

**POLYMERIZATION OF OLEFINS. THE ACTION OF
SULFURIC ACID ON METHYLISOPROPYLCARBINOL**

BY

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of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy**

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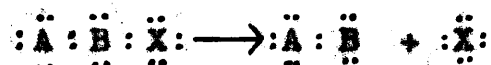
INTRODUCTION

The formation of high molecular weight olefins by the action of sulfuric acid and other dehydrating and polymerizing agents on alcohols and olefins is well known. This reaction has important industrial applications in the manufacture of synthetic lubricating oils¹ and synthetic resins^{2,3}. The literature on this subject up to 1931 has been covered in the theses of Cooke⁴ and Wheeler⁵ and will not be repeated at this time.

A series of articles by F. C. Whitmore and his students on the dehydration of alcohols and the mechanism involved therein has appeared in the literature since 1931. The theory proposed to explain the formation of the various products found should also be applicable to the anyl alcohol involved in the present investigation. A brief review of their work is, therefore, presented below.

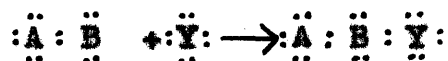
Whitmore⁶ proposed the following mechanism to explain the formation of "abnormal" or rearranged products in the course of many organic reactions. When a molecule containing a strongly electronegative atom (or group), such as oxygen or halogen is brought into a reaction which results in the removal of that atom, the electronegative atom takes a completed octet of electrons with it. The atom which shared an electron pair with the electronegative group (X)

is thus left with only a sextet of electrons. This process may be represented as follows:

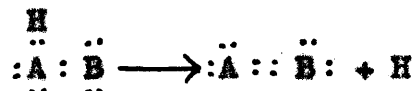


Four different changes may then take place.

(1) The positive organic fragment may have a life long enough to allow it to combine with a negative ion Y in the reaction mixture to give the "normal" product:



(2) If the atom A has a hydrogen attached to it the fragment can be stabilized by the loss of a proton.

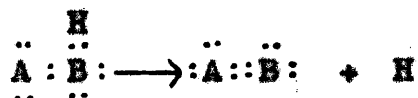


(3) If B has a greater attraction for electrons than A, an electron pair including the atom or group which it holds will shift to B, leaving A with only a sextet of electrons. The new fragment can then recombine with the ion X or with a new negative ion Y from the reaction mixture to give an "abnormal" or rearranged product.



(4) If atom B in the rearranged positive fragment has a hydrogen attached to it, the system may lose a proton and depending on the other groups attached to A and B, the resulting unsaturated compound may or may not be identical with that obtained by the loss of a proton from the original

fragment.



The dehydration of 2,3,4-trimethylpentanol-3 according to Whitmore and Laughlin⁷ yielded the normal products 3-methyl-2-isopropylbutene-1 and 2,3,4-trimethylpentene-2 in the ratio 1:2. No rearrangement products were detected.

A study of the dehydration of tertiary aliphatic alcohols containing an adjacent tertiary hydrogen was made by Whitmore and Evers.⁸ The group of alcohols worked with may be represented by the formula $\text{R}(\text{CH}_3)(\text{iso-C}_3\text{H}_7)\text{COH}$. Two adjacent carbons hold respectively a tertiary hydroxyl and a tertiary hydrogen which are readily removed to form a tetrasubstituted olefin. It had previously been shown that the first member of the series in which R is methyl yields the expected tetramethylethylene and amounts of 2,3-dimethylbutene-1 varying with the conditions of dehydration. With the four higher members (R = ethyl, n - propyl, n - butyl and n-amyl) the ozonolysis products indicated that the dehydration took place exclusively from the isopropyl and R groups with the former predominating about 2:1.

Whitmore and Church⁹ in a study of the dehydration of 2,2-dimethylhexanol-1, an alcohol of the type $\text{R}_2\text{CCH}_2\text{OH}$,

found that four products were formed, corresponding to the following courses: (1) shift of butyl and loss of proton from amyl to yield $(CH_3)_2C=CHO_4H_9$; (2) shift of butyl and loss of proton from methyl to yield $CH_2=C(CH_3)(C_3H_7)$; shift of methyl and loss of proton from butyl to yield $C_3H_7CH=C(CH_3)(C_2H_5)$; and shift of methyl and loss of proton from ethyl to yield $(CH_3)(C_4H_9)C=CHOH_3$. The first and second olefins appeared in the ratio 18:1 indicating a predominant loss of hydrogen from the newly formed amyl group as compared with the two methyl groups; the third and fourth olefins were in the ratio 1:2 in favor of the loss of hydrogen from the newly formed ethyl group as compared with the butyl group. Dehydration of methylethyl-n-butylcarbinol, corresponding to the positive fragment formed by the butyl shift gave the first and second olefins in the ratio 1.4:1. Dimethyl-n-amylcarbinol, corresponding to the positive fragment formed by the methyl shift, gave the third and fourth olefins in the ratio 1:1.6 and also a six percent yield of olefin corresponding to the loss of a proton from a methyl group, namely $CH_2=C(C_2H_5)(C_4H_9)$. The difference between the ratios 18:1 and 1.4:1 for the first and second olefins formed by dehydration with rearrangement of the primary alcohol and by dehydration of the tertiary alcohol respectively is noteworthy.

Whitmore and Herndon¹⁰ found that octanol-2 on dehydration yields a mixture of octene-1 and octene-2 in approximately the ratio 1:4. The dehydration of octanol-1 involves a rearrangement and the product is a mixture of octene-1 and octene-2 in approximately the ratio 2:1.

Whitmore and Homeyer¹¹, in a study of the dehydration of 4,4-dimethylpentanol-2, obtained 4,4-dimethylpentene-2 and 4,4-dimethylpentene-1 in the ratio 4.5:1. Contrary to expectation the dehydration took place mainly from the neopentyl group rather than the methyl group.

Whitmore and his students¹² made a study of the dehydration of secondary carbinols containing a neopentyl system. Tertiary-butylmethylecarbinol (pinacolyl alcohol) yielded tetramethylethylene and unsym-methylisopropylethylene in the ratio 2:1, and a small amount of the normal dehydration product, tertiary-butylethylene. The dehydration of 6,6-dimethyldecanol-5 and 3-methyl-3-butylheptanol-2 gave mixtures of the three olefins, 5,6-dimethyldecene-5 and -4, and 2-methyl-3-butylheptene-2. Relatively more of the two decenes were obtained from the second carbinol indicating the greater mobility of the butyl group than the methyl group. Neither alcohol gave a detectable amount of normal dehydration without

rearrangement. 3-Isopropylnonanol-5 dehydrated to give 2-methyl-3-butylheptene-2 and -3, the dehydration involving mainly the tertiary hydrogen rather than the butyl group. Dehydration of di-tert-butylcarbinol yields unstable nonenes which break up to form trimethylethylene and diisobutylene and their polymers. A significant feature of this dehydration is the apparent transfer of an electron pair from a tertiary butyl group without the transfer of that group.

Whitmore and Laughlin¹³ studied the dehydration of tertiary alcohols containing a neopentyl system. Methylethyl-tertiary-butylcarbinol yielded the normal product, 2,2,3-trimethylpentene-3 and the rearranged olefin 2,3,3-trimethylpentene-1 in the ratio 4:1. Dimethyl-tertiary-amylcarbinol gave mainly the normal product 2,3,3-trimethylpentene-1. Methylisopropyl-tertiary-butylcarbinol gave 3,3-dimethyl-2-isopropylbutene-1 by normal dehydration involving the methyl group and the rearrangement product 2,3,3,4-tetramethylpentene-1 in the ratio 3:1, with only traces of 2,3,4,4-tetramethylpentene-2 by normal dehydration involving the isopropyl group. The sluggishness of the isopropyl group in this reaction in losing a proton is noteworthy. Methyl-di-tert-butylcarbinol gave mainly 2-tert-butyl-3,3-dimethylbutene-1 by dehydration involving the methyl group. Methylethylneopentylcarbinol

dehydrated without rearrangement to give mainly 2,2,4-trimethylhexene-4 (from the ethyl group) with less than five percent of 2,2,4-trimethylhexene-3 (from the neopentyl group) and only traces of 4,4-dimethyl-2-ethylpentene-1 (from the methyl group). Their results showed the tendency of these tertiary alcohols to dehydrate without rearrangement, in contrast to related primary and secondary alcohols containing a neopentyl group which dehydrated mainly with rearrangement.

Whitmore and Simpson¹⁴ investigated the dehydration of n-amyl, isoamyl and capryl alcohols by the Tschugaeff xanthate method which avoids rearrangements. n-Amyl alcohol gave pentene-1, isoamyl alcohol gave isopropylethylene and capryl alcohol gave a mixture of equal parts of octene-2 and octene-1.

Church, Whitmore and McGrew¹⁵ studied the behavior of the five simplest normal alkyl radicals in the dehydration of tri-n-alkyl tertiary alcohols. In the case of the twenty-two alcohols studied the order of decreasing ease with which the different alkyl groups supplied the hydrogen to form water was: ethyl, n-propyl, n-butyl, n-amyl, methyl. All of these tertiary alcohols were dehydrated by iodine without rearrangement.

The extensive literature on the polymerisation of ethylene has been reviewed by Stanley¹⁶ and Carothers¹⁷.

Mignone and Saint-Aunay¹⁸ succeeded in isolating as the first products formed in the action of the silent discharge on ethylene butene-1 and hexene-1. Pease¹⁹ found butene-1 in the products of the thermal polymerization and from a study of the kinetics has concluded that this is a chain reaction. Carothers states that in effect at least this reaction involves at the first step the addition of ethylene, as $H + CH = CH_2$, to the double bond of another molecule of ethylene, and then a similar addition to butylene.

Lebedev and Koblyanski²⁰ have investigated the polymerization of isobutylene. They found that the trimer was not polymerized under the conditions that lead to the production of higher polymers from either the monomer or the dimer. Hence the higher polymers must be built up by the successive addition of monomer or dimer. The structure of the polymerized olefins was not determined.

The isomers present in diisobutylene prepared by the action of sulfuric acid on tertiary butyl alcohol were found by Whitmore and his students²¹ to be 2,4,4-trimethylpentene-1 and -2, confirming the previous work of McCubbin and Adams²². The trimethylpentene-1 and -2 isomers are present in approximately the ratio of 4:1.

Whitmore²³, in a discussion of the polymerization of olefins by acid catalysts predicts that the most probable products in the disubstituenes would be 3,5,5-trimethylheptene-2 and -3, 2,3,4,4-tetramethylhexene-1 and -2, and

2-ethyl-4, 4-dimethylhexene-1.

In the thesis of Cooke⁴, of which this work is a continuation, the preparation of methyl isopropyl carbinol by a Grignard reaction and the formation of an olefin containing ten carbon atoms per molecule by the action of sulfuric acid was described. In the thesis of Wheeler⁵ it was shown by fractional distillation of the decenes through an ordinary 100 cm. long, bead filled column with an electrically heated jacket and subsequent ozonization that at least two isomers were present. The products of ozonolysis were acetaldehyde and a liquid fraction containing at least two eight carbon ketones, one of which gave a semicarbazone melting at 143.5 - 144.5°C. and the other a semicarbazone melting at 170-171°C. Fractionation and identification of the two ketones was not possible with the small amount of material obtained.

The purpose of the present work was to prepare sufficient of the decene mixture so that it could be fractionated in the most efficient equipment available, to ozonize the nearly pure isomers thus obtained, and to determine the structure of the aldehydes and ketones formed, in order to add further to our knowledge of the mechanism of polymerization of simple olefins to complex oils and resins.

still had been found to give an efficient separation of a 50 mol percent mixture of benzene and ethylene dichloride, substances having boiling points differing by only 3.42°C. Twenty-eight fractions varying in volumes from 46 to 71 ml. and a residue of 210 ml. were obtained. The temperature and refractive indices of the various fractions indicated that the material distilled consisted primarily of two substances having the following physical properties:

1st Decene	Boiling point-215 mm. = 110.8°C	$n_D^{25} = 1.4344$
2nd Decene	Boiling point-215 mm. = 116.8°C	$n_D^{25} = 1.4376$

The first decene, when ozonized, yielded acetaldehyde and a ketone boiling at 147.2°C. at 766 mm., the semicarbazone of which melted at 147.6-8°C. The second decene, when ozonized, yielded acetaldehyde and a ketone boiling at 154.4°C. at 768 mm., the semicarbazone of which melted at 169.5°C. Thorough examination of fractions 2,5,13,19,25 and the residue failed to reveal the presence of any other decene. It was, therefore, concluded that there are only two isomeric decenes present and that these isomers are present in equal proportions since the curve obtained by plotting the refractive index against the percent distilled shows a sharp rise between the two plateaus corresponding to the two decene isomers when approximately fifty percent of the mixture has been distilled.

Inasmuch as acetaldehyde was formed by ozonolysis of both decenes, it was known that the group $\text{>C} = \overset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{H}$ was

present in both decenes. Both ketones gave the Hofmann test characteristic of methyl ketones, thereby extending the known portion of the decene molecules to $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ -\text{C} = \text{C}-\text{H} \end{array}$. The identity of the remaining C_7H_{13} radical was established by W. Gordon Rose²⁶ for the first decene and by the author for the second decene.

Oxidation of the methyl ketone to a seven carbon acid with sodium hypobromite took place with good yields. The amide of the seven carbon acid melted at 76.5°C . There are seventeen possible structurally isomeric saturated seven carbon acids. Beilstein lists the amides of thirteen of these, only one of which melted in the neighborhood of the unknown amide. This acid was methyldiethylacetic acid whose amide was reported by Haller and Bauer²⁷ to melt at $78-79^\circ\text{C}$. This acid was synthesized by the Grignard reaction from the chloride of methyldiethylcarbinol and carbon dioxide, and was found to boil at the same temperature as the unknown seven carbon acid, namely 104°C ., a mixed melting point, however, showed a depression of approximately thirty degrees.

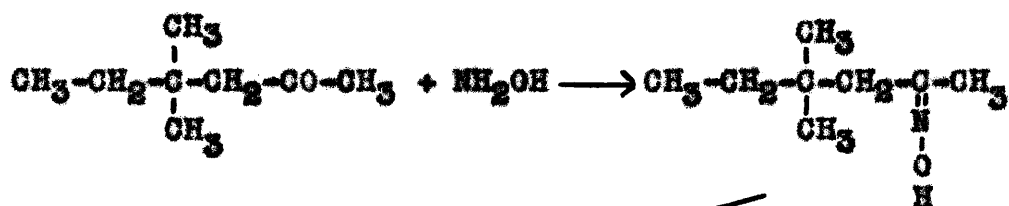
Twelve of the seventeen possible structurally isomeric saturated eight carbon methyl ketones are described in the literature. The boiling point of the ketone and the melting point of the semicarbazone of one of these are very close to those of the unknown ketone. This was 3-methyl-3-ethyl-pentanone-2, which was found by Nyberg²⁸ to boil at $153.5-154.0^\circ\text{C}$.

at 756 mm. and to yield a semicarbazone melting at 168°C . This methyl ketone should yield on oxidation with sodium hypobromite the same seven carbon acid that had already been synthesized. In view of the remarkable similarity in physical constants of the two ketones and acids, 3-methyl-3-ethylpentanone-2 was synthesized in order to check on possible rearrangement during the preparation of the acid. The method of Nyberg was used for the synthesis, involving the reduction of methylethylketone with magnesium amalgam and rearrangement of the symmetrical pinacol to the pinacolone with sulfuric acid at -10°C . The semicarbazone of the ketone fraction boiling from 153° to 155°C . melted at 167.5°C .; a mixed melting point with the unknown semicarbazone showed a depression of about thirty degrees.

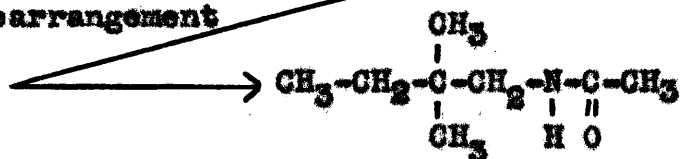
Inspection of the data in the literature revealed that there were only three methyl ketenes whose semicarbazones or derived seven carbon acid amides were unknown. One of these three, namely 4,5-dimethylhexanone-2, had previously been made in this laboratory by Wheeler⁵ and its semicarbazone found to melt at $159-160.5^{\circ}\text{C}$.(corr.). There remained only the following possible methyl ketenes: 3,4,4-trimethylpentanone-2 and 4,4-dimethylhexanone-2. Evidence accumulated in the meantime by W. Gordon Rose²⁶ indicated that the ketone obtained from the lower boiling decene was 3,4,4-trimethylpentanone-2. It remained to prove that the

second ketone was 4,4-dimethylhexanone-2.

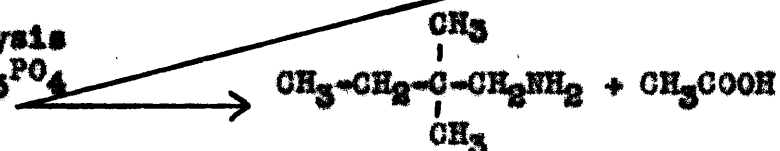
The ketone was converted to the oxime by treatment with hydroxylamine and the ketoxime was subjected to a Beckmann rearrangement by treatment with phosphorus pentachloride. The rearrangement proceeded in the desired "anti" sense with twenty percent yield of a substituted acetamide. The substituted amide was hydrolyzed by a 1:1 aqueous syrupy phosphoric acid solution in a sealed tube at 230-40°C. Solid derivatives of the resultant amine were prepared with picryl chloride and benzenesulfonyl chloride. The picramide melted at 88-88.5°C. and the benzenesulfonamide at 59-59.5°C. The reactions involved in the above degradation of the ketone are as follows:

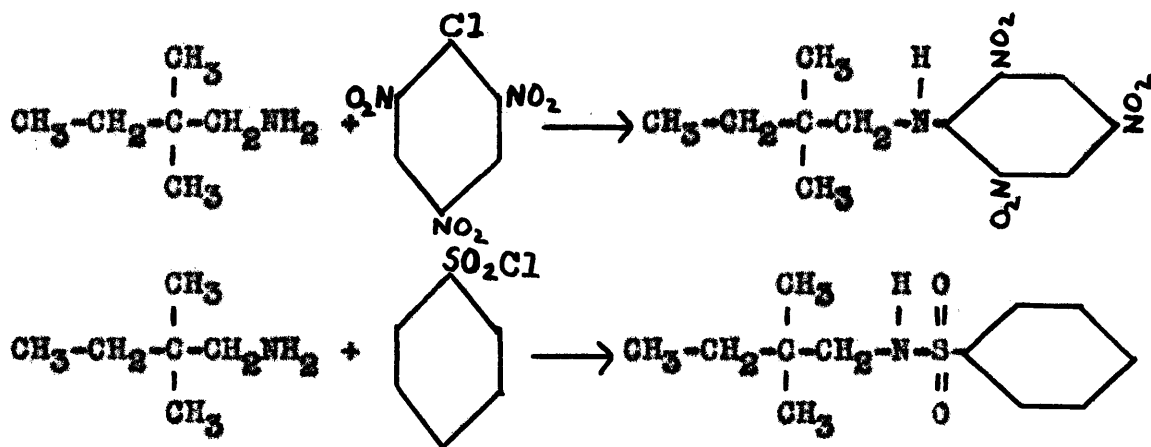


Beckmann rearrangement
with PCl_5

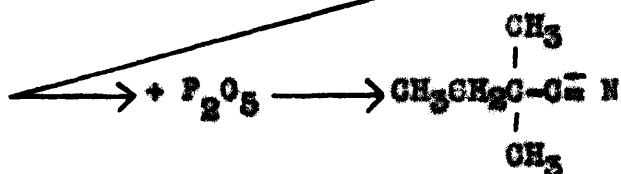
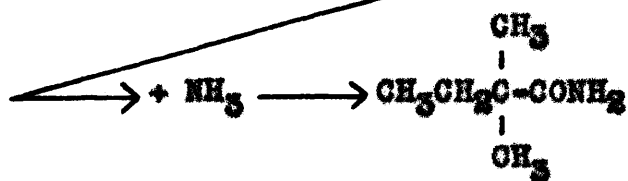
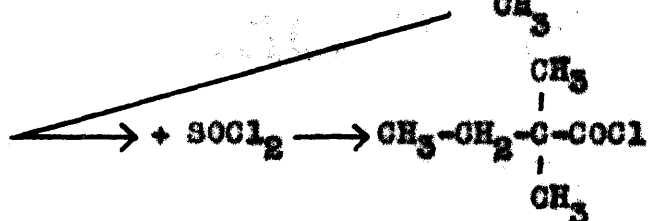
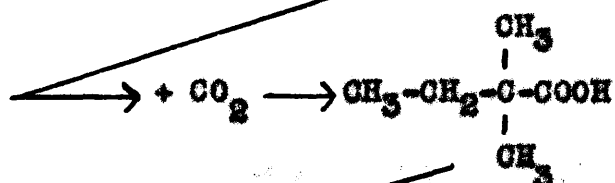


Hydrolysis
with H_3PO_4

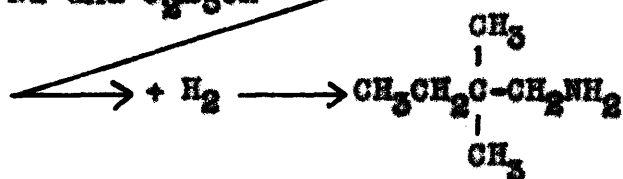




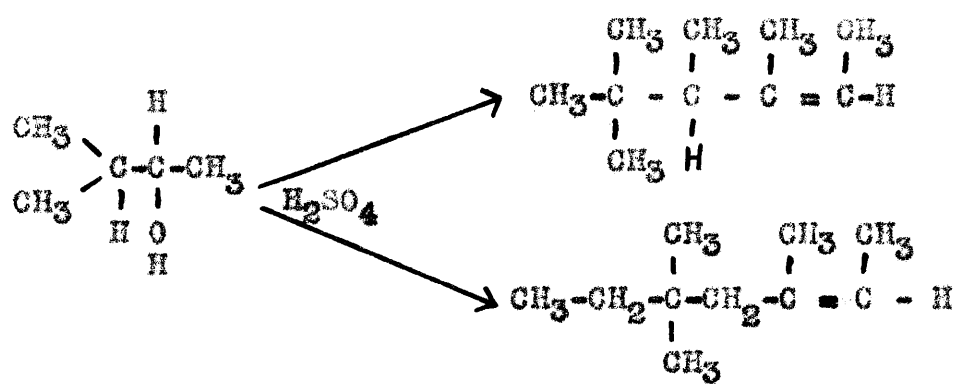
The above picramide and benzenesulfonamide were prepared synthetically in the following manner. Dimethyl-ethyl acetic acid was made through the Grignard reaction from tertiary amyl chloride and carbon dioxide. The acid was converted to the chloride with thionyl chloride and then to the amide by treatment with ammonium hydroxide. The amide was dehydrated to the nitrile with phosphorus pentoxide, and the nitrile reduced to the amine with sodium and alcohol. The picramide and benzenesulfonamide were prepared in the usual manner. The picramide melted at 87.8-88.6°C. and the benzenesulfonamide at 59-59.5°C. Mixed melting points with the derivatives obtained from the unknown ketone gave no depressions of the melting points. The reactions involved in this synthesis are as follows:



Na and $\text{C}_2\text{H}_5\text{OH}$

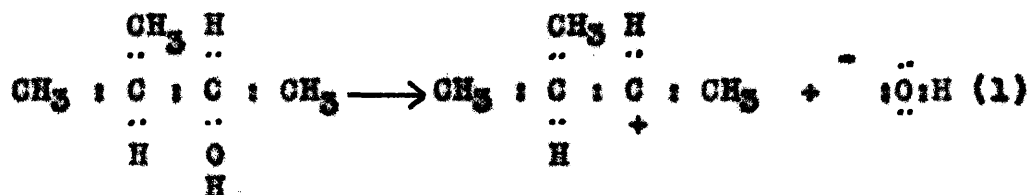


The action of 75% sulfuric acid on methylisopropylcarbinol at 80°C . results, therefore, in the formation of two isomeric decenes, namely 3,4,5,5-tetramethylhexene-2 and 3,5,5-trimethylheptene-2:

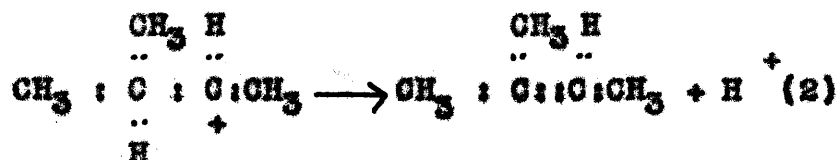


DISCUSSION OF RESULTS

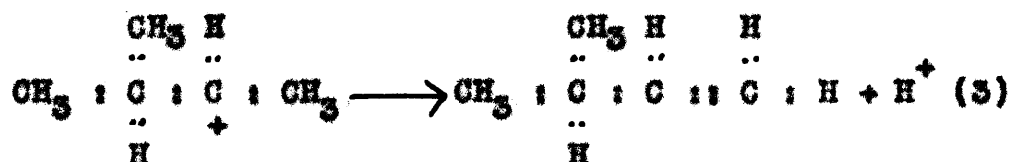
According to the theory of Whitmore for the dehydration of alcohols, methylisopropylcarbinol would lose the hydroxyl group and become a positive organic ion:



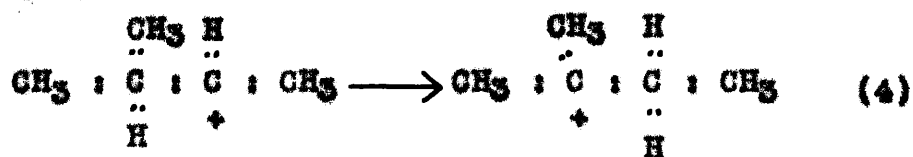
This positive fragment may lose a proton from the isopropyl group to form trimethylethylene:



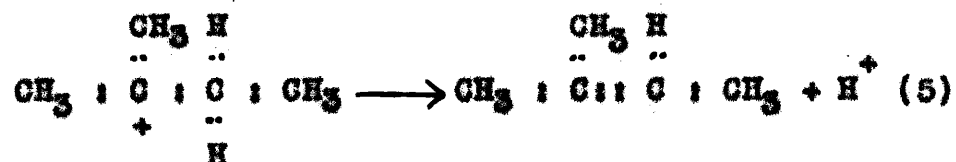
or from the methyl group adjacent to the positive carbon to form isopropylethylene:



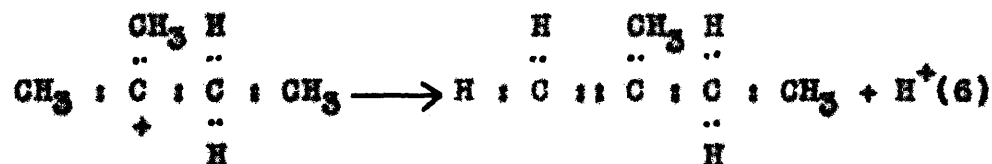
If the positive carbon of the organic fragment has a greater attraction for electrons than the adjacent secondary carbon, the hydrogen may shift with its electrons to form a new positive ion:



A shift of a methyl group in this case would not result in any change in structure of the positive ion. A loss of hydrogen from the newly formed ethyl group would produce trimethylethylene:

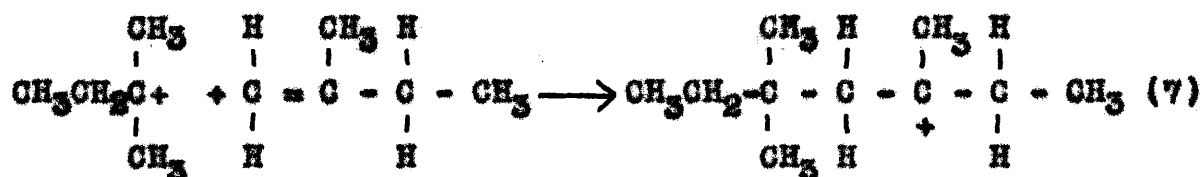


Loss of hydrogen from the adjacent methyl group would produce 1-methyl-1-ethylethylene.

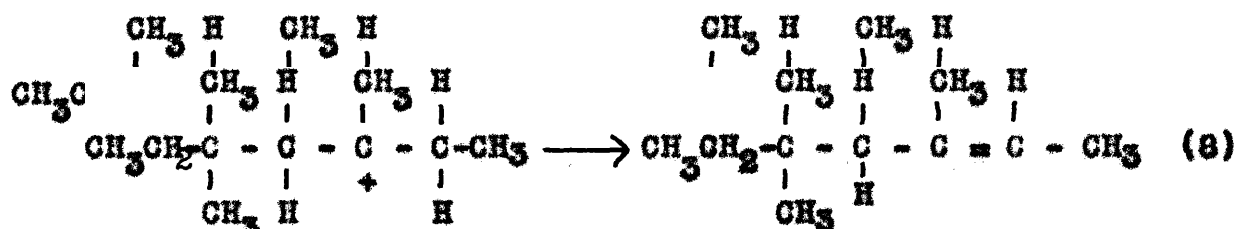


Inasmuch as the carbon atom having the most electronegative groups attached to it has the least attraction for electrons, positive ion (4) would be expected to predominate rather than fragment (1).

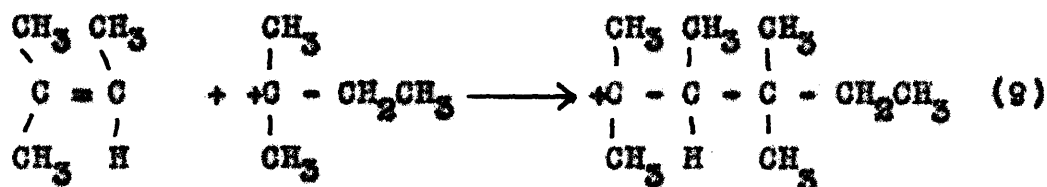
Union of fragment (4) with olefin (6) would take place as follows:



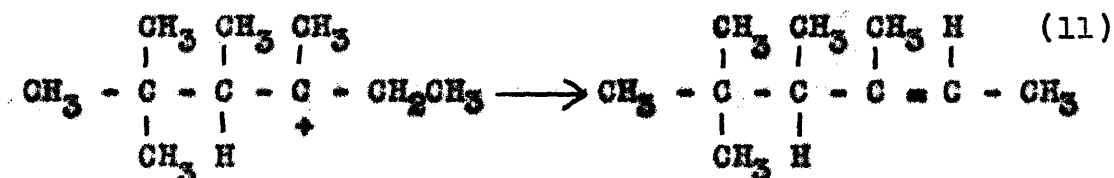
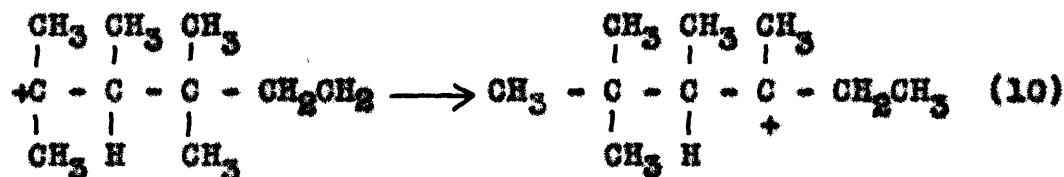
Loss of hydrogen from the ethyl group would be expected, as in the case of methylethylneopentylcarbinol¹³, and would form 3,5,5-trimethylheptene-2, observed as one of the products:



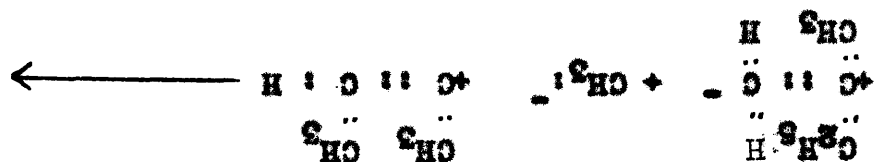
Union of fragment (4) with olefin (5) would proceed in the following manner:



In order to account for the 3,4,5,5-tetramethylhexene-2 observed as the second product of the reaction investigated, the positive fragment in (9) would have to undergo a shift of a methyl group and a loss of hydrogen from the ethyl group:



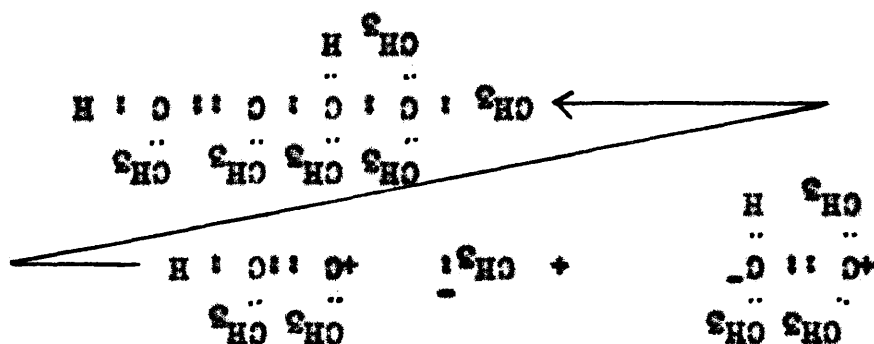
If the explanation of the formation of the above products is sought in the theory of a chain reaction analogous to the polymerization of ethylene, the mechanism is much simpler.



The addition of the two fragments to the double bond of 1-methyl-1-ethylcyclohexene would take place as follows:

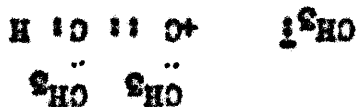
3,4,5,6-tetramethylcyclohexene-2.

This is one of the observed products, namely



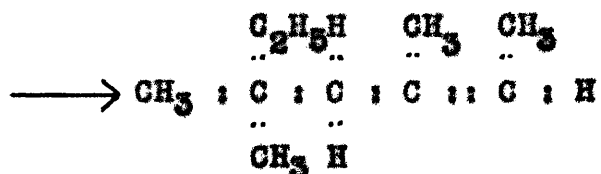
electronegativities, as follows:

ethylene would take place, in accordance with the relative electronegativity of the two adjacent carbon atoms involved. The addition of these two fragments to the double bond of a nonactivated molecule of trimethyl-



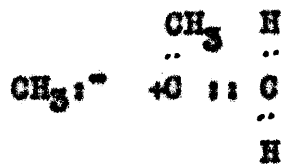
namely:

In effect at least the molecule of trimethylcyclohexene behaves as though it were activated in the following manner:

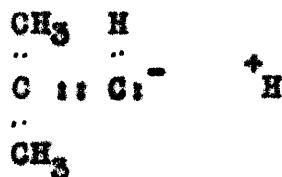


This is the other observed product, namely 3,5,5-trimethylheptene-2. If this mechanism is correct, trimethylethylene and 1-methyl-1-ethylethylene must be produced by the dehydration of methylisopropylcarbinol in the ratio 3:1.

The products formed by the polymerization of isobutylene can be predicted by the same mechanism. From a consideration of the relative electronegativities involved, isobutylene would be expected to behave as



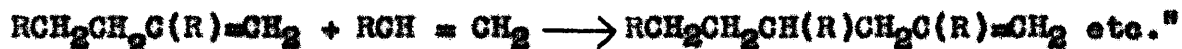
rather than



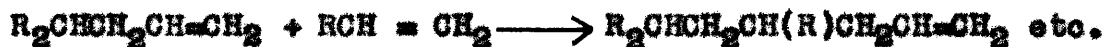
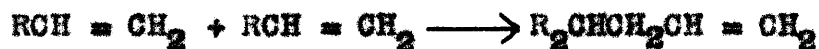
The products observed in the formation of the dipolymer can be accounted for on the basis of the "activation" taking place eighty percent in the first sense and twenty percent in the second sense with subsequent addition to a molecule of isobutylene.

It has already been stated in the introduction that the first step in the polymerization of ethylene is the formation of butene-1 and the second step is the formation

of hexene-1. Similar terminal unsaturations have been found by Whitby and Kats³⁰ in a study of the polyindenes, $\left(\begin{smallmatrix} \text{CH}_2 - \text{C}_6\text{H}_4 \\ | \\ \text{CH} = \text{CH} \end{smallmatrix} \right)_n$. Carothers¹⁷ has reviewed the evidence regarding the polymerization of vinyl compounds and states that the facts indicate that the formation of the high polymer is a chain reaction. "The collision of an activated molecule of monomer with another molecule of monomer yields an active dimer capable of coupling with another molecule of monomer, and the activating energy persists in the polymeric chain until it has been built up to a considerable length". "This mechanism may be formulated as follows:



However if R is a strongly electronegative group such as the phenyl group in styrene, it is believed that the following course would predominate:



Experimental evidence regarding the structure of even the relatively simple dimer of styrene is lacking. The validity of the interpretation of olefinic polymerizations on the basis of the relative electronegativities of the groups involved must necessarily await further evidence.

It should be noted that this reaction makes available a source not only of two new decenes, but also the corresponding decanes (which it is planned to prepare and study later), and the corresponding eight carbon methyl ketenes and seven carbon acids. Previous attempts³¹ to synthesize one of these acids, dimethylethylpropionic acid, failed. Cressley and Perkin³¹ isolated a heptylic acid from the decomposition products of camphoric acid by fusion with potash. This acid had a boiling point 209-210° and gave an anilide melting at 105-105.5°. They believed it to be dimethylethylpropionic acid but synthesis by the interaction of ethyl sodiomalonate and dimethylethylcarbinylbromide was not successful. It is interesting to note that the melting point of their anilide is within 0.5°C of the value found for dimethylethylpropionic acid in the present investigation.

EXPERIMENTAL DATA

Preparation of isopropyl bromide

Isopropyl bromide was first prepared by treating a mixture of isopropyl alcohol and naphthalene with bromine. Two parts by weight of naphthalene were mixed with one part of isopropyl alcohol in a round-bottom short neck flask fitted with a dropping funnel, distillation tube and thermometer. The mixture was heated to 60°C and bromine added drop by drop until excess hydrogen bromide gas was evolved. The ester was distilled, washed successively with water, sodium bicarbonate solution, and water, and dried over ignited potassium carbonate. Fractional distillation yielded about sixty percent of isopropyl bromide (b.p. $59-61^{\circ}\text{C}$.).

Inasmuch as this method involved the loss of one part bromine for each part converted to hydrogen bromide, another process was used to prepare most of the isopropyl bromide required. Hydrogen and bromine were passed over a platinum catalyst and the resulting hydrogen bromide was bubbled through isopropyl alcohol. When the alcohol was saturated, the ester was distilled and worked up as described above. A total of 8455 grams of pure isopropyl bromide was prepared.

Preparation of methylisopropylcarbinol

Methylisopropylcarbinol was made from isopropyl bromide and acetaldehyde through the Grignard reaction. The amounts of materials used and the yields obtained are given in Table 1. The procedure used was that described by Drake and Cooke³². The magnesium was dried in a desiccator over phosphorus pentoxide. The ether was prepared by drying with calcium chloride, sodium wire and finally by distilling from a solution of ethyl magnesium bromide. The isopropyl bromide was dried over ignited potassium carbonate. The magnesium and a portion of the ether were placed in a 3-necked flask of suitable size, provided with a mercury sealed mechanical stirrer, a reflux condenser closed with a calcium chloride tube and a dropping funnel, also fitted with a calcium chloride tube.

Table 1
Preparation of methylisopropylcarbinol

Run	Isopropyl bromide grams	mols	Magnesium grams	mols	Acetalde- hyde grams	mols	Ether ml	Yield of car- binol grams	Percent theoreti- cal yield based on bromide %
1	600	4.9	146	6	200	4.6	800	187	44
2	900	7.3	219	9	370	8.4	1200	357	56
3	1200	9.8	292	12	467	10.6	1450	433	50
4	1200	9.8	292	12	411	9.3	1825	135	16
5	1200	9.8	292	12	461	10.5	1825	287	33
6	1200	9.8	292	12	433	9.8	1825	655	76
7	1850	15.0	440	18	653	14.8	3100	770	58

No catalysts or heating were required to start the reaction in any of the runs. The mixture of isopropyl bromide and ether were added slowly through the dropping funnel at a rate sufficient to cause a gentle refluxing. Upon completion of the addition of the bromide, refluxing was continued on a water bath for forty minutes. The flask was then cooled in an ice-salt bath to -8°C . Acetaldehyde, freshly prepared by distillation of paraldehyde with p-toluene sulfonic acid, was mixed with ether and added drop by drop to the flask through the dropping funnel. It is important to note that calcium chloride should not be used in drying the paraldehyde, inasmuch as it was found to promote the formation of metaldehyde in the distilled acetaldehyde, even though the undissolved calcium chloride was removed by filtration before distillation.

The poor yields in runs 4 and 5 were due to this factor. When all of the aldehyde had been added, the product was allowed to stand overnight and then poured on cracked ice. The basic magnesium halide was dissolved by neutralizing with dilute sulfuric acid. The ether layer was separated and the aqueous layer extracted at least four times with ether. The combined ether solutions were dried over anhydrous sodium sulfate and fractionally distilled. The portion boiling from 109° to 115°C. was collected and saved for refractionation. Refractionation of 3440 grams of methylisopropylcarbinol collected at 109-115°C. yielded 1111 grams boiling at 110-111° and 1749 grams boiling 111-112°C.

Preparation of decene

The experimental conditions found by Cooke⁴ to give the best yield of dipolymer were employed. The amounts of material used and the yields obtained are given in Table 2. Methylisopropylcarbinol was added rapidly with vigorous stirring to one and one-half times the molecular equivalent of sulfuric acid in 75 per cent aqueous solution, specific gravity 1.67, in a three neck flask, fitted with a mercury sealed stirrer, reflux condenser and separatory funnel. It is important to add the alcohol rapidly as the lower yields

obtained in the first five runs were due to the slow addition of the alcohol over periods of 55, 38, 22, 10 and 16 minutes respectively. The temperature was raised rapidly to 80°C. and kept there for 20 minutes. The usual time for the addition of 200 grams of carbinol to 450 grams sulfuric acid solution and subsequent elevation of the temperature to 80°C. was five minutes. Refluxing occurs during the period of heating, due probably to the formation of low boiling olefins. At the end of twenty minutes the contents of the flask were quickly cooled to room temperature and the layer of hydrocarbon separated. It was washed with sodium bicarbonate solution, then with water, and dried over calcium chloride. The dry product was fractionally distilled and the fraction boiling from 149° to 169°C., containing the decenes, was saved for further purification. The 149-169°C fractions from all runs were mixed and placed over sodium wire. After standing overnight the material was refluxed for six hours and again allowed to stand overnight. The decene was distilled from the sodium through a short column packed with small pieces of glass tubing. A total of 1880 ml distilled between 147° and 163°C.

Table 2

Preparation of Decene

Run	Methyl- isopropyl carbinol used grams	Yield of decene grams	Percent of theore- tical yield %
1	100	33.	41.5
2	100	36.	45.5
3	50	18.5	46.5
4	50	20.	50.5
5	50	17.5	44.
6	50	21.	53.
7	100	46.5	58.5
8	200	91.	57.
9	200	87	54.5
10	204.5	93.5	57.5
11	208	100.	61.
12	202	95.5	59.5
13	200	83.	52.
14	202	96.5	60.5
15	200	192.	60.5
16	200	195	60.5
17	203	195	60.5
18	203.5	195	60.5
19	200	101.0	63.5
20	194	100.5	65.
21	112	44	49.5
22	49	23	59.

Fractionation of the decene

Inasmuch as the isomers of decene have boiling points within a narrow temperature range, it was known that a very efficient fractionating column would be required to separate the mixture under investigation. The Bureau of Standards in collaboration with the American Petroleum Institute has built several efficient laboratory stills for the fractional distillation of fairly large volumes of hydrocarbons. Arrangements were made through the kindness of S. T. Schickens and his colleagues to fractionate the decene mixture obtained from methylisopropylcarbinol through one of these stills. This still has been fully described in the literature²⁵. It consists, briefly, of a 3-liter still pot, supporting a column 2.5 cm. in diameter and 250 cm. long; the column is filled with approximately 3600 feet of jewelers brass locket chain, size number 13-18. The rectifying column is surrounded by a column jacket which is wired with four independent heating units in order to control the temperature gradient along the packed column. The reflux ratio is regulated by a reflux head which permits the major part of the vapor to pass into a condenser and be returned to the column while the remaining part of the vapor leaves the column through a side arm. The distillate is run into a

boiling-point apparatus of the Cottrell type and the boiling point of each fraction determined. Schickelanz found that this still running at a rate of 0.5 ml. of distillate per minute, with a reflux ratio of 22:1, a vapor velocity of 7.57 m per minute, and having a "hold up" of 180 ml, readily separates a mixture of benzene and ethylene dichloride. Starting with 1500 ml of a 50 mol percent mixture of benzene and ethylene dichloride, substances having boiling points differing by only $3.42^{\circ}\text{C}.$, it was possible to obtain 450 ml of almost pure benzene as distillate and 350 ml of almost pure ethylene dichloride as residue.

The results of the fractionation of 1820 ml of decene are presented in Table 3. The still was run at the average rate of 0.4 ml of distillate per minute and with a reflux ratio of 22:1. The temperature of distillation is plotted against the percent distilled in Figure 1. The refractive index of each fraction is plotted against the percent distilled in Figure 2. The latter curve consists of two well-defined plateaus with a fairly sharp rise between them in the 50-60 percent distilled area, suggesting the presence of two isomers in equal proportions. The temperature curve shows these same two plateaus but at least one other minor break is also present.

Table 3

Fractionation of decene

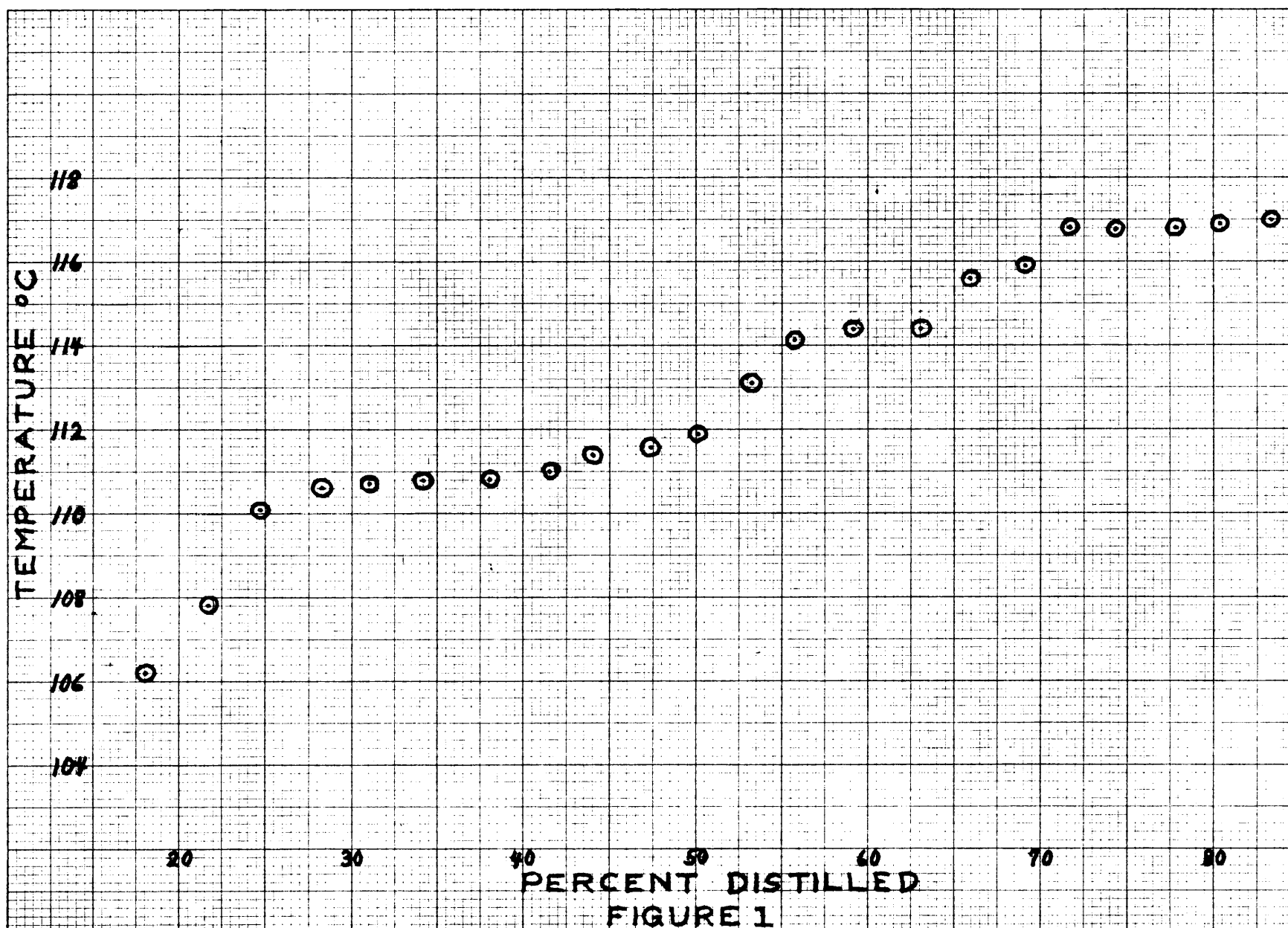
Volume of charge = 1820 ml.

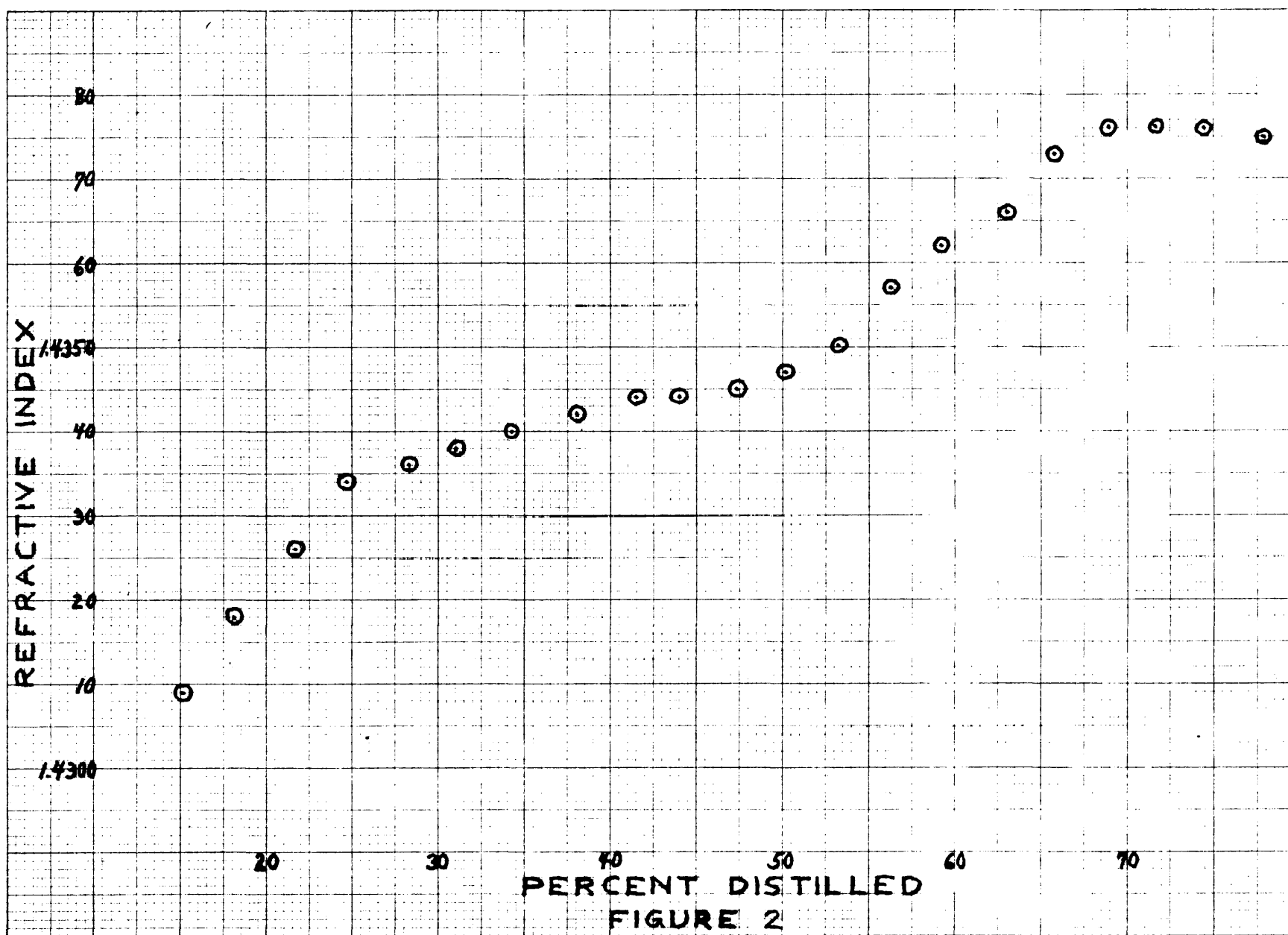
Refractive index(n_D^{25}) of charge = 1.4346

Fraction No.	Volume ml.	Percent distilled %	Temperature °C at 215 mm.	Refractive index n_D^{25}
1	52	2.9	<90°	1.4202
2	60	6.2	91.6	1.4252
3	52	9.0	103.1	1.4274
4	54	12.0	107.2*	1.4283
5	57	15.1	108.0*	1.4309
6	54	18.1	106.2	1.4318
7	64	21.6	107.8	1.4326
8	57	24.7	110.1	1.4334
9	66	28.3	110.6	1.4336
10	49	31.0	110.7	1.4338
11	58	34.2	110.8	1.4340
12	69	38.0	110.8	1.4342
13	63	41.5	111.0	1.4344
14	50	44.0	111.4	1.4344
15	56	47.3	111.6	1.4345
16	51	50.1	111.9	1.4347
17	57	53.2	113.1	1.4350
18	55	56.2	114.1	1.4357
19	52	59.2	114.4	1.4362
20	71	63.0	114.4	1.4366
21	54	65.8	115.6	1.4373
22	56	69.0	115.9	1.4376
23	50	71.6	116.8	1.4376
24	50	74.4	116.8	1.4376
25	51	77.8	116.8	1.4375
26	59	80.4	116.9	1.4375
27	53	83.4	117.0	1.4369**
28	46	85.9	117.3	1.4373
29	210	-	Residue	1.4403

* Leaks in system

** Still shut down for four days prior to taking this fraction.





Ozonization of the decene

The ozonizer described by Cooke⁴ was used in this investigation. The decene sample (20 ml) was mixed with three volumes of ethyl acetate and cooled in the ozonizing tube to -25°C . Ozome was passed through the solutions at varying rates, corresponding to flowmeter readings of 4 to 10 and to ozone values of 1.5 to 2.0 grams per hour. The upper limit was found to give satisfactory absorption and was used in most of the experiments. The amount of ozome was determined by passing the gas through 80 ml of 5 percent aqueous potassium iodide solution for five minutes and titrating the iodine, liberated after acidification, with standard thiosulfate solution. After the solution had been treated with the theoretical amount of ozone, the ozonide was decomposed by mixing with 100 ml 10 percent acetic acid and 7 grams zinc, and warming gradually on the steam bath with stirring. A water trap was used at the top of the reflux condenser to catch acetaldehyde vapors. The ethyl acetate layer was separated and the aqueous layer extracted four times with ethyl acetate. The ethyl acetate solution was washed with saturated sodium bicarbonate solution until free from acid, and then washed once with water. The solution was dried with ignited sodium sulfate and distilled through a small fractionating column filled with small pieces of glass tubing.

The presence of acetaldehyde was indicated in the first portion of each distillate by its characteristic odor; it was identified through the p-nitrophenylhydrazone, confirming the previous work of Wheeler⁵. The formation of formaldehyde toward the end of the ozonization period was noted, particularly when high concentrations of ozone were used. Qualitative tests with fuchsin and resorcinol reagents for formaldehyde gave positive tests on the aqueous solution obtained by passing the gas from the ozonizing tube through a water trap. Passage of ozone through ethyl acetate alone did not produce formaldehyde. Only traces of formaldehyde were obtained and its presence is believed to be due to decomposition of the decene ozonide by excess ozone.

Exploratory ozonolysis of the decene fractions

Fifteen gram portions of the decene fractions which were representative of the various plateau areas on the temperature curve (Figure 1) were ozonized and the ketones recovered in the manner described above. These were fractionally distilled through a small Claisen flask and a ml portion of each fraction treated with semicarbazide hydrochloride and sodium acetate in alcoholic solution to precipitate the semicarbazones of the ketones. In this

way a thorough examination of the fractionated decene for any isomers present was accomplished. The essential details of this exploration are presented below. The letter "s" in parentheses after the melting point of the semicarbazone indicates that only a small amount was obtained, usually only enough for a melting point determination.

Decene Fraction 2				Decene Fraction 5			
Bolling range of ketone cut	Amount	M.P. in °C.	1st crop of semicarbazone	Bolling Point = 91.6°C at 215 mm.	2nd crop of semicarbazone	M.P. in °C.	1st crop of semicarbazone
82-180	5.2	144-154 (s)	none	148-149 (s)	140	none	148-149 (s)
120-140	2.5	160-161	133	140-150	3.2	150	160-161
140-150	2.8	150	135	150-160	2.8	none	150
160-180	2.6	none	none	160-180	2.6	none	none
190-200	2.6	none	none	190-200	2.6	none	none
Decene Fraction 13				Decene Fraction 13			
Bolling Range of ketone cut	Amount	M.P. in °C.	1st crop of semicarbazone	Bolling Point = 111.0°C at 215 mm.	2nd crop of semicarbazone	M.P. in °C.	1st crop of semicarbazone
82-140	3.6	148-149	none	148-149	none	none	148-149
140-150	5.7	158-159	177-180 (s)	158-159	none	none	158-159
150-170	1.1	170-173 (s)	170-173 (s)	170-173 (s)	none	none	170-173 (s)
170-186	1.8	none	none	170-186	none	none	none
186-191	1.7	none	none	186-191	none	none	none
110-145	4.0	144	144	144	144	144	144
145-144	3.8	139	139	139	139	139	139
144-153	1.8	139	139	139	139	139	139
153-191	1.6	139	139	139	139	139	139

Decene Fraction 19		Bolling Point = 114.4°C at 215 mm.
Bolling Range of ketone cut °C	Amount ml.	1st Crop of semicarbazone M.P. in °C
80-130	1.6	158-164 (s)
130-150	1.4	153
150-160	4.7	146
160-180	2.4	131
>180	1.7	none
		2nd Crop of semicarbazone M.P. in °C
		151 (s)
		124 (s)
		132 (s)
		122
		none

Recrystallization from dilute alcohol raised the melting point of the 130-150° out from 153° to 164°C.; that of the 150-160° out from 146° to 168°; and that of the 160-180° out from 131 to 160°.

Decene Fraction 25		Bolling Point = 116.8° at 215 mm.
Bolling Range of ketone cut °C	Amount ml.	1st Crop of semicarbazone M.P. in °C
130	0.4	-
150-155	5.8	167
>155	1.0	-
		2nd Crop of semicarbazone M.P. in °C
		134 (s)

Decene Fraction 29		Bolling Point = Residue(>117.3°C at 215 mm)
Bolling Range of ketone cut °C	Amount ml.	1st Crop of semicarbazone M.P. in °C
80-150	1.6	162
150-160	5.5	160
160-180	2.2	150
>180	1.2	131 (s)
		2nd Crop of semicarbazone M.P. in °C.
		153 (s)
		none
		121 (s)
		none

Recrystallization from dilute alcohol raised the melting point of the 80-150° out from 162° to 168°C.; that of the 150-160° out from 160° to 165.5°C.; and that of the 160-180° out from 150° to 161-163°C.

It was observed that decene fractions 5 and 13 yielded primarily a ketone which boiled below 150°C and gave a semicarbazone which melted at about 144°C , whereas decene fractions 25 and 29 yielded a ketone which boiled above 150°C and gave a semicarbazone melting at about 168°C . Decene fraction 2 which was about 18° below the boiling range of the decenes evidently contained some other product besides the low boiling ketone, but it was not investigated further. Decene fraction 19 was a mixture of the two decenes with the higher boiling isomer predominating. It was, therefore, evident that there were only two isomers of decene present.

Preparation of the two ketones

Decene fractions 21 to 29 were ozonized in 20 to 25 ml portions, the ethyl acetate removed by distillation through a small column, and high boiling residue fractionated in a Claisen flask. The results are given in Table 4. The higher boiling ketone thus obtained (fraction $150-160^{\circ}\text{C}$.) was redistilled (Table 5) through a Podbielniak vacuum-jacketed column at the rate of 0.25 ml per minute. The refractive index, density and Cottrell boiling point were determined for various fractions. The ketone was found to have the following properties: Cottrell boiling point $768 = 154.4^{\circ}\text{C}$.; $d_{\frac{20}{4}} = 0.829$; $n_D^{25} = 1.4183$. Fraction 11, the

properties of which were considerably different from the above ketone, would not yield a semicarbazone and was not investigated further.

Decene fractions 3 to 9 were ozonized in 20 to 25 ml portions and the decomposition products distilled in the same manner as the higher fractions. The yields as given in Table 4 are lower than those obtained with the higher boiling ketone. Inasmuch as this lower boiling ketone was later found to have a boiling point of 147.2°C at 766 mm pressure, considerable amounts of this ketone are probably in the fraction boiling above 150°C . This ketone was turned over to W. Gordon Rose for further investigation. Its properties were found by him²⁶ to be as follows: Cottrell boiling point = 147.2°C ; $d_4^{20} = 0.826$; $n_D^{25} = 1.4136$; semicarbazone melting point = $147.6-8^{\circ}\text{C}$.

Table 4

Ozonization of decene

Sample No.	Composition of sample Fract. No.	Composition of sample Amt. in ml.	Fraction 1 boiling range °C	Fraction 1 Amt. g.	Fraction 2 boiling range °C	Fraction 2 Amt. g.	Fraction 3 boiling range °C	Fraction 3 Amt. g.	Percent of theoretical yield of ketone (based on fract. 2)
1	28	44	80-150	4.5	150-160	23.5	>160	4.5	64.4
2	22	54.5							
3	21	6.0	80-150	7.0	150-160	34.5	>160	8.0	68.8
4	29	12.0	80-150	8.0	150-160	52.0	>160	31.0	52.2
5	29	60	80-150	5.0	150-160	31.0	>160	14.0	62.3
	21	44							
	27	20	80-150	8.0	150-160	38.5	>160	9.0	72.5
6	7	63							
	8	52.5							
7	9	65.5	80-135	30.0	135-150	86.5	>150	33.5	57.6
	5	15.0							
	6	54.0							
8	8	3.0	80-135	7.0	135-150	35.0	>150	20.0	39.6
	3	44.5							
	4	52.5	80-135	21.0	135-150	47.0	>150	17.0	52.9

Table 5

Distillation and properties of higher
boiling ketone

Charge = 188 ml Pressure = 188 mm

Fract. No.	Amount ml.	Percent distill- ed %	Thermo- couple temper- ature °C	Refractive Index n_{25}^D	Density d_{20}^4	Cottrell boiling point at 768 mm °C
1	9.65	5	66.5-104	1.4064	-	-
2	9.55	10	104-105	1.4195	-	-
3	18.60	20	105-107.5	1.4196	0.826	-
4	18.60	30	107.5	1.4195	-	152.8
5	18.85	40	107.5	1.4190	0.828	153.7
6	18.85	50	108	1.4186	-	154.1
7	18.85	60	108	1.4184	-	154.2
8	18.75	70	108	1.4183	0.829	154.4
9	18.70	80	108	1.4183	-	154.45
10	18.60	90	108-124	1.4205	-	-
11	10.30	95.5	124-129	1.4309	0.842	-

Derivatives of ketone (b.p. 154.4°C.)

Preparation of semicarbazone of ketone (b.p. 154.4°C.)

Three grams of semicarbazide hydrochloride and 3.4 g. sodium acetate were dissolved in 30 ml of water and 30 ml 95% ethyl alcohol. 2.4 ml of ketone fraction 8 were added with stirring. The mixture was neutralized with 10% sodium hydroxide solution and five drops of glacial acetic acid were added. The precipitate, which formed rapidly, was filtered off and recrystallized from 50% ethyl alcohol to constant melting point. Melting point = 169.5°C.(corr.). Analysis of this derivative is reported in Wheeler's thesis⁵.

Preparation of 2,4-dinitrophenylhydrazone of ketone(b.p.154.4°C.)

Eight-tenths of a gram of 2,4-dinitrophenylhydrazine and 0.7 ml ketone fraction 8 were dissolved in 40 ml of 95% ethyl alcohol and brought to a boil under a reflux condenser. The solution was allowed to cool one minute and 0.8 ml concentrated hydrochloric acid added. The solution was then boiled for two minutes and allowed to cool. The precipitate was recrystallized from 95% ethyl alcohol to constant melting point. Melting point = 146.5 - 147°C. This derivative is very insoluble in alcohol and petroleum ether.

Analysis:

Sample mg.	H ₂ O mg.	CO ₂ mg.	Hydrogen %	Carbon %
3.742	2.103	7.429	6.29	54.14
4.229	2.408	8.386	6.37	54.09
Calculated for C ₈ H ₁₆ N ₂ HO ₆ H ₃ (NO ₂) ₂			6.54	54.50



Iodoform test on ketone (b.p. = 154.4°C.)

Seven and one-half ml iodine solution (8 g. iodine and 24 g. potassium iodide in 120 ml water) were added to 1 ml of 10% sodium hydroxide. Three drops of ketone fraction 8 were then added, the mixture was heated to 60°C., and shaken vigorously for 15 to 30 minutes. A yellow precipitate formed and settled to the bottom, indicating the presence of a methyl ketone.

Oxidation of ketone (b.p. 154.4°C.) with sodium hypobromite

Thirty-three grams of sodium hydroxide were dissolved in 280 ml water and cooled to 0°C. in a 3-necked 1-liter flask, fitted with a stirrer, reflux condenser, dropping funnel and thermometer. Four and eight-tenths grams of bromine were added in 25 minutes keeping the temperature below 3°C. The solution was cooled to 0°C. again and 13 g. of ketone boiling at 154.4°C. were added in 15 minutes. The temperature did not rise above 1°C. The solution was stirred vigorously for 1 hour

with the temperature between 0° and 50°, then stirred for five hours at room temperature, warmed to 60°C. and stirred for 1 hour at that temperature. The reflux condenser was changed to distilling position and the bromoform and carbon tetrabromide steam distilled. After cooling to 50°C. and adding 40 ml concentrated sulfuric acid, the organic acid present was steam distilled. The distillate was extracted thoroughly with ether and dried over ignited sodium sulfate. Fractional distillation yielded 7 grams of an acid boiling at 103-104° at 15 mm. Yield = 83% theoretical. Repetition of the above reaction with 51.8 grams of ketone and proportionately larger amounts of reagents yielded 23 grams of acid, which is 45 percent of the theoretical yield. A boiling point determination made at atmospheric pressure gave the value 215°C at 776 mm.

Analysis:

Sample	H ₂ O	CO ₂	Hydrogen	Carbon
mg.	mg.	mg.	%	%
2.890	2.663	6.626	10.56	64.02
Calculated for C ₉ H ₁₄ O ₂			10.34	64.59

Derivatives of acid (b.p. 213°)

Preparation of the amide of $C_7H_{14}O_2$ (b.p. $\approx 213^{\circ}C.$)

One ml of the acid was refluxed one-half hour with 1.2 ml thionyl chloride and poured into 15 ml concentrated ammonium hydroxide with cooling. The precipitate was filtered and recrystallized from petroleum ether ($60-67^{\circ}C.$) to constant melting point. Melting point = $76.5^{\circ}C$ (corr.)

Analysis:

Sample mg.	H_2O mg.	CO_2 mg.	Hydrogen %	Carbon %
3.569	3.749	8.504	11.75	64.98
3.558	3.721	8.461	11.70	64.85
Calculated for $C_7H_{15}ONH_2$			11.70	65.02

Preparation of the anilide of $C_7H_{14}O_2$ (b.p. $213^{\circ}C.$)

One ml of the acid was refluxed one-half hour with 1.2 ml thionyl chloride and poured into 2.5 ml aniline dissolved in chloroform. The excess aniline was removed by washing with dilute hydrochloric acid. The anilide was obtained by evaporating the chloroform and recrystallized from petroleum ether ($60-67^{\circ}C.$) to constant melting point. Melting point = $105.5 - 106^{\circ}C.$ (corr.)

Analysis:

Sample mg.	H ₂ O mg.	CO ₂ mg.	Hydrogen %	Carbon %
3.502	2.942	9.751	9.40	75.93
3.555	3.003	9.865	9.45	75.68
Calculated for C ₇ H ₁₃ ONHC ₆ H ₅			9.34	76.00

Preparation of the p-phenylphenacyl ester of C₇H₁₄O₂
(b.p. = 213°C.)

Approximately 0.005 mol of the sodium salt of the acid was refluxed with 0.005 mol of p-phenylphenacyl bromide in 15 ml of 75% ethyl alcohol for one hour. Sufficient alcohol was added to keep the ester in solution. The precipitate which separated on cooling was filtered off and recrystallized from alcohol to constant melting point. Melting point = 74°C. (Corr.)

Analysis:

Sample mg.	H ₂ O mg.	CO ₂ mg.	Hydrogen %	Carbon %
3.231	2.186	9.182	7.57	77.50
3.323	2.249	9.475	7.57	77.77
Calculated for C ₇ H ₁₅ O ₂ CH ₂ COC ₆ H ₄ C ₆ H ₅			7.45	77.70

Attempted preparation of $C_6H_{12}O_2$

There are only eight six carbon fatty acids as compared with seventeen seven carbon fatty acids. Isolation of a six carbon acid would, therefore, have simplified the problem of identification of the decene. This was first attempted by the transformation of the carboxyl group of the seven carbon acid to a diphenylcarbinol group and subsequent oxidation of the tertiary carbinol which should split off benzophenone to form the six carbon acid. The diphenylalkylcarbinol was prepared from the seven carbon acid methyl ester and bromobenzene through the Grignard reaction.

Preparation of the methyl ester of $C_7H_{14}O_2$ (b.p. $213^{\circ}C.$)

Seventeen ml of methylnitrosourethane were diluted with 85 ml of absolute ether and heated to boiling in a 500 ml distilling flask. Approximately 25 ml of a 25% of potassium hydroxide in methyl alcohol were added, keeping the solution boiling without additional heat. The contents of the flask were distilled until colorless. The diazomethane was collected in 100 ml absolute ether with an adapter dipping below the surface. The yield was determined by adding an aliquot of the ether solution to a weighed amount of

p-nitrobenzoic acid and titrating the excess acid, and was found to be 0.23 g. diazomethane per ml methylnitrosourethane. There was, therefore, available 3.17 g. of diazomethane for methylation. Seven grams of $C_7H_{14}O_2$ of boiling point $213^{\circ}C$. (requires 2.26 g. CH_2N_2) were added to the cold diazomethane solution. The ether was evaporated and the ester vacuum distilled. Five and one-half grams of the ester boiling at $49-50^{\circ}C$ at 17 mm. were collected. Yield = 71 percent theoretical.

Preparation of the diphenylalkylcarbinol

Eighteen grams (0.12 mol) of brombenzene in dry ether were added slowly to 4 g. (0.16 mol) magnesium covered with dry ether. The solution was refluxed on the steam bath for 15 minutes after the first vigorous reaction had subsided and then cooled to $0^{\circ}C$. Five and one-half grams (0.04 mol) of the acid methyl ester in dry ether solution were added and the solution warmed gradually and finally refluxed on the steam bath for one-half hour. It was then poured on ice, neutralised with dilute hydrochloric acid and extracted with ether. The ether extract was dried over sodium sulfate. After evaporation of the ether about 8 g. of semi-solid residue remained.

Oxidation of the tertiary carbinol

Six grams of chromic acid anhydride were dissolved in 10 ml glacial acetic acid and 10 ml water, and added drop by drop to the 8 g. crude tertiary carbinol in 30 ml glacial acetic acid. The solution was warmed on the steam bath for 15 minutes, poured into 200 ml water and extracted thoroughly with ether. The ether was evaporated and the residue made alkaline with sodium hydroxide. The benzophenone was extracted with ether. When this fraction was distilled, 5.5 grams of high boiling residue was obtained which did not solidify. The alkaline aqueous fraction was made acid to Congo Red with sulfuric acid, extracted with ether, and the ether extract dried over ignited sodium sulfate. Fractional distillation failed to yield any organic acid.

Oxidation of the ketone with chromic-sulfuric acid mixture.

Methyl ketones when oxidized with chromic-sulfuric acid mixture usually split off acetic acid as one of the main products. This should have resulted in the formation of a six carbon acid or a lower molecular weight ketone with the ketone (b.p. $154.4^{\circ}\text{C}.$) under investigation. Nineteen and one-half grams of chromic acid anhydride were dissolved in

120 ml water and 16 ml concentrated sulfuric acid. Fifteen ml of $C_8H_{16}O$ were added and the solution boiled in a 1 liter flask for one and one-half hours. An emulsion was noted in the reflux condenser. The contents of the flask were steam distilled until nearly dry; 30 ml of water were added and the solution distilled to nearly dryness again. The distillate was made alkaline with sodium hydroxide and the ketone extracted with ether. Eight and one-half ml of ketone were recovered. The aqueous solution was acidified with sulfuric acid and extracted with ether. A small amount of organic acid was noted. The 8.5 ml of ketone was boiled with chromic-sulfuric acid mixture for 24 hours. Only 1 ml of ketone was recovered which was shown to be the original ketone by preparation of the semicarbazone. The ether extract containing the organic acid formed in this second treatment was added to the first portion and dried over ignited sodium sulfate. Fractional distillation yielded 2 ml of acid boiling at 96-100°C. at 16 mm. Oxidation of the ketone with chromic-acetic acid mixture did not result in better yields of organic acid.

The amide of the organic acid fraction was prepared as previously described. Fractional crystallization from petroleum ether seven times yielded a small amount of the less soluble fraction melting at 82-88°C. and the residue as an amide melting at 73.5-74.5°C. A mixed melting point of the latter material with the amide of the seven carbon acid

melting at 76.5^o C. gave no depression of the melting point. Recrystallization of the 82-88^o material from petroleum ether two more times gave a very small amount of material melting at 90-100^oC. Mixed melting points of this material with the seven carbon acid amide and acetamide gave depressions of the melting point below 70^oC. A mixed melting point with dimethylethylacetamide, which melts at 103^oC., did not depress the melting point but melted indefinitely at about 90^oC. It was, therefore, evident that the ketone was abnormal in its behavior and tended to split off the methyl group to yield a seven carbon acid rather than form the six carbon acid. This behavior is not surprising in view of the structure of the ketone as later established, since Whitmore has found that a CH₂ group attached to a tertiary carbon is very non-reactive.

Synthesis of methyldiethylacetic acid

The amide of this acid is reported by A. Haller and E. Bauer²⁷ to melt at 78-79^oC. As this was within two degrees of the melting point of the amide obtained from the unknown C₇H₁₄O₂ (b.p. 213^oC.) the above acid was synthesized by a method not heretofore reported in the literature for this acid, namely by the addition of carbon dioxide to methyl-diethylcarbonyl magnesium chloride.

Preparation of methyldiethylcarbinol

One hundred twenty-seven grams (5.2 mols) of magnesium turnings were placed in a 2-liter 3-necked flask fitted with a stirrer, reflux condenser and separatory funnel. The magnesium was covered with 200 ml dry ether. Five hundred grams (4.6 mols) ethyl bromide mixed with 350 ml ether were added over a period of five hours. The solution was refluxed on a water bath for one-half hour and then cooled to 5°C. One hundred eighty grams (2 mols) of ethyl acetate in 125 ml of ether were added over a period of 3 hours, maintaining the temperature at about 20°C. The solution was refluxed a half hour and allowed to stand overnight. Thirty-five grams (0.4 mol) of ethyl acetate in 15 ml of ether were added rapidly. The solution was refluxed a half hour, then poured on cracked ice, neutralized with dilute sulfuric acid and extracted with ether. The ether extract was dried over potassium carbonate. Fractional distillation yielded 125 grams of methyldiethylcarbinol boiling between 120-125°C. Percent yield = 53.4% theoretical.

Preparation of methyldiethylcarbiny chloride

Hydrochloric acid gas was generated by dropping sulfuric acid on sodium chloride covered with aqueous hydrochloric acid and dried by passing through two washing

towers containing sulfuric acid. The dry hydrochloric acid gas was passed into 125 grams (1.2 mols) of methyl-diethylcarbinol containing 45 grams of calcium chloride for three hours. After one and one-half hours the calcium chloride had taken up sufficient water to form a separate layer. This was removed and 45 grams fresh calcium chloride was added. The solution was filtered and refluxed at 90 mm pressure for three-fourths of an hour. Vacuum distillation yielded 100 grams (.83 mol) of tertiary chloride distilling at 55-56° at 90 mm pressure. Yield = 69% theoretical. The chloride was kept over ignited potassium carbonate.

Preparation of methyldiethylacetic acid

Twenty-five grams (1 mol) of dried powdered magnesium were placed in a 2-liter 3-necked flask fitted with a stirrer, reflux condenser, and a separatory funnel. One hundred twenty-five ml of dry ether (distilled from Grignard reagent) and 3 grams of the tertiary chloride were added. It was necessary to add iodine and methyl iodide to start the reaction, which was initiated only after one hour elapsed time. The remaining 84 grams (.72 mol) of tertiary chloride contained in 500 grams ether (total used = 8 mols) was added over a period of 4 hours. The solution was

refluxed a half hour and cooled to -9°C . Carbon dioxide gas was passed into the flask for two and one-fourth hours. A slight pressure was obtained by a 2" mercury seal at the top of the condenser. The solution was allowed to stand overnight, then poured on cracked ice and acidified to Congo Red with dilute sulfuric acid. The acid was extracted with ether and the ether extract dried over sodium sulfate. The ether was distilled off and the residue extracted with sodium bicarbonate solution and finally with 20% sodium hydroxide solution. It was boiled for a half hour, then acidified to Congo Red with sulfuric acid and extracted with ether. The ether extract was dried with sodium sulfate. Distillation yielded 7.5 grams (0.06 mol) of acid boiling at 104° under 14 mm pressure. Yield of methyl-diethylacetic acid = 8% theoretical. The usual fatty acid odor was lacking in the case of this acid, the product being odorless.

Derivatives of methyl-diethylacetic acid:

Preparation of the amide of methyl-diethylacetic acid

The amide of this acid was prepared by the method previously described and recrystallized from petroleum ether ($60-67^{\circ}$) to constant melting point. Melting point = 78.5°C . (corr.). A mixed melting point with the amide melting at 76.5°C ., prepared from the unknown acid of boiling point

213°C, melted from 52° to 62°C., remelting in the same range. The two amides were therefore derived from two different acids.

Preparation of the anilide of methyldiethylacetic acid.

The anilide of this acid was prepared by the method previously described. The product was recrystallized from petroleum ether (60-67°C.) to constant melting point. Melting point = 88.5°C. (corr.)

Preparation of p-phenylphenacyl ester of
methyldiethylacetic acid

The p-phenylphenacyl ester of this acid was prepared by the method previously described. The product was recrystallized from alcohol to constant melting point. Melting point = 76°C. (corr.).

Synthesis of 3-methyl-3-ethylpentanone-2

The semicarbazone of this ketone is reported by Nyberg²⁸ as melting at 168°C. The boiling point of the ketone is given as 153.5-154°C. at 756 mm. Inasmuch as these physical properties are remarkably like those of our ketone, it was believed worth while to prepare this ketone

in order to take mixed melting points of the semicarbazones, although the Hofmann oxidation should yield methyldiethylacetic acid which had already been synthesized. Synthesis of this ketone would show whether rearrangement had taken place during the preparation of the acid.

Preparation of symmetrical-methylethylpinacol

One kilogram of methylethylketone was refluxed with calcium oxide for one hour. A fresh 200 gram portion of calcium oxide was added and refluxing continued for another hour. Distillation yielded 760 grams boiling 77° to 84°C . Eighty grams (3.29 mols) of magnesium were placed in a 5-liter flask and covered with 800 ml dry benzene. Ninety grams (.3 mol) of mercuric chloride in 500 g. (7 mols) methylethylketone were added rapidly, followed by the addition of 260 g. (3.5 mols) ketone in 200 ml dry benzene before refluxing ceased. The solution was heated on the steam bath for 15 hours. Vigorous refluxing took place for 2 hours and then subsided. The contents of the flask became a solid smooth mass. Two hundred ml of water were added and the solution was refluxed gently overnight, cooled and decanted. Two hundred fifty ml of benzene and 20 ml water were added, and the mixture heated on the steam bath for a half hour, cooled and decanted. Two hundred fifty ml benzene were added and the above process repeated. The

benzene was distilled from the decanted solution. When the temperature of the vapor reached 84° water appeared again in the column. The contents of the flask were then transferred to a Claisen flask and vacuum distilled. The material boiling below 64° at 13 mm was taken off and then the following fractions collected at 11 mm:

Fraction	Temp. distillate	Amount
1	$64-87^{\circ}\text{C.}$	104 g.
2	$87-100^{\circ}\text{C.}$	137 g.
3	$100-120^{\circ}\text{C.}$	49 g.
4	$120-145^{\circ}$	44 g.
5	Residue	60 g.

Fraction 2 represents the best material. Fractions 1 and 3 undoubtedly contain some of the pinacol. The yield was therefore approximately 50 percent of the theoretical based on the amount of magnesium used.

Rearrangement of the pinacol to the pinacolone:

Eight hundred grams of sulfuric acid in a 1-liter 3-necked flask fitted with a stirrer, separatory funnel and thermometer were cooled to -10°C. and 100 g. of pinacol (51 g. Fraction 2 and 49 g. fraction 3) were added slowly over a period of one and one-half hours, keeping the temperature about -6°C. The solution was stirred vigorously for 2 hours longer at -6°C. , poured on finely cracked ice and steam distilled, collecting about one and one-half liters.

Seventy-one grams of oily insoluble material were separated and dried over calcium chloride. The ketones were distilled through a Claisen flask at ordinary pressure (747 mm) and the following fractions collected:

Fraction	Temperature	Amount
1	127-150	7.0 g.
2	150-151.5	2.5 g.
3	151.5-153	2.5 g.
4	153-155	7.0 g.
5	155-160	6.5 g.
6	Residue	37.0 g.

Nyberg states that the rearrangement goes 20 percent involving the migration of a methyl group to give an ethyl ketone boiling at 151.5° (semicarbazone M.P. 98°C.) and 80 per cent involving the migration of an ethyl group to yield a methyl ketone boiling at 153.5-154° (semicarbazone M.P. 168°C.).

Derivatives of 3-methyl-3-ethylpentanone-2:

Preparation of the semicarbazones of Nyberg's ketones

One ml. of fractions 1 to 4 was mixed with 1.5 g. semicarbazide hydrochloride and 1.7 g. sodium acetate in 50% alcohol solution. The solution was neutralized with 10 percent aqueous sodium hydroxide solution and 0.25 ml acetic acid added. After 24 hours the precipitate was filtered off, water added to the filtrate and a second

crop of crystals collected. The following melting points were observed:

Fraction	1st Crop M.P. °C	2nd Crop M.P. °C
1	149-159	129-139
2	159-163	143-146
3	162-166	154-159
4	167.5	159.5-161.5

Fraction 4 material had been recrystallized from 50 percent alcohol. A mixture of the 167.5° semicarbazone above with the semicarbazone (M.P. 169.5°) of the unknown ketone boiling at 154.4°C., melted indefinitely from 136 to 150°. The unknown ketone is, therefore, not 3-methyl-3-ethylpentanone-2, despite the similarity in physical properties.

Preparation of the 2,4-dinitrophenylhydrazone of
3-methyl-3-ethylpentanone-2

A 0.7 ml portion of fraction 4 (b.p. 153-155°) was used to prepare the 2,4-dinitrophenylhydrazone by the method previously described. The product was recrystallized three times from alcohol and once from 36-52°C. petroleum ether to constant melting point. Melting point = 92-92.5°C. This derivative will therefore serve to differentiate this ketone from the one boiling at 154.4°C. obtained by ozonolysis of the higher boiling decene.

Preparation of $C_6H_{13}NH_2$ from ketone (b.p. $154.4^\circ C.$)

The Beckmann rearrangement³⁵ of the oximes of ketones to substituted amides is very often a useful method for the degradation of ketones to smaller molecular weight products. It was realized that if the ketone under investigation ($C_6H_{13}COCH_3$) rearranged in the "anti" sense, a substituted acetamide ($C_6H_{13}NHCOCH_3$) would be produced which probably could be hydrolyzed to yield a six carbon amine. This would considerably simplify the problem of identification of the structure of the six carbon alkyl radical.

Preparation of the oxime of the ketone (b.p. $154.4^\circ C.$)

Thirty-five grams hydroxylamine hydrochloride in 60 ml water, 31 g. ketone, and 200 ml 95% alcohol were mixed together in a 500 ml flask connected to a reflux condenser. Fifty-seven grams potassium hydroxide in 57 ml water were added with vigorous shaking. The mixture was refluxed for two hours, cooled and extracted with ether without acidifying. The ether extract was dried over sodium sulfate and distilled. This procedure gave a clear distillate whereas when the mixture was acidified before the ether extraction, the oxime fraction was rendered

turbid by the presence of hydroxylamine hydrochloride. Twenty-nine grams of ketoxime boiling at 101°C . at 13 mm was obtained. Yield = 81 percent theoretical. The yields obtained in two preparations when the solution was acidified before extraction were as follows:

20 g. ketone yielded 14 g. ketoxime = 62.5 percent theoretical; 23 g. ketone yielded 15 g ketoxime = 58 percent theoretical. The ketone used in these two latter preparations was made available for this investigation through the courtesy of W. Gordon Rose. It was obtained by him from one of the decenes present in Sharples "Diamylene" and was shown to be identical with the author's ketone by a mixed melting point of the semicarbazones.

Analysis:

Sample mg.	H ₂ O mg.	CO ₂ mg.	Hydrogen %	Carbon %
2.931	3.061	7.158	11.68	66.57
Calculated for C ₈ H ₁₆ NOH			11.97	67.06

Beckmann rearrangement of the oxime.

Twenty-five grams of ketoxime were dissolved in 220 ml ether. Thirty-seven grams of phosphorus pentachloride were added with vigorous shaking over a period of one hour while cooling to -5°C . in an ice-salt bath. A precipitate

formed in the flask during the first few minutes and redissolved before the addition of the phosphorus pentachloride was completed. After standing overnight, the ether was removed by distillation and the residue poured on cracked ice. The aqueous solution was made alkaline with sodium hydroxide and extracted thoroughly with ether. The ether extract was dried over sodium hydroxide and distilled. Five grams of amide boiling at 125°C . at 13 mm was obtained. Yield = 20 percent theoretical. Approximately the same yield was obtained in two other preparations using 14 g. and 9.5 g ketoxime.

The use of benzene sulfonyl chloride instead of phosphorus pentachloride as the reagent for effecting rearrangement was also tried. Five grams ketoxime were dissolved in 25 ml pyridine and 6.1 ml benzene sulfonyl chloride added while cooling. The mixture was allowed to stand at room temperature for one hour. The precipitate which formed in the ice bath dissolved at room temperature with evolution of heat. The solution was poured on a mixture of 15.5 g sulfuric acid and cracked ice. The aqueous solution was extracted with ether and the ether extract was dried over ignited sodium sulfate. Distillation yielded one gram of amide boiling at 125° at 13 mm and 1.5 g of a high boiling (approximately 225° at 13 mm) material. The yield of the amide boiling at 125° at 13 mm was, therefore, the same as that obtained by the use of

phosphorus pentachloride. All attempts to effect the crystallization of this amide were without success.

Hydrolysis of the unknown amide.

The amide was found to be very stable to both alkaline and acid hydrolysis at ordinary pressure. Hydrolysis was effected, however, by acid in a sealed tube. Five grams of amide were heated in a sealed tube with 15 ml of a 1:1 aqueous phosphoric acid solution at 230-240° for five hours. Ten ml concentrated hydrochloric acid were added and the solution extracted with ether several times to remove any unhydrolyzed amide. The solution was saturated with potassium hydroxide while cooled in an ice bath. The amine was distilled into 1:1 aqueous hydrochloric acid and the amine hydrochloride obtained as a solid by evaporation of the aqueous acid on a steam bath. It was dried in a vacuum dessicator over potassium hydroxide. Approximately five grams of amine hydrochloride were obtained.

Derivatives of $C_6H_{13}NH_2$

Preparation of the picramide of the unknown amine.

One gram of the amine hydrochloride was dissolved in a little water and saturated with potassium hydroxide.

The amine was extracted with several portions of ether, the ether solution added to 1 g picryl chloride dissolved in 50 ml of 95% ethyl alcohol, and the ether evaporated on a steam bath. The solution was cooled and the precipitate separated by filtration. It was recrystallized from 60-67° C. petroleum ether to constant melting point. Melting point = 88-88.5°C. (corr.)

Analysis:

Sample mg.	H ₂ O mg.	CO ₂ mg.	Hydrogen %	Carbon %
4.577	2.113	7.717	5.17	45.97
4.688	2.188	7.929	5.22	46.12
Calculated for C ₈ H ₁₃ NHOC ₆ H ₄ (NO ₂) ₃			5.16	46.12

Preparation of the benzenesulfonamide of the unknown amine.

One gram of the amine hydrochloride in 30 ml of five percent potassium hydroxide was mixed with 1.2 ml benzenesulfonyl chloride, shaken vigorously for several minutes and then warmed on the steam bath to hydrolyze the excess chloride. The solution was cooled and the side of the flask scratched to crystallize the heavy oil which remained undissolved. The precipitate was filtered and recrystallized from 35-50°C. petroleum ether to constant melting point. Melting point = 59-59.5°C. (corr.).

Analysis:

Sample mg.	H ₂ O mg.	CO ₂ mg.	Hydrogen %	Carbon %
3.305	2.294	7.231	7.78	59.66
4.268	2.984	9.338	7.82	59.68
Calculated for C ₈ H ₁₃ NH ₃ SO ₂ C ₆ H ₅			7.94	59.70

(All analyses recorded in this thesis were made by J. R. Spies.)

Synthesis of 1-amino-2,2-dimethyl-butane

This amine was desired in order to compare the melting points of its picramide and benzenesulfonamide with those of the six carbon amine obtained by degradation of the unknown eight carbon ketone of boiling point 154.4°C.

Preparation of dimethylethylacetic acid.

A few small crystals of iodine were placed in a 2-liter 3-necked round bottom flask, fitted with a reflux condenser, stirrer and graduated dropping funnel, all connections being made with ground glass joints. The iodine was covered with 98 g. (4 mols) of magnesium turnings dried overnight over phosphorus pentoxide. The flask was heated to vaporize the iodine and allowed to cool. A mixture of 426 g. (4 mols) of tertiary amyl chloride (b.p. 84-86°C.) dried over ignited potassium carbonate and 500 ml ether dried by distilling from ethyl magnesium bromide was prepared. Thirty ml of the halide mixture were added to the reaction flask. The reaction was well started

in eight minutes. Two hundred ml of dry ether were then run in rapidly, followed by 475 ml of the halide mixture at a maximum rate of one drop per second (3 ml per minute). Three hundred ml of dry ether were added to the remaining halide mixture and this mixture run into the reaction flask at the same slow rate as above. Addition of the halide mixture took nine hours. The solution was stirred one hour longer and cooled to -20°C . with dry ice in carbon tetrachloride-toluene mixture. Carbon dioxide gas was passed in for three hours, maintaining a slight pressure by a mercury seal at the top of the condenser. The solution was allowed to stand overnight, then poured on cracked ice, made acid to Congo Red with dilute sulfuric acid and extracted five times with ether. The ether extract was dried over sodium sulfate. Fractional distillation yielded 255 g (2.2 mols) of acid boiling at 85°C . at 13 mm. Yield = 55% of theoretical.

Preparation of dimethylethylacetyl chloride.

Fifty-eight grams (0.5 mol) of dimethylethylacetic acid were added to 68 g (0.57 mol) thionyl chloride dropwise over a period of one hour while warming on a steam bath under a reflux condenser. The solution was refluxed for one hour longer and distilled. There was obtained 58 g.

(0.43 mol) of acid chloride boiling at 132-134° C. at atmospheric pressure. Yield = 86% of theoretical.

Preparation of dimethylethylacetamide.

The acid chloride from 56 g. (.5 mol) of dimethylethylacetic acid, prepared as above, was run dropwise into an ice-ammonium hydroxide mixture without isolating the chloride by distillation. The precipitate was filtered on a Buchner and washed with a small amount of cold water. The yield of amide was 44 g. (0.38 mol), equal to 76% of the theoretical amount based on the acid used.

Preparation of dimethylethylaceto-nitrile.

Twenty-two grams (0.19 mol) of the amide and 32 g phosphorus pentoxide were mixed thoroughly and heated gently in a round bottomed flask for ten minutes. The mixture was distilled until no more nitrile came off. One part by volume of water was added to 2 parts of the nitrile and the solution saturated with potassium carbonate. The nitrile layer was separated, a small amount of phosphorus pentoxide added and the nitrile redistilled. There was obtained 15.8 g (0.16 mol) nitrile boiling at 128-129° at 760 mm. Yield = 86% theoretical.

Preparation of 1-amino-2,2-dimethylbutane.

Fifteen and eight-tenths grams (0.16 mol) of the nitrile were mixed with 250 ml absolute ethyl alcohol and 20 g. of sodium, cut up in small pieces, were added. The flask was cooled under a reflux condenser until the vigorous reaction had subsided, then heated until the sodium was completely used up. The solution was cooled and hydrochloric acid added until the reaction mixture was acid to Congo Red. A considerable excess of hydrochloric acid was added and the alcohol removed by distillation. The aqueous residue was saturated with potassium carbonate and the amine distilled into 1:1 hydrochloric acid. The hydrochloric acid solution was evaporated nearly to dryness on the steam bath. Drying was completed in a vacuum dessicator over potassium hydroxide.

Derivatives of 1-amino-2,2-dimethylbutane

Preparation of the picramide of 1-amino-2,
2-dimethylbutane.

The picramide was prepared in the manner previously described and recrystallized from 60-67°C. petroleum ether to constant melting point. Melting point = 87.8-88.6°C.(corr.). Mixed melting point with picramide of unknown six carbon amine

which melted at 88-88.5°C. gave no depression of the melting point.

Preparation of the benzenesulfonamide of 1-amino-2,
2-dimethylbutane

The benzenesulfonamide was prepared in the manner previously described and recrystallized from petroleum ether to constant melting point. Melting point = 59-59.5°C.(Corr.). Mixed melting point with benzenesulfonamide of unknown six carbon amine which melted at 59-59.5°C. gave no depression of the melting point.

SUMMARY

1. Methylisopropylcarbinol has been shown to be dehydrated and the resulting olefins polymerized by the action of seventy-five percent sulfuric acid at 80°C. to yield a mixture of two decenes, namely 3,4,5,5-tetramethylhexene-2 and 3,5,5-trimethylheptene-2, present in equal proportions.

2. A mechanism has been postulated for this polymerization, based on the apparent activation of trimethylethylene as $\text{CH}_3 + \text{C}(\text{CH}_3) = \text{CH}(\text{CH}_3)$ and subsequent addition to another molecule of olefin.

3. This reaction makes available a source not only of the two new decenes mentioned above, but also of the corresponding decanes, 2,2,3,4-tetramethylhexane and 3,3,5-trimethylheptane, the two eight carbon methyl ketones, 3,4,4-trimethylpentanone-2 and 4,4-dimethylhexanone-2, and the two seven carbon saturated monocarboxylic acids, α, β, β -trimethylbutyric acid and β, β -dimethylvaleric acid.

4. 4,4-Dimethylhexanone-2 has been found to have the following properties: b.p. 768 154.4°C.; d_{20}^{20} 0.829; n_D^{25} 1.4183; m.p. semicarbazone 169.5°C.; m.p. 2,4-dinitrophenylhydrazane 146.5-147°C.

5. 3-Methyl-3-ethylpentanone-2 has been synthesized by Nyberg's original method and the following derivatives prepared: semicarbazone m.p. 167.5°C. (Nyberg 168°C.);

2,4-dinitrophenylhydrazone m.p. 92-92.5°C. This ketone can be distinguished from 4,4-dimethylhexanone-2 by the 2,4-dinitrophenylhydrazine derivative.

6. β,β -Dimethylvaleric acid (dimethylethylpropionic acid) has been found to have the following properties: b.p. 213°C.; b.p.₁₃ 103-104°C.; m.p. amide 76.5°C.; m.p. anilide 105.5-106°C.; m.p. p-phenylphenacyl ester 74°C.

7. α -Methyl- α -ethylbutyric acid has been synthesized and the following derivatives prepared: amide m.p. 78.5°C. (Haller and Bauer 78-79°C.); anilide m.p. 88.5°C.; p-phenylphenacyl ester m.p. 76°C. This acid can be distinguished from β,β -dimethylvaleric acid by the aniline derivative.

8. 1-Amino-2,2-dimethylbutane has been synthesized and the following derivatives prepared: benzenesulfonamide m.p. 59-59.5°C.; picramide m.p. 88-88.5°C.

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