trimethylheptene-2 would be predicted according to the theory advanced by Whitmore¹⁰ to explain the mechanism of the polymerization of olefins by acid catalysts. However, only a radical intramolecular rearrangement of one of the hypothetical intermediates which would be expected according to Whitmore's theory could result in the formation of 3,4,5,5-tetramethylhexene-2.

The proof of the structures of the two decenes was obtained as follows. Ozonolysis yielded acetaldehyde and two ketones, C₈H₁₆O, which were demonstrated to be methyl ketones by the haloform reaction. The two decenes must, therefore, possess the structure



(10) Whitmore, *Ind. Eng. Chem.*, 26, 94 (1934).

- (1) From the Ph.D. dissertations of G. M. Kline and W. G. Rose
- (2) Wischnegradsky, *Ber.*, 8, 434 (1875).
- (3) Schneider, *Ann.*, 157, 207 (1871).
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Many of the theoretically possible methyl ketones could be eliminated as a result of information available in the literature. The melting point of either the semicarbazone of the ketone, or of the amide or anilide of the seven carbon acids which would be formed from the ketone by the haloform reaction, is recorded for all but three of the theoretically possible eight-carbon methyl ketones. One of these, *viz.*, 4,5-dimethylhexanone-2 has been synthesized in this Laboratory by Wheeler,⁹ and found to yield a semicarbazone melting 159–160°. It remained to eliminate one of the three following ketones: 4,4-dimethylhexanone-2,3,4,4-trimethylpentanone-2, and 3-methyl-3-ethylpentanone-2. The last-mentioned ketone has been prepared by Nyberg, who recorded¹¹ the melting point of its semicarbazone as 168° (*cf.* semicarbazone of (I) below, *m. p.* 169.5°). Additional evidence in favor of the possible identity of (I) and 3-methyl-3-ethylpentanone-2 is to be found in the fact that Haller and Bauer¹² report that the amide of the related diethylmethylacetic acid melts at 78–79° (*cf.* amide of (V), *m. p.* 76.5°). Synthesis of 3-methyl-3-ethylpentanone-2, however, proved that it was not identical with ketone (I).

The ketoximes, $R(\text{CH}_3)\text{C}=\text{NOH}$, were converted by the Beckmann rearrangement into substituted acetamides, RNHCOCH_3 , whose hydrolysis yielded the corresponding amines. The latter were identified by comparing several of their derivatives with the same substances prepared synthetically.

Experimental

Methylisopropylcarbinol.—The carbinol was prepared from acetaldehyde and isopropyl bromide.¹³

The Decenes.—The above carbinol was added rapidly from a separatory funnel to one and one-half times its molecular equivalent of 75% sulfuric acid contained in a flask equipped with stirrer and condenser. The temperature of the mixture was then raised rapidly to 80° and held there for twenty minutes. Five minutes sufficed to add 200 g. of carbinol to the acid and to raise the temperature of the mixture to 80°; slower addition of the carbinol resulted in a low yield of decenes. After twenty minutes the mixture was cooled, the hydrocarbon layer separated, washed with bicarbonate solution, and with water, and dried over calcium chloride. Distillation of this product through a short column yielded a fraction boiling from 149–169° which was subjected to further purification. The yield was 55–60%. The 149–169° fractions from several experiments were combined, allowed to stand over

sodium for about eight hours, then refluxed over sodium for six hours, and allowed to stand in contact with the sodium overnight. The resulting product was distilled through a short column; 1880 ml. of decenes boiling from 147–163° was so prepared, and further fractionated as described below.

Fractional Distillation of the Decenes.—Through the courtesy of the late E. W. Washburn, arrangements were made to fractionate the decene mixture in one of the very efficient columns at the National Bureau of Standards. The column used had been described by Schickltanz,¹⁴ and is capable of separating a 50 mole per cent. mixture of benzene and ethylene dichloride so that 30% of practically pure benzene and 23% of practically pure ethylene dichloride are obtainable by a single distillation.

The decene mixture (1820 ml., n_D^{25} 1.4346) was separated into 28 fractions of about 60 ml. each, and a residue of 210 ml. The total volumes, *b. p.* (215 mm.) and n_D^{25} were as follows: Nos. 1–2, 112 ml., to 91.6°, 1.4202–52; Nos. 3–7, 281 ml., to 107.8°, 1.4274–1.4326; Nos. 8–17, 576 ml., to 113.1°, 1.4334–1.4350; Nos. 18–20, 178 ml., to 114.4°, 1.4357–1.4366; Nos. 21–28, 416 ml., to 117.3°, 1.4373–6; residue, 210 ml., above 117.3°, 1.4403.

Indication of the presence of at least two isomers is apparent; the refractive index of one is near 1.4340, that of the other near 1.4375. Since other work had convinced us that it was futile to attempt a separation of pure individuals by further distilling the purest fractions, ozonolyses were carried out on the fractions listed above.¹⁵

Exploratory Ozonolyses of the Decene Fractions

Fifteen-gram portions of fractions 2, 5, 13, 19, 25, and of the residue, (29), were ozonized and the ozonides decomposed. Acetaldehyde, a trace of formaldehyde, and a mixture of ketones resulted. The ketones were converted into their semicarbazones and the latter fractionally crystallized. *No evidence of more than two semicarbazones was obtained.* Decomposition of the ozonides was effected by several different procedures: the zinc-acetic acid method, the catalytic hydrogenation method,¹⁶ and the zinc-water catalyst method¹⁷ were all used. The most satisfactory results with these particular decenes are obtained by the use of ethyl acetate or petroleum ether as solvent for ozonolysis, and the zinc-water catalyst method for decomposition of the ozonide. Ozonolyses were conducted at –15 to –25°.

Very careful exploratory ozonolyses of representative fractions of a purified specimen of the so-called "Diamylene" marketed by the Sharples Solvents Company of Philadelphia revealed no products other than those mentioned above.¹⁸

(14) Schickltanz, *Bur. Standards J. Research*, **11**, 89 (1933); *cf.* also **7**, 852 (1931).

(15) We wish to express our thanks to S. Schickltanz and the others of the Petroleum Research Section of the Bureau of Standards for their valuable assistance in fractionating the decene mixture.

(16) F. G. Fischer, *Ber.*, **65**, 1467 (1932).

(17) Whitmore and Church, *THIS JOURNAL*, **54**, 3710 (1932).

(18) Space does not permit including the detailed evidence which indicates the absence of any considerable quantity of decenes other than those mentioned above. For detailed evidence the original dissertations of G. M. Kline and W. G. Rose (U. of Md., 1934) should be consulted.

(11) Nyberg, *Ber.*, **55B**, 1960 (1922).

(12) Haller and Bauer, *Compt. rend.*, **148**, 130 (1909).

(13) "Organic Syntheses," Vol. XII, p. 48.

The Eight-Carbon Ketones.—By ozonolysis of fractions 21 to 29, and of fractions 3 to 9, two ketones, (I) and (II) were obtained. The yield of ketones was about 60%. Both ketones were obtained from all fractions, but (I) was present in greater abundance in the products of ozonolysis of fractions 21–29, and (II) was present in larger quantity in the products of ozonolysis of fractions 3–9. (I), later shown to be 4,4-dimethylhexanone-2, has the following properties: b. p. (Cottrell)¹⁹ 154.4° at 768 mm.; d_4^{20} 0.829; n_D^{25} 1.4183. (II), later shown to be 3,4,4-trimethylpentanone-2, has the following properties: b. p. (Cottrell) 147.2° at 766 mm.; d_4^{20} 0.826; n_D^{25} 1.4136.

Table I lists the derivatives prepared from ketones (I) and (II).

verted into diethylmethylcarbinylmagnesium chloride and treated with carbon dioxide. The resultant acid yielded an amide which melts at 78.5°. A mixture of the synthetic amide with the amide of (V) melted from 52–62°. This acid has been characterized only by its amide; the anilide and *p*-phenylphenacyl ester were consequently prepared for future reference. These substances melt at 88.5 and 76°, respectively.

3-Methyl-3-ethylpentanone-2 was made according to Nyberg's directions. Its semicarbazone melts at 167.5°, but a mixture with the semicarbazone of (I) melted from 136 to 150°. The 2,4-dinitrophenylhydrazones serve well to differentiate 3-methyl-3-ethylpentanone-2 from (I). The melting points of these derivatives are 92–92.5°

TABLE I
DERIVATIVES OF KETONES (I) AND (II)

	M. p., °C.	B. p., °C.	Carbon, %			Hydrogen, %		
			Calcd.	Found	Found	Calcd.	Found	Found
Semicarbazone of (I)	169.5	58.33	58.36	58.60	10.34	10.04	10.28 ²⁰
Semicarbazone of (II)	148	58.33	58.53	58.07	10.34	10.20	10.42
2,4-Dinitrophenylhydrazone of (I)	146.5–147	54.50	54.14	54.09	6.54	6.29	6.37
2,4-Dinitrophenylhydrazone of (II)	109.5	54.50	54.73	54.45	6.54	6.52	6.41
Oxime, (III), of ketone (I)	101 (13 mm.)	67.07	66.57		11.97	11.68	
Oxime, (IV), of ketone (II)	113 (27 mm.)	67.07	66.97	67.10	11.97	12.22	11.83
<i>p</i> -Nitrophenylhydrazone of (II)	73	63.83	64.16	64.30	8.04	7.78	7.97

The Degradation of (I) and (II) to Seven-Carbon Acids.—(I) and (II) were degraded to the corresponding seven-carbon acids by the haloform reaction. The method employed was like that described²¹ for the conversion of pinacolone into trimethylacetic acid. The yield of *t*-amylacetic acid (V) from (I) was 45–53%; that of methyl *t*-butylacetic acid (VI) from (II) was 35%. The following properties of (V) and (VI) were observed: (V) boils at 213° at 778 mm. (Cottrell), and distils at 103–104° at 13 mm.; (VI) melts at 24.5°, and distils from 103–104° at 20 mm., or at 76° under 5 mm. pressure; the methyl ester of (V) boils at 49–50° at 17 mm., that from (VI) at 46° under 18 mm. pressure. (VI) has a n_D^{25} 1.4182.

Table II lists the derivatives of (V) and (VI).

and 146.5–147° (in the order that the ketones are mentioned).

The Beckmann Rearrangement of the Oximes (III) and (IV).—The oximes (III) and (IV) were rearranged by means of phosphorus pentachloride in dry ether. A typical example is as follows: 25 g. of (III) was dissolved in 220 ml. of ether which had been carefully dried, rendered alcohol free, and finally distilled from ethylmagnesium bromide; 37 g. of phosphorus pentachloride was added to the ethereal solution while the mixture was shaken and cooled to –5°. After addition of the phosphorus pentachloride was completed, the reaction mixture was allowed to stand overnight. The ether was then removed by distillation, and the residue poured over cracked

TABLE II
THE ACIDS (V) AND (VI) AND THEIR DERIVATIVES

	M. p., °C.	Carbon, %			Hydrogen, %		
		Calcd.	Found	Found	Calcd.	Found	Found
Amide of (V)	76.5	65.05	64.98	64.85	11.71	11.75	11.70
Amide of (VI)	106.0	65.05	64.73	64.84	11.71	11.28	11.80
Anilide of (V)	105.5–106.0	76.04	75.93	75.68	9.33	9.40	9.45
Anilide of (VI)	104.5	76.04	76.57	76.68	9.33	9.22	9.32
<i>p</i> -Phenylphenacyl ²² ester of (V)	74	77.73	77.50	77.77	7.46	7.57	7.57
<i>p</i> -Phenylphenacyl ester of (VI)	68.5	77.73	77.67	77.41	7.46	7.29	7.55
<i>t</i> -Amylacetic acid (V)	...	64.54	64.02	7.46	10.84	10.56	
Methyl- <i>t</i> -butylacetic acid (VI)	24.5	64.54	64.64	64.09	10.84	10.78	10.62

Synthesis of Diethylmethylacetic Acid and 3-Methyl-3-ethylpentanone-2 and their Derivatives.—Ethyl acetate was treated with ethylmagnesium bromide to yield diethylmethylcarbinol. The chloride of this carbinol was con-

ice. The aqueous solution was made slightly alkaline with sodium hydroxide and extracted thoroughly with ether. The ether extract was dried over sodium hydroxide and the ether removed by distillation. Five grams of amide (VII) boiling at 125° at 13 mm. was obtained. A very similar process resulted in the production of 9 g. of amide (VIII) boiling at 130–131° at 20 mm. from 11.6 g. of (IV). The yield of amide obtainable from (IV) was much better than that from (III). There was always

(19) Boiling temperatures (Cottrell), and melting points have been corrected, or were taken with standardized Anschütz thermometers.

(20) Analyses reported by Wheeler, Ref. 9.

(21) "Organic Syntheses," Coll. Vol. I, p. 510.

(22) Drake and Bronitsky, THIS JOURNAL, 52, 3715 (1930); Drake and Sweeney, *ibid.*, 54, 2059 (1932).

a very considerable amount of high boiling residue left after distillation of (VII). Rearrangement of (III) through its benzenesulfonyl ester resulted in no increase in yield; the rearrangement takes place smoothly, however. The high boiling residue is probably the result of rearrangement in the other sense.

The Hydrolysis of the Amides.—Both amides (VII) and (VIII) are very stable toward hydrolysis. Boiling them with alkali or sulfuric acid was found to be without any appreciable effect. However, by heating the amides for five hours at 230–240° in a sealed tube with 85% phosphoric acid diluted with an equal volume of water, hydrolysis was effected. After opening the tubes, the acid solution was extracted with ether to remove unhydrolyzed amide and acidic products, and then cooled strongly and saturated with potassium hydroxide. The amine was either separated in a separating funnel and distilled, or distilled directly from the alkaline solution into 1:1 aqueous hydrochloric acid. From 5 g. of (VII) approximately 5 g. of amine (IX) hydrochloride was obtained; 9 g. of (VIII) yielded 5.5 g. of amine (X).

2-Amino-3,3-dimethylbutane (XII).—Pinacolylamine was prepared by the reduction of pinacone oxime by sodium and alcohol.

1-Amino-2,2-dimethylbutane (XI).—Dimethylethylacetic acid was made from *t*-amyl chloride by use of the Grignard reagent and carbon dioxide. The acid was converted into its chloride by means of thionyl chloride and then into its amide; 22 g. of amide was mixed thoroughly with 32 g. of phosphorus pentoxide and heated gently for about ten minutes. The mixture was then heated more strongly until no more nitrile distilled. After washing the nitrile with water and saturated potassium carbonate solution, it was dried and distilled from a bit of phosphorus pentoxide; 15.8 g. of dimethylethylacetone nitrile boiling at 128–129° at 760 mm. was obtained, a yield of about 86% of that theoretically possible. The entire quantity of nitrile was dissolved in 250 ml. of absolute alcohol, and 20 g. of clean sodium cut into small pieces was added. The flask was cooled while the reaction was very vigorous, and finally heated under reflux until all the sodium had dissolved. The solution was then cooled and acidified strongly with hydrochloric acid and most of the alcohol removed by distillation. The aqueous residue was next saturated with potassium carbonate and the amine distilled into 1:1 hydrochloric acid. After evaporation of the solution nearly to dryness on the steam-bath, drying was completed in a vacuum desiccator over potassium hydroxide.

Table III lists the derivatives of amines (IX) and (X).

The Comparison of the Derivatives of Table III with the Corresponding Substances from (XI) and (XII).—The synthetic amines (XI) and (XII) were converted into the P and B derivatives of Table III. The resulting substances were identical in melting point with the compounds listed in the table, and a mixture of approximately equal

TABLE III

THE DERIVATIVES^a OF THE UNKNOWN AMINES (IX) AND (X)

	M. p., °C.	Carbon, %		Hydrogen, %			
		Calcd.	Found	Calcd.	Found		
P—IX ^b	88–88.5	46.12	45.97	46.12	5.16	5.17	5.22
P—X	107	46.12	46.29	46.30	5.16	4.94	5.12
B—IX	59–9.5	59.70	59.66	59.68	7.94	7.78	7.82
B—X	96.0	59.70	59.76	59.29	7.94	7.90	7.65
Amide VIII	68–68.5	67.07	67.23	66.74	11.97	11.63	11.95
Chloro- aurate X ^c	189, 195d	16.31	16.08	16.48	3.69	3.85	3.72
		Au 44.67		Au 44.88, 44.71			

^a In the above table N-(2,4,6-trinitrophenyl)-amines are designated by P, and N-benzenesulfonylamines by B. Thus, P—IX is the N-(2,4,6-trinitrophenyl) derivative of the unknown amine (IX). ^b Prepared from the amine and 2% alcoholic picryl chloride. ^c Cf. Markownikoff, *Ber.*, **32**, 1448 (1899).

parts of known and unknown melted at exactly the same point. Amide (VIII) was also prepared from amine (XII); analysis and a "mixed melting point" determination proved the synthetic product identical with the substance obtained from oxime (IV).

Conclusion

It is apparent, from the structure of amines (IX) and (X), that amides (VII) and (VIII) from which the amines are produced by hydrolysis must be $C_2H_5C(CH_3)_2CH_2NHCOCCH_3$ and $(CH_3)_3CCH(CH_3)NHCOCCH_3$. The oximes (III) and (IV), therefore, have the structures $C_2H_5C(CH_3)_2CH_2C=(NOH)CH_3$ and $(CH_3)_3CCH(CH_3)C=(NOH)CH_3$. Ketones (I) and (II), consequently, are $C_2H_5C(CH_3)_2CH_2COCH_3$ and $(CH_3)_3CCH(CH_3)COCH_3$, respectively, and the original decenes are $C_2H_5C(CH_3)_2CH_2C(CH_3)=CHCH_3$ and $(CH_3)_3CCH(CH_3)C(CH_3)=CHCH_3$.

Summary

1. The action of 75% sulfuric acid at 80° on methylisopropylcarbinol has been shown to yield 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2.

2. These same two substances are also present in the "Diamylene" formed as a by-product during the chlorination of mixed pentanes.

3. Whitmore's theory of the mechanism of the polymerization of olefins by acid catalysts accounts adequately for the formation of 3,5,5-trimethylheptene-2, but not for the production of 3,4,5,5-tetramethylhexene-2.

COLLEGE PARK, MARYLAND

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