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TECHNICAL NOTE

No. 1247

THE PREPARATION AND PHYSICAL PROPERTIES OF SEVERAL ALIPHATIC HYDROCARBONS AND INTERMEDIATES

By Frank L. Howard, Thomas W. Mears, A. Fookson,
Philip Pomerantz, and Donald B. Brooks
National Bureau of Standards

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SUMMARY

In the course of an investigation of the knock ratings of aliphatic hydrocarbons, pure paraffins and olefins were prepared in quantities sufficient for engine tests. This report describes the methods of preparation and purification of three pentanes, four hexanes, three heptanes, four octanes, eight nonanes, seven decanes, four hexenes, five octenes, six nonenes, six decenes, and a number of alcohols, ketones, esters, and alkyl halides. Most of these compounds were highly purified. Physical constants measured included freezing point, boiling point and its variation with pressure, refractive index and density, and their variations with temperature.

INTRODUCTION

In 1934 the Automotive Section of the National Bureau of Standards undertook an investigation of the impurities present in the certified isooctane (2,2,4-trimethylpentane) used as a primary standard in the knock rating of fuels. In the course of this work, about a score of paraffin hydrocarbons were isolated and their physical properties and knock ratings were determined. (See reference 1.) The information obtained in this work indicated that some of the higher paraffin hydrocarbons should be decidedly superior to isooctane in knock rating.

The results of this work led to a research project that was initiated with the objective of preparing, in quantities sufficient for engine tests, the paraffin hydrocarbons likely to be of interest as components of combat aviation fuel. This project was begun in 1937 under joint sponsorship of the National Advisory Committee for Aeronautics, the Army Air Forces, and the Navy Bureau of Aeronautics and has been actively prosecuted since that time. The results of portions of this investigation

completed prior to 1940 have been presented in references 2 to 5, and the syntheses and physical properties of a number of additional aliphatic hydrocarbons are described in the present paper.

Since the objective of this work was the preparation of pure hydrocarbons for engine testing to determine knock rating, it was generally necessary to subordinate other considerations to this purpose. In many cases, it was therefore not possible to make detailed studies of the reactions or to determine properties of some of the new or little-known intermediates.

Acknowledgments are due the following people for aid and advice on various phases of this work: Dr. Cecil E. Boord, Ohio State University, Dr. George Calingaert and Dr. Harold A. Soroos, Ethyl Corporation Research Laboratories, Dr. Nathan L. Drake, University of Maryland, Dr. Merrill R. Fenske and Dr. Frank C. Whitmore, Pennsylvania State College, and Dr. Frederick D. Rossini, National Bureau of Standards.

APPARATUS

Reaction Vessels

Small-scale exploratory reactions were generally carried out in 5-liter glass flasks. In some cases, where an unusually low yield of final product was expected, 12-liter flasks were used. The use of these larger flasks was discontinued in 1944, and reactions of this size were then conducted in 14-liter brass double-walled vessels. For synthesis on a larger scale, two copper reactors were used initially. Each of these reactors had a capacity of 60 liters and was double walled. Water at any desired temperature between 5° and 75° C could be circulated in the space between the walls to control the temperature of the reaction. The reactors were equipped with multiple-paddle stirrers (60 to 200 rpm), reflux condensers (multiple copper tube), separatory funnels for addition of reactants, and draw-off valves for removal of products. These reactors were used until early in 1944, when two 50-gallon kettles (one glass lined, one stainless steel) were put into service. The copper reactors were then used as distillation receivers in conjunction with the large kettles. The large kettles were standard commercial items and were installed so that any temperature between 5° and 150° C could be maintained in the jackets.

Hydrogenation Equipment

Hydrogenation reactions were accomplished in high-pressure hydrogenators, designed after those described by Adkins in reference 6.

Three sizes were used, with capacities of 1, 3, and 20 liters. The catalyst used was a commercial nickel-on-kieselguhr preparation, which proved to be economical and efficient. No difficulty was encountered in hydrogenating any of the materials, provided they were halogen-free. Most of the hydrogenation reactions took place at temperatures below 160° C and pressures below 2000 pounds per square inch.

Stills

For convenience, the various stills used in this work are designated in the text by numbers. The salient features of these stills are given in table 1. Some of these columns are no longer in use, having been supplanted by others of later designs. Operations formerly performed in Columns 1 and 2 were later carried out in 19 and 20, and Columns 8 and 9 were replaced by 17 and 18. Column 10 was abandoned in 1942, when Column 11 was put into operation. Columns 3 to 7 were replaced by 21 to 27 late in 1945.

Still 1.- This still is of the total-reflux, intermittent take-off type, and has been previously described in reference 5. The reflux rate was approximately 1500 ml per hour in most cases, the take-off rate being governed by the composition of the charge and the purity desired in the product. Samples of 78 ml each were removed automatically at predetermined intervals varying from 0.5 to 24 hours. The efficiency is approximately ninety to ninety-five theoretical plates, and the hold-up is 260 ml.

Still 2.- The column of this still consists of 150 actual plates, following the design by J. H. Brunn. (See reference 7.) The volume of each fraction removed was 65 ml. Reflux rate was about 800 ml per hour. This still has also been described in reference 5. The mechanisms of operation and sample removal are the same as for Still 1. In both Stills 1 and 2 the head temperature was followed during the day by means of a platinum resistance thermometer, and the timing operations were scheduled so that samples were removed when this temperature (corrected to 760 mm Hg) became reasonably constant (generally to within a change of less than 0.005° C per hr).

Stills 3 to 9.- Small stills patterned after those described by Whitmore and Lux (reference 8) were used to remove other from reaction mixtures, for purification of intermediates, for preliminary purification of final products, and for fractionation of small charges. These stills are designated as 3 to 9 in table 1.

Still 10.- Prior to the construction of other large-capacity stills, Still 10 was used for preliminary fractionation of commercial synthetic crudes. The pot was part of a domestic hot-water tank, the column a

length of 2-inch pipe. The take-off was governed by a 1/8-inch needle valve.

Still 11.- In order to have a higher-capacity, higher-efficiency still than 10, Still 11 was constructed. The entire still is made of monel metal. The reflux rate is about 4 liters per hour, as measured by gain in temperature of the condenser water. The take-off rate is governed by a commercial 1/8-inch solenoid valve, operated by an automatic timing device. The efficiency of the still is about sixty-five theoretical plates under operating conditions (3.5 to 4.5 liters per hr reflux). Safety devices include overflow tanks for the salvaging of material distilled through the condenser if the water is accidentally cut off, a product overflow tank for retaining material which may be delivered because of faulty operation of the solenoid valve, and a pot-temperature-limit control. All openings to the still are vented to the outside of the building.

Stills 12 to 16.- These columns were constructed for analysis of commercial crudes, purification of large quantities of material, and isolation of hydrocarbons from commercial mixtures. These were put into operation in 1943, and later (1945) Column 11 was lengthened by 4 feet and added to the group. The take-off on all these stills is governed by a timer and small solenoid valves. Condensers in the larger columns are of the multiple cold-finger type. The columns are heated by resistance wire controlled by variable transformers. Temperatures are measured by copper-constantan thermocouples. Safety devices include overflow tanks, automatic pot-temperature-limit control, forced ventilation, automatic carbon-dioxide fire control (controlled by thermal-plugs), and automatic warning if the atmosphere approaches a combustible mixture. The pots of Stills 12 to 16 are made of mild steel. The columns of 12 and 13 are made of galvanized pipe, and the columns of 14 and 15 are made of stainless steel. Condensers are of copper, brass, or monel metal.

DETERMINATION OF PHYSICAL PROPERTIES

From the plots of refractive indices, boiling points, or freezing points of fractions with respect to volume of distillate, those fractions containing the best material were selected and used for the determination of physical constants.

The methods used for the determination of physical constants have been described in reference 4. The freezing-point apparatus was modified in December 1944, so that additional control of the rate of cooling could be obtained. This was done by installing a pumping system on the evacuated chamber surrounding the sample, so that the rate of cooling could be governed by the pressure in the evacuated chamber. This modification of

the equipment has been adequately described by Mair (reference 9). Table 2 lists the measured physical properties of the compounds described herein.

The freezing-point data on 2,2,5,5-tetramethylhexane are considered representative, and are illustrated in figure 1. Boiling-point data on four compounds are shown in figure 2. These figures are presented as typical examples of measured physical properties. Refractive indices were measured on an Abbe type (Valentine) refractometer until 1943 when a Bausch and Lomb precision-oil refractometer (also Abbe type) was put into use. An estimate of the purity of the individual compounds may be made from the data listed in table 2 under the heading ΔT:20 to 80 percent, which indicates the number of degrees difference between the temperature at which 20 percent of the material had distilled and the temperature at which 80 percent had distilled. The presence of peroxides in the olefin samples tended to make this difference extraordinarily large.

PREPARATION OF MATERIALS

Grignard Reagents

The preparation of Grignard reagents in large quantities (up to 330 moles) has been found to be subject to the same limitations as the preparation of small amounts, except that the yields, in general, are slightly larger. The methods used in typical runs of representative members of the aliphatic series are given as follows, and are not repeated in the discussion of the various syntheses. Decomposition of reaction complexes formed by the action of Grignard reagents on various compounds followed the classical methods and need not be repeated.

Methylmagnesium bromide.- To the reactor was added 100 gram atoms (2.43 kg) of magnesium turnings and enough ether to cover the magnesium. A small amount of methyl bromide was added. If reaction did not start immediately, a little methyl iodide (or previously prepared Grignard reagent) was added. After reaction had been initiated the stirrer was started, and methyl bromide from a cylinder supported from a steelyard was allowed to flow through a coil of copper tubing surrounded by a dry-ice bath where it condensed and dropped into the reaction mixture. Flow was regulated by a small needle valve. After the reaction was well started, cooling water was admitted to the jacket, and an excess of methyl bromide was added as fast as it would react. During the addition of methyl bromide, ether was added in 2-liter portions until the total ether added was 20 liters (200 ml per gram atom of magnesium). The amount of methyl bromide added was determined by the loss of weight of the cylinder, and it was found that practically no methyl bromide was lost during the operation. After addition of methyl bromide was

complete, the reaction mixture was warmed for 2 to 3 hours. If the mixture contained sludge or pieces of unreacted magnesium, it was allowed to stand until the sludge had settled, and then the clear solution was siphoned off. The sludge was next washed with dry ether and allowed to settle, then the siphoning procedure was repeated. If the amoung of sludge was small, this last operation was carried out advantageously in a separatory funnel, in which the sludge could be drawn off easily.

The yields varied from 88 to 95 percent, based on magnesium, as determined by titration. Similar yields were realized when ethyl magnesium chloride was prepared, but in this case slower addition of halide was necessary in order to avoid the formation of appreciable amounts of sludge.

Isopropylmagnesium chloride.- Magnesium turnings (1.5 kg, 63 gram atoms) and 5 liters of ether were placed in the reactor, and reaction was started by the addition of a small amount of isopropyl chloride. After the reaction was initiated, the stirrer was started and 1 liter of isopropyl chloride in 2 liters of ether was added slowly. After this first charge of chloride was complete, 5 liters of ether and the rest of the magnesium (1.5 kg, 63 gram atoms) were added, and cooling water was circulated through the jacket. Then the rest of the chloride and ether was added in the ratio of 1 liter of chloride for 2.0 to 2.5 liters of other, until a total of 125 moles of chloride and 37.5 liters of ether had been used. This addition was carried out as fast as possible, still keeping the reflux from the condenser dropwise and not in a steady stream. About 35 hours were required for a 125-mole run. After removal of the clear solution from the sludge, the yield, calculated from titration data, amounted to 90 to 93 percent of the theoretical quantity.

t-Butylmagnesium chloride.- This preparation was carried out in essentially the same manner as described for the preparation of isopropylmagnesium chloride, except that the addition of chloride was necessarily slower in order to retard formation of hexamethylethane, isobutylene, and diisobutylene. A 70-mole run required approximately 35 hours. The latter half of the chloride added was more dilute than the first half (reference 10) and the rate of addition was slowed up progressively as the reaction neared completion. The jacket of the reactor was not cooled so much in this preparation as with the less highly branched halides. The tendency of t-butyl chloride to form sludge is much greater than that of the simpler halides, although many runs were made in which practically no sludge was observed. The yields varied from 80 to 92 percent.

n-Pentane

One gallon of commercial n-pentane was fractionated in Still 1. From this distillation there was obtained 1792 ml of material, the

fractions of which had a refractive index n_D^{20} of 1.3574 to 1.3575. A "best" sample was selected for determination of physical constants.

2-Methylbutane (Isopentane)

One gallon of commercial isopentane was fractionated in Still 1. There was obtained 2200 ml of material, n_D^{20} = 1.3535 to 1.3536, which was collected while the head temperature of the column was 27.87° to 27.88° C. Later a total of 47 liters of high-purity material was prepared from the same source by fractionation in Still 11.

2,2-Dimethylpropane (Neopentane)

In 1933, Whitmore and Fleming (reference 11) described the preparation of neopentane by reaction between methylmagnesium chloride and t-butyl chloride in toluene at 45° to 50° C. Yields of 42 to 50 percent were reported. In the present work, a method is described whereby somewhat larger yields of purer product were obtained.

In this work, neopentane was prepared by action of dimethyl zinc on t-butyl chloride in toluene at 5° C. The advantage of causing reaction at this temperature, rather than the often used higher temperature (35° to 50° C) for reactions of this type has been previously demonstrated. (See reference 2.) Dimethyl zinc was prepared in the manner described in reference 2; however, certain improvements in the technique of handling this material have been made.

A 5-liter, single-neck flask, which was used for dimethyl-zinc preparation, was placed in an oil bath and fitted with a 400-millimeter reflux condenser. To the top of the condenser was attached a bridge of 10-millimeter glass tubing which led to the top of a similar reflux condenser attached to a 5-liter, three-neck flask. This latter flask, into which dimethyl zinc was distilled, was situated in a cold-water bath and was provided with a separatory funnel (500 ml) and a stirrer. A side arm on the bridge provided for the introduction of inert gas (carbon dioxide).

The zinc-copper couple from 960 grams of zinc dust and 120 grams of cupric oxide was placed in the one-neck flask, and 1100 grams (7.75 moles) of methyl iodide added. The temperature of the oil bath was raised to about 45° C, and a slow stream of carbon dioxide was passed in the side arm of the bridge and out through the separatory funnel into a venting tube made of 25-millimeter glass tubing. Reaction between methyl iodide and the couple was complete after 10 hours, provided that the couple was sufficiently active. When reaction had ceased, as shown by the cessation of reflux, the carbon-dioxide flow was stopped, 500 ml

of toluene was added to the three-neck flask, and the top of the separatory funnel was fitted with a tee tube. The reflux condenser on the one-neck flask was heated with steam, and the temperature of the oil bath was gradually raised over a period of 2 hours to about 180° C. This caused the methylzinc iodide in the flask to decompose into dimethyl zinc and zinc iodide. The dimethyl zinc distilled across the bridge into the toluene in the three-neck flask. Carbon dioxide was allowed to flow through the top of the tee while distillation of dimethyl zinc was in progress.

After distillation of dimethyl zinc was complete, the single-neck flask was allowed to cool and the side arm on the bridge connected to a gas-purification train comprising, in the order named, a wash bottle containing water, two bottles containing 85-percent sulfuric acid, an empty bottle, a bottle containing 40-percent potassium hydroxide, a calcium-chloride drying tower, and a 100- by 1.5-centimeter tube filled with silica gel. After passing through this train, the gas was led into a condensing system comprising a copper coil condenser at -10° C, a receiver at -78° C, and finally a trap at -78° C.

The flask containing toluene and dimethyl zinc was cooled to 5° C, and 525 ml (about 4.8 moles) of t-butyl chloride in 750 ml of dry toluene was added during 5 hours. During the addition of chloride, methane was evolved by the reaction. After the addition of chloride was complete, the reaction mixture was allowed to stand 15 hours. Then the bath temperature was raised gradually to 50° C, during which time more gas was given off which was not affected by the sulfuric acid and which did not condense in the -78° C trap.

Water was then added to the reaction mixture through the separatory funnel. It was necessary to exercise considerable care in this operation, since a violent evolution of neopentane took place at this point. This gas was condensed in the -10° C condenser, and solidified in the receiver. There was no discoloration of the sulfuric acid. After about 200 ml of water had been added and the evolution of gas had subsided, the apparatus was swept out with nitrogen.

The resulting neopentane was transferred to a glass tube and sealed. The yield amounted to 164.5 grams, which is 59 percent of that theoretically possible, based on one half the amount of methyl iodide used (2 moles of methyl iodide give 1 mole of dimethyl zinc). The residue from the dimethyl zinc, which contained zinc iodide, was used to prepare additional methyl iodide by the method described in reference 12.

In assembling the apparatus, corks, rather than rubber stoppers, were used exclusively and after assembly they were coated with shellac. In one preliminary experiment, in which rubber stoppers were used, the product was contaminated with a material which had the odor of methyl

mercaptan. Where rubber tubing was necessary in making connections to the side arm on the bridge, arrangement was made so that a minimum of rubber surface was exposed.

The yield reported on the first run was verified later when nine additional runs of this preparation were made, in which an average yield of 65.6 percent was obtained. In two of these runs, the couple was less active than in the other preparations, and the product was contaminated with methyl iodide. The presence of methyl iodide was characterized by a pink color which developed in the product after a few days. The yield obtained in one run was low because a stoppage developed in the purification train, and some material was lost through a loosened connection.

Freezing-point measurements made on the material from three experiments gave the values -16.61°, -16.61°, and -16.60° C, respectively. These data may be compared with the value -16.63 ±0.10° C, calculated for the freezing point of 100-percent-pure neopentane by Aston and Messerly. (See reference 13.)

3-Methylpentane

From 75.2 moles of ethylmagnesium chloride and 37 moles of ethyl acetate there was prepared 3660 ml of 3-methyl-3-pentanol, which was purified by distillation in Column 7 (b.p. 120° to 124° C at 760 mm). Dehydration of this carbinol by refluxing with 0.2-percent β-naphthalene sulfonic acid yielded a mixture of alkenes which boiled 65° to 71° C at 758 millimeters. This dehydration would be expected to yield chiefly 3-methyl-2-pentane, with a smaller amount of 2-ethyl-1-butene. No attempt was made to separate the two olefins since both compounds yield the same alkane when hydrogenated. Hydrogenation of this mixture gave crude alkane which was filtered through silica gel and distilled in Column 4 to yield 1980 ml of material which boiled 64.5° to 65.5° C (uncorrected). Redistillation in Column 1 gave 1420 ml of hydrocarbon made up of fractions removed while the head temperature was 63.319° to 63.322° C (761.1 mm Hg) and for which n_D^{20} = 1.3764 to 1.3765.

2,2-Dimethylbutane (Neohexane)

The synthesis of neohexane has been reported previously in reference 4. Since then commercial neohexane has become available. Several charges of this material were fractionated in Stills 1 and 2. From each run, only the latter half of the distillate consisted of material having the properties of neohexane. The forerun contained an impurity of higher refractive index and slightly lower boiling point. No extensive investigation was made of this forerun, but the most likely impurity was cyclopentane. This fact was later substantiated by the manufacturer.

A total of 38 liters of purified neohexane was propared by fractionation of 75 liters of the commercial crude mixture in Still 11.

2-Methylpentane

About 75 liters of commercial crude neohexane was fractionated to prepare 38 liters of 2,2-dimethylbutane. From the distillations of this material, there was obtained 3320 ml of residue, which was fractionated in Column 2 into 46 fractions:

Fraction	Boiling range (Head temperature) (°C)	Volume (ml)	Refractive index, n_D^{20}
1 to 22	58.8 to 60.2	1500	1.3748 to 1.3717
23 to 44	60.2 to 60.4	1500	1.3715 to 1.3717
45 to 46	60.4	140	1.3717 to 1.3744

Fractions 35 to 37 were combined, filtered through silica gel, and used in the determinations of physical properties of 2-methylpentane.

Investigation of Butene Alkylate

Seventy-five liters of Butene Alkylate was fractionated in Still 10. The head temperature was measured by means of a recording thermometer of the gas-expansion type. The reflux ratio was maintained at about 100 to 1. Fractions of not more than 3.87 liters each were collected, the volume of the fraction depending on the time-temperature curve. After measurement of refractive indices, like fractions from different runs were combined and refractionated in Still 2. Fractionation of the lowest boiling portion from Still 10 was carried out first, then the second lowest boiling was added to the residue and fractionated, and so on. The refractive index of each fraction was measured, and a plot of refractive index versus fraction number was made. Samples represented by single plateaus were combined and redistilled in Column 1 or 2. Several hydrocarbons were isolated thereby, and are listed in table 3.

2,3-Dimethylbutane.- The 2,3-dimethylbutane from Butene Alkylate (2213 ml) was added to 1255 ml of 2,3-dimethylbutane of approximately the same purity from another source. The combined material was washed with sulfuric acid, water, sodium-carbonate solution, and again with water. After it was dried and filtered through silica gel, it was fractionated in Still 2, and gave 2300 ml of material for which n_D^{20} = 1.3748 to 1.3749.

2,4-Dimethylpentane.- The 2,4-dimethylpentane from Butene Alkylate (2610 ml) was refractionated in Still 2. The fractions for which n_D^{20} = 1.3816 to 1.3817 were reserved as the best portion, and amounted to 985 ml.

2,3-Dimethylpentane from Isooctane

Seventy-five liters of isooctane (a commercial mixture of branched chain hydrocarbons) was fractionated in Still 10 in the manner described in the preceding section. Fractions which distilled between 85° and 95° C (n_D^{20} = 1.3886 to 1.3914) were combined (28,051 ml) and refractionated in Still 11. From this distillation there was obtained 7165 ml of hydrocarbon which boiled 89.7° to 90.0° C (n_D^{20} = 1.3918 to 1.3921) which was refractionated in Still 2. The purified 2,3-dimethylpentane thereby obtained amounted to 4790 ml after filtration through silica gel. The refractive index range n_D^{20} of various fractions was 1.3919_1 to 1.3919_6.

2,2,3-Trimethylbutane (Triptane)

The synthesis of triptane involved two reactions: (a) the preparation of 2-chloro- 2,3-dimethylbutane, and (b) the reaction of this chloride with dimethyl zinc.

2-Chloro- 2,3-dimethylbutane.- The apparatus used was similar to that described in reference 2 for the preparation of 4-chloro- 2,2,4-trimethylpentane. It was modified so that rubber stoppers were replaced with ground-glass connections. The alkene used was a mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, which was formed by dehydration of pinacolyl alcohol (3,3-dimethyl-2-butanol). (See reference 5.) The original alkene mixture contained a small amount of 3,3-dimethyl-1-butene, in addition to the hexenes, but this hydrocarbon was removed for use in another synthesis.

In 2 hours, 1500 ml of the alkene mixture, along with excess hydrogen chloride, was passed through two chambers kept in a bath at -78° C. Occasionally it was necessary to remove the baths in order to allow the solidified chloride to melt and pass on through the apparatus. The product was washed with water, with 5-percent sodium-bicarbonate solution, again with water, and dried with two successive portions of fresh anhydrous potassium carbonate. Distillation of the resulting material in Column 3 gave, after a forerun of unchanged alkene, 675 grams of 2-chloro-2,3-dimethylbutane (b.p. 69° to 70° C at 190 mm Hg).

Synthesis of triptane.- With apparatus like that used in the preparation of neopentane, dimethyl zinc was prepared from 1100 grams (7.75

moles) of methyl iodide and distilled into a 5-liter flask containing 500 ml of toluene. The flask was surrounded by ice, and the chloride 600 grams, 5 moles) in 1000 ml of toluene was added during 4 hours. The mixture was allowed to stand for 16 hours, and was then treated with water and with dilute hydrochloric acid. The reaction product, 2060 ml, was fractionated in Column 5 to give a small amount of methyl iodide, some olefinic material, presumably dimethylbutenes formed by dehydrochlorination of the alkyl chloride, and 297 ml of crude triptane boiling at 78° to 83° C, with $n_D^{20} = 1.3932$. Two passages through silica gel gave a product of the following properties, compared with those of high-purity material:

Property	Present preparation	High-purity material (reference 5)
Refractive index, n_D^{20}	1.3897	1.38947
Density, d_4^{20}	0.6896	0.69000
Freezing point, °C	-26.1	-25.059
Boiling point, °C	81.0 (Cottrell)	80.879

The yield of crude triptane amounted to 51 percent of the theoretical.

In subsequent experiments it was found that a large excess of alkyl chloride offered no addvantage, a 2- to 3-percent excess giving a comparable yield. The excess chloride was found to be easily removed by boiling the crude mixture with a 5-percent solution of potassium hydroxide in alcohol.

In each of several experiments, the yield amounted to 46 to 52 percent of crude triptane. The time allowed for addition of chloride was varied from 3 to 8 hours, and the temperature of reaction from 0° to 30° C without any appreciable change in yield. In one experiment, in which isooctane (2,2,4-trimethylpentane) was used as a solvent, the yield was 48 percent.

Under the conditions of hydrochlorination, 2,3-dimethyl-1-butene was found to add hydrogen chloride more easily than 2,3-dimethyl-2-butene. The unreacted alkene which was recovered when a mixture of the two was hydrochlorinated was found to be practically pure 2,3-dimethyl-2-butene. Very slight decomposition of 2-chloro- 2,3-dimethylbutane takes place when it is boiled at atmospheric pressure.

2-Methyl-3-Ethylpentane

This octane was prepared by hydrogenation of the olefins which resulted from the dehydration of 2-methyl-3-ethyl-3-pentanol. The carbinol was prepared by the action of ethylmagnesium chloride on isobutyl isobutyrate.

To a solution containing 90 moles of ethylmagnesium chloride in 20 liters of ether was added 6335 grams (44 moles) of isobutyl isobutyrate in 10.5 liters of ether. The product was dried with sodium carbonate and distilled in Column 6. There was obtained 5680 ml of 2-methyl-3-ethyl-3-pentanol (55° to 57° C at 48 mm Hg). Dehydration was effected by refluxing the carbinol with 0.2 percent by weight of β-naphthalene sulfonic acid, which gave 5235 ml of crude alkene mixture, boiling at 114° to 119° C. Since dehydration of 2-methyl-3-ethyl-3-pentanol should yield two alkenes: namely, 2-methyl-3-ethyl-2-pentene (b.p. about 117° C) and 4-methyl-3-ethyl-2-pentene (b.p. about 116° C), both of which yield the same alkane on hydrogenation, no attempt was made to separate the two. The alkene mixture was dried with calcium chloride and distilled from sodium. A portion of the distillate (4721 ml) was hydrogenated to the alkane, which, after two distillations from sodium and filtration through silica gel, amounted to 4050 ml. The compound was finally fractionated in Still 1, yielding 3300 ml of material, which had a refractive index constant within 0.0001.

2,3,3-Trimethylpentane

This hydrocarbon resulted from the reaction between isopropylmagnesium chloride and t-amyl chloride.

To 90.5 moles of isopropylmagnesium chloride in 30.9 liters of ether solution was added 9600 grams (90 moles) of t-amyl chloride during a period of about 12 hours. Stirring was continued until separation of solid material prevented adequate mixing. Then the reaction mixture was allowed to stand 2 to 3 weeks at 15° to 20° C until no more Grignard reagent was present. The product was treated with ice and dilute hydrochloric acid and the resulting organic material distilled in Column 3. After a forerun of ether, isoamylene, and t-amyl chloride, there was obtained 4400 ml of crude 2,3,3-trimethylpentane (31-percent yield) which boiled 112° to 115° C. When refractionated in Column 1, the crude paraffin gave 3600 ml of fractions for which $n_D^{20} = 1.4074$ to 1.4075. Redistillation of accumulated foreruns from several batches gave an additional quantity of pure material. From several runs a total of 39 liters of pure 2,3,3-trimethylpentane was prepared.

Early experiments on this preparation were made in which a large excess of Grignard reagent was assumed to be desirable, but it was found

that the yield of product was actually decreased by an excess of Grignard reagent. For example, in one run in which 72 moles of isopropylmagnesium chloride was allowed to react with 57 moles of t-amyl chloride, the yield of 2,3,3-trimethylpentane was only 21 percent.

2,2,3-Trimethylpentane and 2,3,4-Trimethylpentane

By fractionation of several cuts of alkylate mixtures, 38.6 liters of 2,2,3-trimethylpentane and 37.9 liters of 2,3,4-trimethylpentane were prepared. The source materials were alkylates, hydro-codimers, and isooctanes which had accumulated at the laboratory. These materials totaled approximately 85 gallons. Some of them were partially fractionated, some were "as received."

The unresolved alkylates and residues were roughly fractionated in Stills 10 and 11 into concentrates rich in 2,2,3-trimethylpentane and 2,3,4-trimethylpentane. These concentrates were redistilled in Column 11. Most of the material was obtained by these distillations. Foreruns, intermediates, and afterruns were again fractionated in Stills 1 and 2. From a total of 47 distillations there were obtained 38,610 ml (at 25° C) of 2,2,3-trimethylpentane (n_D^{20} = 1.4026 to 1.4029) and 37,955 ml (at 25° C) of 2,3,4-trimethylpentane (n_D^{20} = 1.4041 to 1.4045). Physical constants of the two compounds were measured, and agreed well with those measured on the pure materials, as reported in references 4 and 5.

2,2,5-Trimethylhexane

The presence of 2,2,5-trimethylhexane in isooctane residue was reported by Brooks, Cleaton, and Carter in 1937. (See reference 1.) By distillation of an additional 76 liters of this material in Still 10, a concentrate rich in this nonane was obtained. This concentrate (4525 ml, b.p. 123° to 125° C, n_D^{20} = 1.399 to 1.400) was refractionated in Still 1. There was obtained 2005 ml of 2,2,5-trimethylhexane with a refractive-index range of 1.3995 to 1.3996.

2,3,5-Trimethylhexane

This nonane was prepared by hydrogenating 2,3,5-trimethyl-2-hexena, which resulted from the reaction of isopropylmagnesium chloride on 1-chloro-2,3-dimethyl-2-butene. There was also formed a small amount of 2,3,3,4-tetramethyl-1-pentene in this reaction.

2,3-Dimethyl-1,3-butadiene.- Pinacol hydrate, prepared by the method of reference 5, was dehydrated to anhydrous pinacol by distillation in Columns 4 to 7. These distillations were carried out at atmospheric

Pressure until the head temperature reached 122° C, when the pressure was reduced to 80 millimeters of mercury. At this pressure the anhydrous pinacol distilled at 111° to 114° C.

In order to determine the optimum conditions for conversion of the glycol to 2,3-dimethyl-1,3-butadiene, a series of test runs were made. The results are shown in the following table:

DEHYDRATION OF PINACOL TO 2,3-DIMETHYLBUTADIENE-1,3

AND PINACOLONE (3,3-DIMETHYL-2-BUTANONE)

Run	Pinacol taken (gm)	Catalyst	Yield (percent) of -	
			Dimethyl-butadiene	Pinacolone
1	453	1.5 grams 48-percent hydrobromic acid	45	19
2	500	5.0 grams β-naphthalene sulfonic acid	36	34
3	500	5.0 grams p-toluene sulfonic acid	40	31
4	500	7.0 grams aniline hydrobromide	18	15

In these experiments, the pinacol was refluxed with the catalyst in Columns 5 or 7. The product of each run was washed, dried, and distilled in Column 6 for analysis. From the results of these experiments, it was concluded that 48-percent hydrobromic acid was the best catalyst of those tried for this dehydration. By dehydrating several batches of pinacol (2.5 to 3.0 kg per batch), 17.4 liters of 2,3-dimethyl-1,3-butadiene was prepared which boiled 68.5° to 71.5° C at 758 millimeters.

1-Chloro-2,3-dimethyl-2-butene.- The addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene was accomplished in the apparatus described in reference 2. The reaction chambers were kept at -30° C, and dry hydrogen chloride and alkadiene added simultaneously. The daily output of the apparatus was 1.0 to 1.5 liters of chloride. The product was freed of dissolved hydrogen chloride by aeration with carbon dioxide and stored over sodium carbonate. Distillation analysis showed that the reaction was practically quantitative. The product used for further synthesis boiled at 32° C at 45 millimeters of mercury.

2,3,5-Trimethyl-2-hexene.- To an ether solution of 62 moles of isopropylmagnesium chloride was added 7.32 kilograms of 1-chloro-2,3-dimethyl-2-butene. The reaction mixture became very viscous, and it was necessary to add more ether at intervals. The reaction was worked up after 4 days and the organic material was dried, the ether removed, and the crude residue distilled through Column 3 (b.p. 70° to 71° C at 90 mm, n_D^{20} = 1.4299). Although there was no appreciable forerun, a large amount of high-boiling material (175° to 200° C) was present. This material was not identified, but is presumed to be polymers (dimers and trimers) of the alkadiene formed under the influence of the Grignard reagent.

The crude 2,3,5-trimethyl-2-hexene contained a considerable quantity of chloride, the greater part of which was removed by boiling with alcoholic potassium hydroxide. Hydrogenation of the crude alkene gave 2,3,5-trimethylhexane, which was filtered through silica gel and distilled in Column 3. From 2500 ml of material, there were obtained 900 ml which boiled 131.9° C (n_D^{20} = 1.4060 to 1.4061) and 50 ml of a hydrocarbon which boiled 141.9° C (n_D^{20} = 1.4218). The latter was identified as 2,3,3,4-tetramethylpentane by comparison with a sample prepared in another manner. A residue of about 1 liter which boiled above 165° C resulted from this distillation. This residue was probably formed by the action of potassium hydroxide or hydrogenation catalyst on the unsaturated halide which was present in the crude olefin. Obviously, most of the Grignard reagent was dissipated in side reactions rather than by coupling with the chloride in the expected manner. This tendency could possibly have been decreased by carrying out the reaction in a more dilute solution.

This preparation was made in 1939 at the suggestion of Dr. C. E. Boord of Ohio State University. The goal was the preparation of 2,3,5-trimethylhexane and 2,3,3,4-tetramethylpentane. The reaction yielded about eighteen parts of the former to one part of the latter. These two hydrocarbons probably resulted from the action of the Grignard reagent on two isomers of 2,3-dimethylchlorobutene. These two isomers probably were 1-chloro-2,3-dimethyl-2-butene, formed by 1,4 addition of hydrogen chloride to the diolefin, and 3-chloro-2,3-dimethyl-1-butene, formed by 1,2 addition. The former chloride would be expected to react with isopropylmagnesium chloride to give 2,3,5-trimethyl-2-hexene, and the latter chloride to to give 2,3,3,4-tetramethyl-1-pentene.

E. T. Cline has made a study of this reaction (reference 14), in which hydrogen bromide, rather than hydrogen chloride, was used. He obtained a ratio of alkenes of 1.6 parts of 2,3,5-trimethyl-2-hexene to 1 part of 2,3,3,4-tetramethyl-1-pentene.

2,2,4-Trimethylhexane

In 1937, Brooks, Cleaton, and Carter (reference 1) isolated an unknown nonane from the residue obtained in the distillation of isooctane (2,2,4-trimethylpentane), which was tentatively identified as 2,2,4-trimethylhexane. In order to extablish the identity of this hydrocarbon. a sample of 2,2,4-trimethylhexane was prepared, and a comparison of physical properties made.

Diisobutylene was oxidized by sodium dichromate, as described in reference 15 by Whitmore, Homeyer, and Trent, to give trimethylacetic acid and 4,4-dimethyl-2-pentanone (methylneopentyl ketone). The oxidation of diisobutylene isomers is discussed more fully in later sections.

To 7.0 moles of ethylmagnesium chloride in 1400 ml of ether solution was added 742 grams (6.5 moles) of 4,4-dimethyl-2-pentanone (b.p. 124° C at 760 mm Hg, n_D^{20} = 1.4038) in 800 ml of dry ether. The reaction mixture was allowed to stand at room temperature for 35 hours, refluxed for 6 hours, and then worked up in the standard manner. The organic material was washed, dried, and distilled in Column 4. In addition to ether and recovered ketone, 409 grams (2.9 moles) of 3,5,5-trimethyl-3-hexanol and 84 grams (0.6 mole) of nonenes resulting from premature dehydration of the carbinol were obtained. The purified carbinol was dehydrated by heating with β-naphthalene sulfonic acid (1 gram) to give a mixture of alkenes which boiled 127° to 132° C. The yield was 335 grams (91 percent). This alkene mixture has been analyzed by Whitmore and Cook (reference 16) who found by ozonolysis that it contained approximately three parts of 3,5,5-trimethyl-2-hexene, one part of 2-ethyl-4,4-dimethyl-1-pentene, and a trace of 3,5,5-trimethyl-3-hexene. All these compounds give the same alkane when hydrogenated, so no attempt was made to separate them.

The alkenes were hydrogenated, and the product filtered through silica gel and distilled in Column 5. The middle 70 percent of the distillate, which distilled at a constant temperature, was redistilled in the same column, the middle 25 percent of the distillate from the latter distillation was used in the measurement of physical properties. The properties of the synthetic material are given in table 2 and are compared in the following table with the properties of 2,2,4-trimethylhexane, which was isolated by the present authors. The identity of the two is proved by data on the freezing point of the 50:50 mixture.

Property	Synthetic material 2,2,4-trimethylhexane	Fraction from isooctane residue (reference 1)
Boiling point at 760 mm Hg, °C	126.54	126.51
Change in boiling point with pressure, °C/mm Hg	00.0503	---
Freezing point, °C	-123.4 (mp)	-129.53
Freezing point of mixture, °C	-124.19	-124.19
Refractive index, n_D^{20}	1.4033	1.40312
n_D^{25}	1.4010	---
Density, gm/ml, d^{20}	0.7156	[a]0.7153
d^{25}	0.7118	---

[a]The published density, 0.7048 (reference 1) of the material isolated from isooctane residue was in error. A recalculation of the original data gave 0.7153, redetermination gave 0.7154.

2,2-Dimethyl-3-Ethylpentane

The synthesis of 2,2-dimethyl-3-ethylpentane was carried out in the following steps: (a) Reaction of t-butylmagnesium chloride with carbon dioxide to give the Grignard complex of trimethylacetic acid, (b) reaction of this complex with ethylmagnesium chloride to produce 2,2-dimethyl-3-ethyl-3-pentanol, (c) dehydration of the carbinol to 4,4-dimethyl-3-ethyl-2-pentene, and (d) hydrogenation of the olefin to 2,2-dimethyl-3-ethylpentane.

To 50.2 moles of t-butylmagnesium chloride in 18 liters of ether, cooled to 5° C, was added 3 kilograms of solid carbon dioxide in small pieces while the reaction mixture was being stirred. Stirring was continued while the mixture came to room temperature and while it was heated to reflux for 2 hours. It was then cooled and 104 moles of ethylmagnesium chloride in 20 liters of ether was added slowly. After addition was complete, the mixture was stirred for 6 hours and allowed to stand at room temperature for 2 days. The product was distilled in Column 6. From this distillation was obtained 3485 grams (48.2 percent yield) of carbinol (b.p. 90° to 95° C at 50 mm Hg, 151° to 176° C at 756 mm Hg, $n_D^{20} = 1.4417$, $d^{20} = 0.851$). The carbinol was dehydrated by heating

with β-naphthalene sulfonic acid to give 3600 ml of alkene. Fractionation of the crude alkene in Column 5 gave 2680 ml of purified 4,4-dimethyl-3-ethyl-2-pentene. The alkene was hydrogenated, and the product filtered through silica gel and distilled in Column 1. From this distillation 1650 ml of constant-boiling 2,2-dimethyl-3-ethylpentane (n_D^{20} = 1.41225 to 1.41230) was obtained.

2,4-Dimethyl-3-Ethylpentane

Preparation of 2,4-dimethyl-3-ethylpentane was accomplished by hydrogenation of the alkenes which resulted from the dehydration of 2,4-dimethyl-3-ethyl-3-pentanol. The carbinol resulted from the action of ethylmagnesium chloride on 2,4-dimethyl-3-pentanone (diisopropyl ketone).

To 76.2 moles of ethylmagnesium chloride was added 75 moles of 2,4-dimethyl-3-pentanone during 2 days. The product was recovered by addition of ice and ammonium chloride to the reaction mixture, and by subsequent distillation gave 5650 grams (52.3 percent) of 2,4-dimethyl-3-ethyl-3-pentanol. A pure sample was obtained by redistillation of the best portion of the crude.

The carbinol was dehydrated with β-naphthalene sulfonic acid to give 6110 ml of crude alkene mixture. A charge of 2 liters of the dehydration product was fractionated in Column 5 for analysis. The individual olefins were recovered in the ratio of 77 percent of the lower-boiling 2,4-dimethyl-3-ethyl-2-pentene to 23 percent of the higher-boiling 4-methyl-3-isopropyl-2-pentene. A sample of each of these isomers was redistilled for determination of physical constants. The values obtained were:

Property	2,4-Dimethyl-3-ethyl-2-pentene	4-Methyl-3-isopropyl-2-pentene
Boiling point at 760 mm Hg, °C	130.5	138.7
Refractive index, n_D^{20}	1.4227	1.4349
n_D^{25}	1.4204	1.4326
Density, d^{20}	0.7433	0.7584
d^{25}	0.7385	0.7550

Hydrogenation of samples of both alkenes yielded the same alkane. The alkene mixture (b.p. 128° to 140° C) was hydrogenated and the resulting product distilled in Column 4. The portion boiling 136° to 139° C was filtered through silica gel and refractionated in Column 1.

In 1945 the preparation was repeated on a somewhat larger scale. For this preparation, 2,4-dimethyl-3-pentanone was fractionated in Still 11. Only the purest fractions obtained (b.p. 124.6° to 124.7° C, n_D^{20} = 1.4015 to 1.4017) were used in the subsequent synthesis. The carbinol was the product of reaction of the Grignard reagent prepared from 260 moles of ethyl chloride with 223 moles of redistilled ketone. The reaction product was distilled in Column 21 until the head temperature was 130° C. A sample (1600 grams) of the residue was distilled in Column 4. From this distillation there were obtained 1130 grams of pure carbinol (2,4-dimethyl-3-ethyl-3-pentanol, b.p. 94.5° to 95.0° C at 47 mm Hg) and about 200 grams of less pure material. A sample from the middle cut of this distillation was reserved for physical constants measurements.

The rest of the undistilled residue was dehydrated with β-naphththalene sulfonic acid, and the dehydration products were washed, dried, and distilled in Column 11. Analysis of the distillation curve showed the presence of 77 volume percent (13.4 liters) of lower-boiling olefin, and 23 volume percent (4.0 liters) of the higher-boiling isomer. In this distillation a best sample from each of the plateaus was reserved and redistilled in Column 17 for physical-constants measurements. Hydrogenation of the olefins was carried out as previously described. The paraffin was fractionated in Columns 17, 18, 19, and 20. There was obtained 11,800 ml of pure hydrocarbon for engine tests. Physical constants of materials synthesized in this later preparation are given in table 2.

*2,2,3-3-Tetramethylpentane (Tetrane)[1]

The synthesis of 2,2,3,3-tetramethylpentane (a new compound designated tetrane) was first accomplished in 1940 (October-December). The reaction involved (a) preparation of 2,3,3-trimethyl-2-butanol (triptanol) from 3,3-dimethyl-2-butanone (pinacolone) and methylmagnesium bromide, (b) reaction of this carbinol with hydrochloric acid to give 2-chloro-2,3,3-trimethylbutane (triptyl chloride), and (c) reaction of the chloride with ethylmagnesium chloride to give the nonane and 2,3,3-trimethyl-1-butene (triptene).

From 82 moles of pinacolone and 84 moles of methylmagnesium bromide, 56.5 moles of 2,3,3-trimethyl-2-butanol was prepared. This carbinol was dissolved in ether, and the solution shaken with several portions of concentrated hydrochloric acid. Samples of the ether solution were removed periodically. The sublimation point of the crude chloride from these samples rose to 131° to 133° C. Recrystallized chloride was found to sublime at 133° C. The chloride solution was washed, dried, and added to 115 moles of ethylmagnesium chloride. The mixture was stirred for 3 hours and then allowed to stand for 4 weeks at room temperature.

[1]Compounds designated with asterisks are believed to be new compounds.

After the reaction mixture was worked up, the organic material was distilled in Column 6, and yielded 2100 ml of recovered triptene (trimethylbutene) and 1900 ml of crude 2,2,3,3-tetramethylpentane, which was contaminated by a considerable amount of triptanol. The carbinol was filtered off as the hydrate, and the filtrate dried and filtered through silica gel. The volume of nonane recovered was 1250 ml, which represents a yield of 9 percent, based on the original pinacolone. Distillation of this material in Column 4 gave 1087 ml of hydrocarbon which was collected at 88.6° to 88.7° C at 159 millimeters of mercury. A portion of this material was recrystallized repeatedly, until the refractive index and freezing point were unchanged by further crystallization. Physical constants were measured on this sample. A second run of this preparation was made in March 1941, in which recrystallized triptyl chlaride was reacted with an equimolar quantity of the Grignard reagent. In this case the yield was increased to 22 percent, based on the chloride.

Procurement of 10 gallons of this hydrocarbon was undertaken in 1941. Part of this (2.9 gal) was prepared at Ohio State University the rest was prepared in these laboratories. This large-scale preparation was carried out by a modification of the technique developed at Ohio State University. The chloride was added to the Grignard reagent in eight equal portions, in 8 successive days, while the reaction mixture was kept at 35° C.

An improved method was devised for the preparation of the large quantities of triptyl chloride necessary for this synthesis. The equipment consisted of three reactors, made from 30-inch lengths of 12-inch pipe, closed at both ends with companion and blind flanges. One end of each reactor was fitted with a small steel valve (1/4 in.). These reactors were refrigerated (-30° C) and were connected to a manifold through which hydrogen chloride could be admitted to each. The reactors were charged with triptene in wide-mouth bottles. The flanges of the reactors were secured by bolts and the reactors were allowed to stand until cold. Hydrogen chloride was then admitted until the pressure was 100 to 120 psi. The pressure gradually fell as the gas reacted until the pressure was about 50 to 60 psi. Then the process was repeated until there was no appreciable change in pressure during an hour. The excess gas was released, the system purged with dry air, and the product removed. The yield was practically quantitative. The product was uncolored and contained a small amount of excess hydrogen chloride. This excess was converted to alkyl chloride by adding a small amount of olefin to each jar and allowing to stand until reacted. By means of this technique, 20 to 35 liters of triptene was converted to the chloride in 1 working day.

To 300 moles of ethylmagnesium chloride there was added 300 moles of triptyl chloride in eight equal portions during 8 days. During this time, the reaction mixture was heated to reflux temperature and stirred. At the end of 2 to 4 additional days, when all the Grignard reagent had reacted,

the mixture was worked up with ice and hydrochloric acid and washed four times with water. Distillation of the ether, and of most of the triptene was carried out from the reaction kettle. The distillate was dried and redistilled in Column 12 or 13 for recovery of triptene.

The residue in the reaction kettle was boiled with sodium propylate in propyl alcohol until the product was substatially free of chloride. After the product was washed, it was steam distilled, and the distillate dried and boiled with alcoholic silver nitrate to remove the last traces of chloride. Then the product was filtered, washed several times, dried, and distilled in Columns 11, 18, 19, and 20, From two runs as described, which were worked up together, there was obtained 14.92 kilograms (116.6 moles) of tetrane which was 99.6 mole percent pure. This represents a yield of 19.4 percent. A total of 21.7 kilograms was prepared by this method.

*2,2,3,4-Tetramethylpentane and 2,3,3,4-Tetramethylpentane

The first preparation of these two nonanes was accomplished in June 1941 by hydrogenation of the alkenes (reference 17) formed by the dehydration of 2,2,3,4-tetramethyl-3-pentanol. The carbinol was prepared by the reaction between methylmagnesium bromide and 2,2,4-trimethyl-3-pentanone. This ketone was the result of oxidation of 2,2,4-trimethyl-3-pentanol, one of the products resulting from the action of t-butylmagnesium chloride on isobutyraldehyde.

The method of reference 17 was used to prepare 2,2,4-trimethyl-3-pentanol. To 55 moles of t-butylmagnesium chloride was added 3960 grams (55 moles) of isobutyraldehyde. Distillation of the organic reaction products gave 4290 grams (33 moles, 60-percent yield) of 2,2,4-trimethyl-3-pentanol. The carbinol was oxidized to pentamethylacetone (2,2,4-trimethyl-3-pentanone) with potassium dichromate and sulfuric acid, by method of Faworsky. (See reference 18.) From 32 moles of carbinol, there was obtained 3150 grams (24.6 moles, 77-percent yield) of ketone, which was distilled in Column 5.

The 2,2,4-trimethyl-3-pentanone (24.6 moles) in 6 liters of ether was reacted with 26 moles of methylmagnesium bromide, and the product distilled in Column 5 until the temperature reached 143° C. At this point dehydration of the carbinol was beginning to take place, so the distillation was interrupted, and the clear, slightly yellow residue (2950 ml) was dehydrated with β-naphthalene sulfonic acid.

From the dehydration there resulted 2410 ml of alkene mixture, which was dried and distilled in Column 3. The following fractions were obtained:

Fraction	Boiling Range (Head temperature) (°C)	Volume (ml)	Identification
1	91 to 119	23	Forerun
2	119 to 124	1550	3,3-Dimethyl-2-isopropyl-1-butene
3	124 to 129	200	Intermediate
4	130 to 135	600	2,3,3,4-Tetramethyl-1-pentene
5	>135	120	Residue

Fractions 2, 3, and 4 represent a combined yield of alkenes of 15.9 moles (65 percent, based on 2,2,4-trimethyl-3-pentanone). Samples from the middle of the plateaus represented by fractions 2 and 4 were reserved for physical-constants measurements. No attempt was made to isolate 2,3,4,4-tetramethyl-2-pentene, a very small quantity of which was found by Whitmore and Laughlin in reference 17.

The alkene fraction which distilled 119° to 124° C was hydrogenated, and the product was filtered through silica gel and distilled in Column 3. There was obtained 1070 ml of hydrocarbon which boiled 133.7° to 134.1° C, n_D^{20} (uncorrected) = 1.4147 to 1.4150. ("Uncorrected" means no correction for possible instrument error.) Redistillation of this material gave 930 ml collected at 133.8° C. Physical constants were determined on a sample from the center of this fraction.

The alkene fraction 4 was treated in like manner, and yielded 347 ml of material collected at 142° C (uncorrected), fractions of which showed a refractive-index range n_D^{20} (uncorrected) of 1.4219 to 1.4220. A sample from this distillation was reserved for determination of physical constants. All intermediate fractions, foreruns, residues, and material eluted from silica gel were hydrogenated and distilled in Column 8. In this way, there were obtained an additional 200 ml of 2,2,3,4-tetramethylpentane and 145 ml of 2,3,3,4-tetramethylpentane.

Tests on these two hydrocarbons demonstrated the advisability of preparing larger quantities. Consequently, 10 gallons of each was synthesized at Pennsylvania State College. These hydrocarbons were purified in these laboratories for engine tests by distillation in Column 1. New pure samples for measurement of physical constants were obtained concurrently. The improved data are given in table 2.

Dimethyl-Zinc Synthesis of Three Tetramethylpentanes

An olefin co-polymer fraction containing 3,4,4-trimethyl-2-pentene and 2,3,4-trimethyl-2-pentene was reacted with dry hydrogen chloride until about 60 percent of the olefin was converted to chloride. This chloride-olefin mixture was treated with dimethyl zinc in a solvent of hydrogenated co-dimer, which contained 2,2,3- and 2,3,4-trimethylpentanes. The resultant product was hydrogenated to a mixture of hydrocarbons, all known to have superior characteristics. This study led to the syntheses of these compounds in a pure state by this method.

Secondary and tertiary butyl alcohols were co-polymerized in the presence of sulfuric acid in the manner described in reference 19. A portion of the product was analyzed by distillation in Column 1 and was found to contain the diisobutylenes, 2,4,4-trimethyl-1- and -2-pentenes (25 percent), 3,4,4-trimethyl-2-pentene (23 percent), 2,3,4-trimethyl-2-pentene (37 percent), and higher-boiling material (15 percent). The rest of the olefin mixture was roughly separated by distillation in Column 5. The fractions which boiled 107° to 120° C amounted to 9740 grams and consisted of 2,3,4-trimethyl-2-pentene and 3,4,4-trimethyl-2-pentene as major components. Part of this fraction (6300 grams) was fractionated in Column 2. By this distillation there were obtained 1150 grams of 3,4,4-trimethyl-2-pentene ($n_D^{20} = 1.4230$, $n_D^{25} = 1.4205$, $d^{20} = 0.7392$, $d^{25} = 0.7350$, b.p. 112.1° to 112.8° C) and 1865 grams of 2,3,4-trimethyl-2-pentene ($n_D^{20} = 1.4275$, $n_D^{25} = 1.4250$, $d^{20} = 0.7434$, $d^{25} = 0.7391$; b.p. 116.3° to 116.5° C).

These two alkenes were reacted separately with hydrogen chloride at -60° C in an apparatus described in reference 2 until approximately 60 percent of the alkene had been converted to alkyl chloride. The products were washed, dried, and fractionated in Columen 3. In this way, 716 grams of constant-boiling 3-chloro-2,2,3-trimethylpentane was obtained from the 3,4,4-trimethyl-2-pentene. The chloride from 2,3,4-trimethyl-2-pentene (1410 grams) was probably a mixture of 2-chloro-2,3,4-trimethylpentane and 3-chloro-2,3,4-trimethylpentane. Since these two chlorides were expected to yield two different nonanes (by reaction with dimethyl zinc) with boiling points differing by about 8° C, no attempt was made to separate the chloride mixture. Physical constants measured on the chlorides are included in table 2.

2,2,3,3-Tetramethylpentane.- In the apparatus, and by the technique described previously, 4.15 moles (614 grams) of 3-chloro-2,2,3-trimethylpentane in 700 ml of isooctane (2,2,4-trimethylpentane, S-4 reference fuel) was allowed to react with the dimethyl zinc from 7.75 moles of methyl iodide. The dimethyl zinc was in a solution with 500 ml of isooctane. The bath temperature for the reaction was 7° C. The product was boiled for 2 hours with 5-percent potassium hydroxide in alcohol, washed, and fractionated in Column 4. This distillation gave:

Fraction	Boiling range (Head temperature) (°C)	Volume (ml)	Refractive index, n_D^{20}
1	96 to 100	1130	1.3918
2	100 to 110	65	1.4059
3 to 4	110 to 116	231	1.4195 to 1.4225
5	116 to 138.6	27	1.4226
6	138.6 to 140.3	39	1.4226
7	140.3	150	1.4233
Distillation of the residue was continued in Still 8 and gave:			
8	140.3	77	1.4232
9 (Residue)	>140.3	10	1.4379

Fraction 1 was recovered solvent. Alkene by-products of the reaction, formed by dehydrochlorination of the alkyl chloride, were contained in fractions 2 to 5. By the low refractive indices of these fractions, it is indicated that this material consisted mostly of 3,4,4-trimethyl-2-pentene. The yield of 2,2,3,3-tetramethylpentane (fractions 6,7, and 8) amounted to 37.7 percent based on alkyl chloride. Fraction 7, after filtration through silica gel, had the following properties: freezing point, -11.85° C, boiling point, 140.20° to 140.23° C at 760 millimeters of mercury; refractive index, $n_D^{20} = 1.4233$, $n_D^{25} = 1.4211$; density, $d^{20} = 0.7565$, $d^{25} = 0.7527$. It may be seen that the product was of high purity when these properties are compared with those of the pure sample, as listed in table 2. The freezing point indicates a purity of about 99.5 mole percent.

2,2,3,4- and 2,3,3,4-Tetramethylpentanes.- By use of the same procedure as described, two runs were made in which a total of 8.35 moles of the mixture of 2-, and 3-chloro-2,3,4-trimethylpentanes was reacted, at 10° C, with the dimethyl zinc from 15.5 moles of methyl iodide. The combined products were refluxed with alcoholic potassium hydroxide, washed, dried, and distilled in Column 4. This operation gave:

Fraction	Boiling range (Head temperature) (°C)	Volume (ml)	Refractive index, n_D^{20}
1	95 to 100	2051	1.3917
2	100 to 115	116	1.4080
3 to 4	115 to 119	440	1.4269 to 1.4267
5	119 to 130	31	1.4219
6 to 8	130.0 to 133.5	139	1.4158 to 1.4150
9	133.5 to 134.0	138	1.4152
10	134 to 140	64	1.4183
The residue was distilled in Still 8, and gave:			
11	140.0 to 141.5	10	1.4212
12	141.5 to 142.0	60	1.4218
13	142.0 to 143.0	20	1.4221
14	143 to 165	10	1.4271
15 (Residue)	----------	83	1.4570

Fraction 1 was recovered isooctane; fractions 3 to 4 were alkene by-products, indicated to be mostly 2,3,4-trimethyl-2-pentene by the refractive indices. The total yield of tetramethylpentanes (fractions 6 to 14) amounted to 30 percent, based on alkyl chloride. These tetramethylpentanes consisted of about 71 percent of 2,2,3,4-tetramethylpentane and about 29 percent of 2,3,3,4-tetramethylpentane.

Fraction 9, after filtration through silica gel, had the following properties: freezing point, -122.54° C, boiling point, 133.3° to 133.4° C at 760 millimeters of mercury, refractive index, $n_D^{20} = 1.4148$, $n_D^{25} = 1.4127$; density, $d^{20} = 0.7397$, $d^{25} = 0.7358$. These values are in agreement with those reported for the pure 2,2,3,4-tetramethylpentane in table 2. Fraction 12 was filtered through silica gel, and the eluent used for measurement of physical properties. These properties were found to be: boiling point, 141.3° to 141.4° C at 760 millimeters of mercury; refractive index, $n_D^{20} = 1.4217$, $n_D^{25} = 1.4196$, density, $d^{20} = 0.7545$, $d^{25} = 0.7512$. These data agree with those reported for purer 2,3,3,4-tetramethylpentane in table 2.

A tetramethylpentane, assumed to be 2,3,3,4-tetramethylpentane, was prepared by Dinerstein (reference 20) in 1940, by action of dimethyl zinc on 3-chloro-2,3,4-trimethylpentane. Later work by Enyeart (reference 21 and by the present authors shows that the hydrocarbon described by Dinerstein was 2,2,3,4-tetramethylpentane.

*2,4-Dimethl-3-Isopropylpentane (Triisopropylmethane)

The recent preparations of triisopropylcarbinol by the action of isopropyl lithium on 2,4-dimethyl-3-pentanone (diisopropyl ketone) (see reference 22) and by the action of isopropyl chloride on diisopropyl ketone in the presence of sodium (see reference 23) have made available a method for synthesizing triisopropylmethane (2,4-dimethyl-3-isopropylpentane). A quantity of this compound has been prepared by the use of isopropyl lithium.

Preliminary work on this reaction was performed in several small-scale experiments, in each of which 10 gram atoms of lithium, 6.5 moles of isopropyl chloride, 5.4 moles of diisopropyl ketone, and 2000 ml of solvent were used. During this study, it was found that technical 2,2,4-trimethylpentane (isooctane) served admirably as a solvent when its use was augmented by efficient stirring and external cooling of the reaction mixture. No preliminary purification of the solvent was necessary and the hazards accompanying its use are much less than those of petroleum ether, used by the original investigators. (See reference 22.)

The preparation of the considerable quantities of finely divided lithium required was expedited by the use of a small laboratory rolling mill. While the lithium was being worked in the mill it was lubricated and coated with a mixture of 80-percent isooctane and 20-percent light mineral oil applied by means of an oil can. This technique tended to prevent the lithium from sticking to the rolls and also prevented excessive oxide formation. The rolled pieces, about 0.003 inch thick, were cut into ribbons and then into squares in large shallow pan under isooctane.

The yields in all the preliminary runs amounted to 18 to 22 percent of carbinol. No appreciable change in yield was experienced when the reaction between isopropyl lithium and diisopropyl ketone was carried out at 99° C, the temperature of boiling isooctane, rather than at 35° C, the temperature used by the original investigators.

After the technique of handling the reaction had been sufficiently developed, a large run was carried out in the 50-gallon stainless-steel kettle. The total quantity of reactants used was: 159 gram atoms (1.10 kg) of lithium, 115 moles (9.03 kg) of isopropyl chloride, 80 moles (9.13 kg) of diisopropyl ketone, and 55 liters of isooctane. The quantity of isopropyl chloride was relatively larger than that used by the original investigators in order that a minimum amount of lithium be left unreacted and that any loss occurring through the reflux condenser be replenished. The diisopropyl ketone was constant-boiling material obtained by redistillation of the commercial product in Still 11.

The kettle was flushed with nitrogen and charged with 31 liters of isooctane. About half the lithium was added and the reaction started by the addition of 1 liter of isopropyl chloride in 1 liter of isooctane, and by warming the jacket to 35° C. The remainder of the lithium was added in three additional charges during the next $2\frac{1}{2}$ days. During the first 3 days, a mixture of the remainder of the isopropyl chloride in an equal volume of isooctane was added in four charges.

A solution of diisopropyl ketone in 11.4 liters of isooctane was added during 8 hours, while the reaction temperature was held at 45° to 60° C. After addition was complete, the mixture was warmed and stirred for 5 hours, after which it was cooled. Decomposition of the reaction mixture was effected by the addition of 25 pounds of cracked ice, followed by a solution of 11 pounds of ammonium chloride in 5 gallons of water. The aqueous layer was removed, and the organic layer washed five times, each time with 3 to 5 gallons of water, after which it was withdrawn and dried overnight with potassium carbonate.

Fractionation of the product in Column 6 gave: recovered isooctane, diisopropyl ketone, boiling point 121° to 126° C, 2355 grams; intermediate fractions, 240 grams; and triisopropylcarbinol, boiling point 104° to 110° C at 50 to 55 millimeters of mercury, 2576 grams. This represents a yield of 20.4 percent based on the diisopropyl ketone added. A part of the triisopropylcarbinol was redistilled, and a pure sample collected from the middle of this distillation for the measurement of physical constants.

The carbinol was dehydrated by distillation from anhydrous copper sulfate. From 16 moles of triisopropylcarbinol, 14.4 moles (90 percent) of crude 2,4-dimethyl-3-isopropyl-2-pentene, was obtained. Water recovery amounted to 80 percent. The crude olefin was dried over calcium chloride and distilled in Column 6, from which 1372 grams of material, which boiled 153.2° to 153.6° C at 756 to 759 millimeters of mercury, $n_D^{20} = 1.4368$ to 1.4371 (all values uncorrected), was collected. A sample was removed from the middle of the distillation for the measurement of physical constants.

The olefin was hydrogenated, and distilled in Column 6, and gave 1100 grams (80 percent) of constant-boiling material, boiling point 156.5° C at 749 millimeters of mercury, $n_D^{20} = 1.4234$ to 1.4236 (all values uncorrected). This material contained a trace of olefin which was removed by repeated filtration through silica gel. Refractionation under reduced pressure afforded the means of obtaining a pure sample for physical-constants measurements.

*Pentamethylpentanes

2,2,3,3,4-Pentamethylpentane.- The first preparation of 2,2,3,3,4-pentamethylpentane was carried out in February 1942 by the reaction between 2-chloro-2,3,3-trimethylbutane and isopropylmagnesium chloride.

To 30.5 moles of isopropyl magnesium chloride in 10.53 liters of ether solution, there was added, at room temperature, 26.4 moles of 2-chloro-2,3,3-trimethylbutane (sublimation point 132.7° to 134° C) in 3.5 liters of ether. After standing for 3 weeks at 15° to 20° C, the reaction mixture was worked up in the usual manner. The product, distilled in Column 6, gave:

14.8 moles of 2,3,3-trimethyl-1-butene, formed by dehydrochlorination of 2-chloro-2,3,3-trimethylbutane

0.1 mole of 2-propanol, formed by oxidation of the Grignard reagent, found in an azeotrope with 2,3,3-trimethyl-1-butene

2.2 moles of recovered 2-chloro-2,3,3-trimethylbutane

3.1 moles of 2,3,3-trimethyl-2-butanol, presumably by hydrolysis of the chloride

1.05 moles of crude 2,2,3,3,4-pentamethylpentane

This represents a yield of 4.0 percent. Another run, in which 19.3 moles of the chloride was used and which was kept at 5° C for 3 weeks, then at room temperature for 2 weeks, yielded 0.6 mole of additional crude (3.1-percent yield).

The combined yield of crude material (300 ml) was fractionated in Column 8. From this distillation there was obtained 226 ml of material which boiled 163.7° to 164° C (uncorrected). This product was redistilled in the same column, and there was collected 186 ml of constant-boiling, constant-refractive-index material. The physical constants of this product after filtration through silica gel were: freezing point -37.5° C, $n_D^{20} = 1.4361$, $d^{20} = 0.7803$, boiling point 165.54° to 165.56° C at 750.5 millimeters of mercury.

Later, two other methods for the preparation of this decane were investigated. Both of these methods involved the methylation of 2,2,3,4-tetramethyl-3-chloropentane. This chloride was prepared in good yield from the corresponding alcohol by reaction with concentrated hydrochloric acid. The chloride decomposed easily when a boiling-point determination was attempted at atmospheric pressure. It would not crystallize at dry-ice temperature and had an index of refraction n_D^{20} of 1.4389. The

carbinol was prepared by the reaction between methylmagnesium bromide and 2,2,4-trimethyl-3-pentanone.

In one experiment (November 1943) on the methylation of this chloride, 1.7 moles of the chloride in 320 ml of benzene was added to 2.5 moles of dimethyl zinc, using the previously described technique. Distillation analysis of the product of reaction showed the presence of 0.4 mole (23.5 percent) of 2-isopropyl-3,3-dimethyl-1-butene and 0.81 mole (47.5 percent) of 2,3,3,4-tetramethyl-1-pentene, both formed by dehydrochlorination of the alkyl chloride. In addition, there was found 0.38 mole (assuming $C_{10}H_{22}$) of material which boiled 150° to 160° C, and from which no pure material could be isolated.

In another experiment (May 1944), 10.7 moles of 2,2,3,4-tetramethyl-3-chloropentane was treated with 11.0 moles of methylmagnesium bromide in ether solution. The reaction was allowed to take place over a period of 3 weeks at 15° to 22° C. The products of the reaction, as determined by distillation analysis, consisted of 3.0 moles (28 percent) of 2-isopropyl-3,3-dimethyl-1-butene, and 5.7 moles (53 percent) of 2,3,3,4-tetramethyl-1-pentene, formed by dehydrochlorination of the alkyl chloride. In addition, there was found 0.5 mole (4.7 percent) of crude 2,2,3,3,4-pentamethylpentane (158° to 167° C, n_D^{20} = 1.4354 to 1.4369).

It is interesting to note that in both of these trials, the dehydrochlorination of the alkyl chloride led to approximately the same relative proportions of the two nonenes; namely, one part of 2-isopropyl-3,3-dimethyl-1-butene, and two parts of 2,3,3,4-tetramethyl-1-pentene. This proportion is not the same as occurs when the carbinol itself is dehydrated. In that case the proportions are three parts of 2-isopropyl-3,3-dimethyl-1-butene and one part of 2,3,3,4-tetramethyl-1-pentene. (See reference 15.)

Pentamethylpentanes from 2,2,3,4,4-pentamethyl-3-pentanol - I.- In an attempt to prepare 2,2,3,4,4-pentamethylpentane, it has been found that 2,2,3,4,4-pentamethyl-3-pentanol will dehydrate under the influence of iodine to a mixture of two decenes, which, on hydrogenation, yields both of the pentamethylpentanes.

In 1933 Whitmore and Laughlin (reference 17) reported the dehydration of 2,2,3,4,4-pentamethyl-3-pentanol by means of β-naphthalene sulfonic acid to give 2-t-butyl-3,3-dimethyl-1-butene without appreciable rearrangement. They also reported a small amount of low-boiling, unidentified material.

Since this reaction offered a means of preparing 2,2,3,4,4-pentamethylpentane, a trial run was made. When the carbinol was dehydrated with β-naphthalene sulfonic acid at atmospheric pressure, the products of the reaction consisted of isobutylene, 2,3-dimethyl-1-butene,

2,3-dimethyl-2-butene, and only a small amount of higher-boiling material. No 3,3-dimethyl-1-butene was found in the reaction products. Dehydration of the carbinol with iodine was found to yield a mixture of decenes, composed of 2-t-butyl-3,3-dimethyl-1-butene and 2,3,3,4,4-pentamethyl-1-pentene.

(1) Preparation of 2,2,4-trimethyl-3-pentanone and 2,2,4,4-tetramethyl-3-pentanone

Preparation of 2,2,4-trimethyl-3-pentanone was made by the Haller-Bauer synthesis (reference 24) in toluene solvent by the action of sodium amide and then methyl sulfate on 2,4-dimethyl-3-pentanone. Sodium amide was made in 90- to 94-percent yield by the method described in reference 25. The crude 2,2,4-trimethyl-3-pentanone was methylated a second time by the same method to give 2,2,4,4-tetramethyl-3-pentanone. The manipulative details of these reactions are described by Whitmore and Laughlin in reference 17. The over-all yield was 58 percent of that theoretically possible, calculated without including recovered 2,4-dimethyl-3-pentanone and 2,2,4-trimethyl-3-pentanone, which were recycled in the synthesis. A charge of this ketone was fractionated in Column 1, for the isolation of a pure sample for physical-constants measurements. In the same column, a sample of the 2,2,4,4-tetramethyl-3-pentanone was also distilled for the same purpose.

(2) Preparation of 2,2,3,4,4-pentamethyl-3-pentanol

A solution of 10 moles of methylmagnesium bromide was reacted with 8.75 moles of 2,2,4,4-tetramethyl-3-pentanone and the product worked up in the usual manner. Fractionation of the product in Column 4 at a pressure of 57 millimeters of mercury gave a forerun of 307 ml of material which boiled below 105° C. At this point the carbinol began to solidify in the condenser and the pale yellow material remaining in the pot was found to be quite pure carbinol (melting point above 37° C). A portion was recrystallized from ether for use in the determination of physical properties. The yield amounted to 75 percent of the theoretical quantity.

(3) Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol with β-naphthalene sulfonic acid

Dehydration of 897 grams (5.7 moles) of 2,2,3,4,4-pentamethyl-3-pentanol with 8 grams of β-naphthalene sulfonic acid under a fractionating column resulted in the distillation of a water layer, an organic layer (855 ml), and about 50 ml of material collected in a dry-ice trap. The organic layer, which smelled strongly of sulfur dioxide and hydrogen sulfide, was washed, dried, and distilled from sodium, and gave the following fractions:

Fraction	Boiling range (Head temperature) (°C)	Volume (ml)	Refractive index, n_D^{20}
1	54	4	------
2	54 to 57	65	1.3908
[a]3	51 to 71	26	1.4033
4	71 to 73	23	1.4084
5	73 to 75	365	1.4100
6	75 to 150	35	1.4223
7	150 to 153.2	24	1.4375
8	153.2 to 156.5	33	1.4400
9	156.5 to 157	14	1.4411
Residue	157	22	------

[a]Distillation interrupted.

A considerable quantity of gas was evolved during the distillation. This gas boiled at about -4° C, was readily absorbed in sulfuric acid, and absorbed bromine. Regeneration from sulfuric-acid solution by neutralization resulted in t-butyl alcohol. This identifies the gas as isobutylene. The other principal products of the reaction were fraction 2(2,3-dimethyl-1-butene), fraction 5 (2,3-dimethyl-2-butene), and fractions 7 and 8, which probably contained a mixture of 2,3,3,4,4-pentamethyl-1-pentene and 2-t-butyl-3,3-dimethyl-1-butene. Since the products of this distillation did not yield the desired compounds in any appreciable quantity more elaborate analysis was not undertaken.

(4) Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol with iodine

A charge of 2,2,3,4,4-pentamethyl-3-pentanol (640 grams, 4.1 moles) was refluxed with 4 grams of iodine and the product distilled through a short fractionating column, yielding 70 ml of water and 700 ml of organic material. The organic layer was washed, dried, and fractionated roughly. The distillates from three runs were combined, yielding 1950 ml of material which, on further fractionation, gave 1800 ml boiling 140° to 155° C. The residue was semisolid and had an odor similar to that of a carbinol. The 140° to 155° C fraction was redistilled into the following fractions:

Fraction	Boiling range (Head temperature) (°C)	Volume (ml)	Refractive index, n_D^{20} (uncorrected)
1	100 to 148.2	55	1.4314
2	148.2 to 149.0	43	1.4348
3	149.0 to 149.6	283	1.4355
4	149.6 to 151.0	460	1.4355
5	151.0 to 152.0	190	1.4367
6	152.0 to 153.0	55	1.4381
7	153.0 to 155.0	50	1.4396
8	155.0 to 157.0	26	1.4410

A constant-boiling portion of fraction 3 was reserved for determination of physical constants and ozonolysis. At 157° C, solid material started to form in the condenser; so the distillation was stopped. The cooled residue in the flask was solid, melting at 34.5° to 37.5° C, but a mixture of this compound and the original carbinol was liquid at room temperature. The material was soluble in ether, insoluble in water, slightly soluble in 85-percent phosphoric acid and was unaffected by sodium.

Analysis showed the presence of 83.1 percent carbon and 13.8 percent hydrogen. Because of the volatility of the compound, these results may be low. By extending the CH content to total 100 percent, the analysis was calculated to 85.8 percent carbon and 14.2 percent hydrogen, which agrees with the analysis of an alkene. The molecular weight was found cryoscopically to be 142.4 (theory for $C_{10}H_{20}$ = 140.1).

At this point the distillation of the solid olefin was continued after provision had been made to prevent solidification of material in the condenser. This distillation gave the following fractions:

Fraction	Boiling range (Head temperature) (°C)	Weight (grams)
9	157.0 to 157.2	30.1
10	157.2 to 158.0	18.6
11	158.0 to 158.2	18.4
12	158.2 to 158.2	27.7
13	158.2 to 158.9	28.1
14	158.9 to 159.0	28.3
15	159.0 to 159.0	28.2
Residue		39.1

Ozonolysis was performed on fraction 15.

(5) Ozonolysis of Alkenes

(a) Lower-boiling alkene (2-t-butyl-3,3-dimethyl-1-butene)

Ozonization of 0.21 mole of alkene in 300 ml isopentane at -5° to -10° C was accomplished in 12 hours. Oxygen containing 7.5 percent ozone was used at the rate of 7500 ml per hour. The solvent was not removed prior to decomposition because the ozonide proved to be a solid. Decomposition was effected by means of the technique developed by Whitmore and Church in reference 26. The reaction was of medium violence and gave rise to 36.5 ml of oil and 150 ml of water layer. Analysis of the water layer showed the presence of 0.18 mole of formaldehyde and no other low-molecular-weight aldehyde or ketone. The oil was distilled to yield 24.3 ml of 2,2,4,4-tetramethyl-3-pentanone (b.p. 150° to 155° C), which, when treated with methylmagnesium bromide, gave 2,2,3,4,4-pentamethyl-3-pentanol, the identity of which was proved by a mixed melting point with a known sample.

(b) Higher-boiling alkene (2,3,3,4,4-pentamethyl-1-pentene)

In the same manner as described, 0.11 mole of the higher-boiling alkene was ozonized in 300 ml of isopentane at -10° to -20° C to yield 0.071 mole of formaldehyde and 9 grams of an oil (b.p. 172° C, $n_D^{24} = 1.4149$). This oil gave a positive iodoform test, and was oxidized by 50-percent nitric acid to 2,2,3,3-tetramethylbutanoic acid. (See references 27 and 28.) After several crystallizations from alcohol, this acid melted at 196° to 197° C, the same value reported in reference 29. The neutral equivalent was found to be 147.3. The amide was prepared and found to melt at 201.5° to 202.2° C, which agrees with the melting point (201° to 202° C) found in reference 29. The ketone gave a 2,4-dinitrophenylhydrazone which melted at 182° to 183° C. The ketone was therefore considered to be 3,3,4,4-tetramethyl-2-pentanone. (Analysis: N found; 17.20, 17.28 percent; calculated for $C_{15}H_{22}N_4O_8$; 17.27 percent.)

(6) Hydrogenation of the decenes

The crude lower-boiling alkene from the dehydration of 2,2,3,4,4-pentamethyl-3-pentanol (fractions 2 to 8) was hydrogenated and filtered through silica gel. Distillation in Column 5 gave:

Fraction	Boiling range (Head temperature) (°C)	Volume (ml)	Refractive index, n_D^{20}
1 to 2	153.4 to 158.4	100	1.4296 to 1.4304
3 to 8	158.4	300	1.4306 to 1.4307
9 to 14	158.4 to 159.8	303	1.4307 to 1.4313
15 to 16	159.2 to 161.7	97	1.4320 to 1.4341
Residue	----------	47	1.4360

An analysis of the distillation curve showed the presence of 735 ml of 2,2,3,4,4-pentamethylpentane and 112 ml of 2,2,3,3,4-pentamethylpentane.

Hydrogenation of the higher-boiling alkene was carried out in a solvent (2,2,4-trimethylpentane). Distillation gave, in addition to the solvent, a small forerun and 247 ml of fractions collected at 163° to 164° C (n_D^{20} = 1.4358 to 1.4361). The best samples of both decanes were reserved for measurement of physical constants.

The yield of alkanes isolated in the pure state (calculated on 2,2,4,4-tetramethyl-3-pentanone) amounted to 25.8 percent of 2,2,3,4,4-pentamethylpentane and 11.4 percent of 2,2,3,3,4-pentamethylpentane. These yields could not be used to form a definite opinion of the reaction, nor can much weight be placed on the ratio of products found, since a loss experienced in the distillation and handling of the higher boiling decene is not accounted for.

Pentamethylpentanes from 2,2,3,4,4-pentamethyl-3-pentanol - II.- The second run of this series of reactions was made to increase the stock of hydrocarbons and to obtain more information on the ratio of products formed by dehydration of the carbinol.

(1) Preparation of 2,2,4-trimethyl-3-pentanone

For this second synthesis, an easier method was devised for making 2,2,4-trimethyl-3-pentanone. This method was an adaptation of that described by Nef in reference 30 who obtained this ketone by the exhaustive methylation of acetone, methylisopropyl ketone, diethyl ketone, or pinacolone with methyl iodide and potassium hydroxide in a sealed tube at 140° C. The method used in the present work substituted the less expensive methyl bromide for methyl iodide in the methylation of commercial 2,4-dimethyl-3-pentanone.

Several runs of various sizes were made and the results are summarized in the following table:

METHYLATION OF 2,4-DIMETHYL-3-PENTANONE

Methylating agent (moles)	2,4-Dimethyl-3-pentanone (moles)	Potassium hydroxide (moles)	Temperature (°C)	Duration (hr)	Yield of 2,2,4-trimethyl-3-pentanone[1] (percent)
CH_3I (1.5)	1.2	3.5	140 to 160	7.0	55
$(CH_3)_2SO_4$(1.5)	1.2	3.5	140 to 160	7.2	0
CH_3Br (4)	4	12	160 to 170	6.0	35
CH_3Br (4)	4	12	140 to 150	9.1	15
CH_3Br (4)	4	12	190 to 200	11.7	35
CH_3Br (4)	4	6(CaO)	190 to 200	8.0	0
CH_3Br (47.7)	39.6	120	200 to 215	8.0	57
CH_3Br (47.7)	39.6	120	190 to 200	10.0	54
CH_3Br (47.7)	39.6	120	200 to 230	8.0	47

[1]Based on 2,4-dimethyl-3-pentanone consumed.

These reactions were carried out in hydrogenation bombs. The bomb was chilled by solid carbon dioxide and charged with the reactants, then sealed and heated to the temperature indicated. Since the reaction is exothermic, it was found difficult to hold a predetermined narrow temperature range. (The operation could probably be made more efficient by pumping the methyl bromide into the reaction vessel as it is consumed by the reaction in order to obtain more stable reaction conditions.) When the reaction was complete the bomb was cooled and the contents washed well with water, dried, and fractionated. In one experiment an attempt was made to distill the residue (247 grams). It was found to contain lachrymatory materials, but little, if any, 2,2,4,4-tetramethyl-3-pentanone. None of this compound was found by Nef in any of his methylation products.

(2) Preparation of 2,2,4,4-tetramethyl-3-pentanone

While the preparation of 2,2,4-trimethyl-3-pentanone was in progress, a new and simpler method for synthesizing 2,2,4,4-tetramethyl-3-pentanone was described by Bartlett and Schneider. (See reference 23.) This new procedure eliminated entirely the necessity of using sodium amide in the

synthesis. The Bartlett and Schneider reaction involved interaction between t-butyl chloride, methyl trimethylacetate, and sodium sand to give a mixture of 2,2,4,4-tetramethyl-3-pentanone and 2,2,4,4-tetramethyl-3 pentanol as major products.

Several small-scale runs (1.6 to 2.0 moles) of this reaction were made. There was no appreciable difference in the yields of ditertiary-butyl compounds from reactions in which technical isooctane (2,2,4-trimethylpentane) was used as a solvent and those in which isopentane was used. Since the former solvent is considered safer, it was used in the majority of the trial runs and in the large-scale run. Slightly larger (2 to 5 percent) yields were obtained when sodium sand was used rather than sodium wire. In none of the small-scale runs did the yield of combined ditertiary-butyl compounds exceed 53 percent. (Bartlett and Schneider report yields up to 71 percent.) After the technique for handling this reaction had been sufficiently developed, a large run was made in the stainless-steel kettle.

(a) Methyl trimethylacetate

To a solution of 53 kilograms (177 moles) of sodium dichromate dihydrate (technical) in 98 liters of water in the glass-lined reactor was added 39.9 liters of concentrated sulfuric acid. The solution was heated to 82° C and 6.6 kilograms (59 moles) of 2,4,4-trimethyl-2-pentene (97 percent pure) was added over a period of 5 hours. The rate of addition was regulated so that the temperature of the mixture did not exceed 88° C. Then about 3 liters of methyl alcohol was added to use the excess dichromate, and the mixture was subjected to steam distillation. There were obtained 5.76 kilograms of organic layer and about 30 liters of aqueous layer. The aqueous layer yielded, on distillation, an additional 0.82 kilogram of organic material. The crude product was distilled in Columns 4 and 5, and yielded 3.91 kilograms of trimethyl acetic acid (b.p. 160° to 165° C; 65.0 percent yield). The methyl ester of trimethylacetic acid was prepared in the usual manner by refluxing a solution of the acid in methyl alcohol. Sulfuric acid was used as the catalyst.

(b) 2,2,4,4-Tetramethyl-3-pentanone

Sodium sand, from 6.8 kilograms (300 moles) of sodium was prepared under toluene (22 liters) in the usual manner. The mixture was cooled to 15° C and 16 liters of technical isooctane (2,2,4-trimethylpentane) and 16 kilograms (173 moles) of t-butyl chloride were added. After the reaction was initiated by the addition of a small quantity of ester, the remainder (total 7.98 kg, 68.5 moles) was added during 4 hours, while the temperature was maintained at 35° to 40° C. Stirring was continued for 8 hours, then the mixture was allowed to stand overnight. The product was worked up in the manner described by Bartlett and Schneider in reference 23. Distillation gave 2.57 kilograms (18.1 moles) of 2,2,4,4-

tetramethyl-3-pentanone (b.p. 151.5° to 156.0° C), 666 grams of intermediate, and 2.72 kilograms (18.9 moles) of 2,2,4,4-tetramethyl-3-pentanol (b.p. 167° to 173° C). Including the intermediate, this represents a yield of approximately 61 percent, based on methyl trimethylacetate.

The carbinol fraction and the intermediate containing carbinol were combined and oxidized in two batches. In each batch 1.36 kilograms (9.45 moles) of carbinol and 333 grams of intermediate were suspended in a solution of 1255 grams of sodium dichromate dihydrate in 1170 ml of water. While the reaction mixture was held at 45° to 60° C, a solution of 2300 ml concentrated sulfuric acid in 2170 ml of water was added during 2 days, after which the reaction mixture was stirred and heated to 50° C for 1 day. The organic material was then steam distilled, dried, and fractionated. There was obtained 1.35 kilograms (9.52 moles) of ketone (b.p. 151° to 154° C; 78 percent yield).

In the same manner, all the 2,2,4,4-tetramethyl-3-pentanol obtained in the several preliminary runs was oxidized to ketone, and all the ketone from the several sources, was combined. This included a small amount prepared by the Haller-Bauer reaction. (See reference 24.)

(c) Preparation and dehydration of 2,2,3,4,4-pentamethyl-3-pentanol

The pentamethylpentanol was prepared in the manner already described. From 6.96 kilograms (49.0 moles) of 2,2,4,4-tetramethyl-3-pentanone there was obtained 4.84 kilograms (30.6 moles) of 2,2,3,4,4- pentamethyl-3-pentanol (62.6 percent yield). Dehydration of the carbinol was caused by refluxing with iodine. In a trial run, 332 grams (1.98 moles) of carbinol was boiled with 3.3 grams of iodine. During 2 hours, 93 percent of the theoretical quantity of water was eliminated and collected. The organic layer was washed with sodium thiosulfate solution and with water, dried, and distilled in Column 17. The charge was 246 grams. The decene fractions (b.p. 145° to 158.9° C) weighed 216.6 grams (1.54 moles; 78 percent). Analysis of the distillation curve showed that these fractions consisted of equal parts of the two isomers, 3,3,-dimethyl-2-t-butyl-1-butene and 2,3,3,4,4-pentamethyl-1-pentene. Treatment of the main portion of the carbinol for the preparation of the pentamethylpentanes followed the procedure already described.

2,2,5,5-Tetramethylhexane and 2,2,4,5-Tetramethylhexane

The synthesis of 2,2,5,5- and 2,2,4,5-tetramethylhexanes was accomplished by the following reactions: (a) oxidation of 2,4,4-trimethyl-1-pentene to 4,4-dimethyl-2-pentanone (methyl neopentyl ketone), (b) oxidation of this ketone to t-butylacetic acid, (c) conversion of the acid to methyl t-butylacetate, (d) reaction of the ester with t-butylmagnesium

chloride to give 2,2,5,5-tetramethyl-3-hexanol, (e) dehydration of the carbinol to a mixture of 2,2,5,5-tetramethyl-3-hexene, 2,3,5,5-tetramethyl-2-hexene, and 2,3,5,5-tetramethyl-1-hexene, and (f) hydrogenation of the first-named alkene to 2,2,5,5-tetramethylhexane and of the last two alkenes to 2,2,4,5-tetramethylhexane.

Oxidation of 2,4,4-trimethyl-1-pentene.- The oxidation of 2,4,4-trimethyl-1-pentene was carried out essentially in the manner disclosed by Whitmore, Homeyer, and Trent in reference 15. Several runs were made using olefin of 95-percent or higher purity. (The isolation of this olefin is described later.) In a typical run, 101 moles of alkene was oxidized during 10 days with sodium dichromate by the slow addition of sulfuric acid. There were obtained 1800 grams of acidic material and 9360 ml of neutral oil which, upon distillation in Column 3, gave 2154 ml of forerun, 4150 grams (36.4 moles) 4,4-dimethyl-2-pentanone (b.p. 123° to 126° C), and 2000 ml of residue. This yield of ketone is equivalent to 36 percent of the theoretical amount. The acidic material was found to be a complex mixture containing only minor quantities of trimethylacetic and t-butylacetic acid, and was not further investigated.

Oxidation of methylneopentyl ketone.- The hypohalite oxidation of the methylneopentyl ketone to t-butylacetic acid was accomplished by a modification of the reaction disclosed in reference 15. There sodium hypobromite (prepared from bromine and sodium hydroxide) was used, while in the present work the less expensive, commercially available calcium hypochlorite was used. Several small preliminary runs were made to develop familiarity with the reaction before a large run was undertaken. Three large runs were made, one of which is described.

A solution of 14.0 kilograms of technical sodium hydroxide in 38 liters of water was prepared. This solution was cooled to 19° C and to it were added about 90 kilograms of cracked ice and 13 kilograms of commercial calcium hypochlorite (70 percent chlorine). The temperature thereby obtained was about -4° C. The ketone (50 moles) was then added during 3 hours. The temperature of the reaction mixture remained below +5° C during this addition. An additional 25 kilograms of cracked ice was added and the mixture stirred for 10 hours, after which it was heated to 65° to 70° C for 5 hours. After cooling the mixture to 20° C, 19.7 liters of sulfuric acid was added slowly and the products steam distilled. The crude product was distilled in several batches from a 1-liter Claison flask. There was obtained 4070 grams (31.3 moles; 63 percent) of acid collected between 180° and 190° C. No further purification of the acid was made.

Conversion of t-butylacetic acid to methyl t-butylacetate.- The methyl ester of t-butylacetic acid was made in the orthodox manner. In a typical run a solution of 4140 grams (35.7 moles) of acid and 300 ml of concentrated sulfuric acid in 10 liters (250 moles) of methanol was

heated to reflux for two periods of 7 hours each. The crude product obtained was distilled in Column 5 and gave 3560 grams (27.4 moles; 76.7 percent) of ester, which was collected at 125° to 127° C.

Preparation of 2,2,5,5-tetramethyl-3-hexanol.- The preparation of 2,2,5,5-tetramethyl-3-hexanol was carried out by the use of the reaction described by Moersch (reference 31) which is an adaptation of that used by Heyd (reference 32).

To the Grignard reagent prepared from 326 gram atoms of magnesium and 325 moles of t-butyl chloride, there was added 6815 grams (52.4 moles) of methyl t-butylacetate during 8 hours. The reaction mixture was refluxed 7 hours each day for 3 days and allowed to stand each night. Decomposition was caused by dilute sulfuric acid (17 kg concentrated acid and 20 kg water and ice). The product was steam distilled, and the aqueous layer extracted with ether. The organic layers were combined and the ether removed in Column 11. The residue was redistilled in Columns 24 and 7, yielding 6507 grams of carbinol collected at 166° to 170° C. This is equivalent to 41.2 moles or 79 percent yield. Moersch reported 85 percent yield (reference 31).

Dehydration of 2,2,5,5-tetramethyl-3-hexanol.- Three preliminary experiments were made on the dehydration of this carbinol and on the rearrangement of the resulting olefins. In one run, 117 grams (0.70 mole) of carbinol was passed over 256 grams (330 ml) of alumina (Baker Hydralo, lot 91942) at 300° to 305° C at the rate of 47 grams per hour. The catalyst tube was 2.5 centimeters in diameter. The water recovered amounted to 10.8 ml (0.6 mole; 86 percent). The product was dried and fractionated in Column 17. The yield of decenes amounted to 70 percent (78 percent on basis of carbinol consumed), and consisted of 34.5 mole percent 2,2,5,5-tetramethyl-3-hexene, 35.2 percent 2,3,5,5-tetramethyl-1-hexene, and 30.2 percent 2,3,5,5-tetramethyl-2-hexene.

In another experiment, 118 grams of carbinol was dehydrated under the same conditions, except that the rate was 98 grams per hour. In this case, a yield of 46 percent olefins (73 percent on basis of carbinol consumed) was obtained. The mixture of olefins contained 34.8 percent 2,2,5,5-tetramethyl-3-hexene, 42.0 percent 2,3,5,5-tetramethyl-1-hexene, and 23.2 percent 2,3,5,5-tetramethyl-2-hexene.

To determine the extent of rearrangement of the olefins, a mixture of decenes was passed over the catalyst at 300° to 310° C at the rate of 44 grams per hour. Analysis of the resultant mixture showed that the original mixture was isomerized as follows: 2,2,5,5-tetramethyl-3-hexene; from 13.5 percent to 16.8 percent; 2,3,5,5-tetramethyl-1-hexene; from 46.2 percent to 31.2 percent; 2,3,5,5-tetramethyl-2-hexene, from 40.0 percent to 52.0 percent.

The bulk of the carbinol was dehydrated in the manner used in the first experiment. The resultant mixture was dried and distilled in Column 5. The carbinol recovered was recycled for dehydration. In this way, 4999 grams of crude olefin mixture was obtained (86.6 percent yield). This mixture was separated roughly in Column 5 into concentrates boiling 121° to 127° C, 139° to 145° C, and 152° to 158° C, and intermediate fractions. A sample (500 ml) of each hydrocarbon was redistilled in Column 17 for preparation of pure compounds. The impure fractions from each of these distillations were returned to the appropriate concentrate. These olefins have been identified previously. (See references 31 and 32.)

Hydrogenation.- Each of the olefin concentrates was hydrogenated separately, as was the combined intermediate. The last two olefin concentrates gave the same paraffin and were combined for distillation. Purification of both paraffins was accomplished in Column 18. The best 500 ml samples from each distillation were redistilled in Column 17, and physical constants were measured on the best samples from these distillations.

2,2,3,3-Tetramethylhexane

This hydrocarbon, which was synthesized at Pennsylvania State College, was purified in these laboratories. When received, the sample (2 gal) contained chlorides which were removed by boiling with alcoholic alkali. The product was washed, dried, and fractionated in Columns 19 and 20. The best portion from one of these distillations was refractionated in Column 17. Physical constants were determined on the best fractions from this distillation.

*3,3,4,4-Tetramethylhexane

The method of preparation of this decane is similar to that used in the preparation of 2,2,3,3-tetramethylpentane, and involved the reaction between ethylmagnesium chloride and 2,3,3-trimethyl-2-chloropentane.

In the exploratory synthesis, 2,3,3-trimethyl-1-pentene (b.p. 108.34° to 108.40° C, n_D^{20} = 1.4170 to 1.4172) was converted to the chloride, 2,3,3-trimethyl-2-chloropentane, by reaction with dry hydrogen chloride at -30° C. The product was fractionated in Column 4. The forerun of unchanged olefin was used in the preparation of more chloride. The chloride used in the coupling reaction was that collected between 81° and 82° C at 57 millimeters of mercury.

To the Grignard solution prepared from 10 gram atoms of magnesium and 10 moles of ethyl bromide, there was added, during 7 days, 9.3 moles (1382 grams) of the chloride. On the twelfth day the mixture was worked up. The ether was removed from the organic layer and the residue refluxed 6 hours with alcoholic alkali (10 percent KOH) to remove chlorides. The

washed, dried, chloride-free material was distilled in Column 17. A large run of the preparation of this hydrocarbon is in progress. From this run a considerably purer compound is expected.

2,3-Dimethyl-1-Butene and 2,3-Dimethyl-2-Butene

The preparation and properties of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene have been reported previously in reference 5. While the 2,3-dimethyl-1-butene reported was relatively pure, the 2,3-dimethyl-2-butene was decidedly impure. The boiling range of the best sample of the latter was about 0.4° C, even after repeated fractionation; whereas other hydrocarbons prepared and reported in the same paper had boiling ranges of less than 0.01° C. The wide boiling range has been attributed to the presence of peroxides in the sample. This tendency to form peroxides is much more pronounced in the 2,3-dimethyl-2-butene than in the one isomer. Since both alkenes result from the same reaction, the study of both compounds was repeated. The method of preparing the alkenes was dehydration of 2,3-dimethyl-2-butanol by means of iodine. The carbinol was prepared by action of methylmagnesium bromide on methyl isobutyrate.

Several batches of methyl isobutyrate were made, in each of which 90 moles of methanol and 30 moles of isobutyric acid were refluxed for 6 to 8 hours with 15 ml of concentrated sulfuric acid. The product was recovered by adding water, extracting the unchanged acid by sodium carbonate solution, and saturating the aqueous layer with salt to recover unused alcohol and dissolved ester. The combined, nonacidic organic layer was distilled in Columns 3, 4, 5, and 6. Only constant-boiling (±0.1° C) material was reserved for subsequent steps. The yield amounted to 71 percent of the theoretical based on original isobutyric acid.

In a typical run of the preparation of 2,3-dimethyl-2-butanol 42 moles of methyl isobutyrate was added to 90 moles of methylmagnesium bromide in 12 hours. After the reaction mixture had been allowed to stand for 15 hours, it was warmed for 4 hours and then treated with ice and dilute hydrochloric acid. The organic material was dried and distilled in Column 6. After ether and unchanged ester had been removed, the carbinol was distilled at 76.4° to 76.6° C at 152 millimeters of mercury. The yield was 3120 grams (73 percent, based on ester).

The dehydration of 2,3-dimethyl-2-butanol was accomplished by heating it with 1 gram of iodine per liter of carbinol. The olefinic material thereby obtained was roughly separated in Column 4 and consisted of approximately three parts of 2,3-dimethyl-2-butene and one part of 2,3-dimethyl-2-butene. The residue from this distillation consisted of unchanged carbinol which had steam distilled during the dehydration step. This carbinol was returned to the dehydration process as it accumulated. In this way, a practically quantitative yield of alkenes was obtained.

Two charges of crude 2,3-dimethyl-2-butene were fractionated in Column 1. The middle cuts from these distillations, the fractions of which had a constant refractive index (±0.00005), were combined, and amounted to 3.6 liters of material. The 2,3-dimethyl-1-butene was fractionated in like manner, and 3.5 liters of material was obtained. The two hydrocarbons were then subjected to distillation in Column 5 under conditions designed to destroy any peroxides present and to prevent their formation in the distillate. This was accomplished by adding hydroquinone to the distillation charge and by keeping the column, take-off, and delivery systems flushed with nitrogen. In this way, thirty-three 100-ml fractions of each hydrocarbon were obtained.

For measuring the physical properties of these olefins the same apparatus and methods previously described were used, but care was exercised to displace air in the apparatus with nitrogen during the determinations. Refractive indices were measured in the usual manner. Peroxide numbers (moles of active oxygen in 1000 liters of solution) were determined by the method of Yule and Wilson (reference 33).

For 2,3-dimethyl-1-butene, fraction 17 was used for determination of refractive index and density. The peroxide number of this fraction was 0.03. Measurements of boiling points of this olefin were made with fractions 16 and 19. The distillate from these determinations contained an unmeasurably small amount of peroxide. The freezing point of 2,3-dimethyl-2-butene was made on fraction 17 (0.07 peroxide number). Refractive-index and density measurements were made on fraction 21 (0.03 peroxide number), and boiling-point measurements on fractions 18, 19, and 20 (0.04 to 0.06 peroxide number). The measured values of the properties are given in table 2.

Considerable difference of opinion exists regarding the freezing point of 2,3-dimethyl-1-butene. Schurman and Boord (reference 34) report a "melting" point of -120° to -123° C on material having a boiling range of 0.4° C. Brooks, Howard, and Crafton (reference 5) report a freezing point of -140.1° C on a sample of high purity which, however, undoubtedly contained some peroxide. Kistiakowsky and coworkers (reference 35), using a sample having a boiling range of 0.01° C for use in determining the heat of hydrogenation, reported that the material congealed to a glass at low temperatures. Two attempts were made in this work to freeze samples which were peroxide-free, but both were unsuccessful. An attempt to freeze samples recovered from the boiling-point distillates, which had been exposed to air for 2 weeks also failed. Attempts were made to freeze samples containing small amounts of 2,2,4-trimethylpentane; those samples containing 0.58 and 2.4 mole percent of this impurity failed to freeze. One sample containing 1.43 mole percent 2,2,4-trimethylpentane gave an indefinite freezing point at -145.4° C. This value seems to substantiate the previous value of -140.1° C (reference 5) and would indicate a very low heat of fusion, which may be a controlling factor in the determination of the freezing point.

The presence of peroxides caused a marked change in the boiling ranges of these olefins. When samples of pure 2,3-dimethyl-1-butene were distilled in the boiling-point apparatus, the observed temperature changes (from 20 to 80 percent distilled) were less than 0.004° C. The same material, after exposure to air for 2 months showed a distillation range (20 to 80 percent) of 0.11° C. Still more pronounced is the effect of peroxides on 2,3-dimethyl-2-butene. Samples containing a small quantity of peroxide (peroxide number 0.04) distilled over a range of 0.007° C or less, but after this material had accumulated peroxides for 10 days the distillation range was found to be 1.03° C.

In order to determine the rate of peroxide formation under normal laboratory conditions, samples of purified alkenes were allowed to stand at room temperature in contact with air. Periodically, portions were withdrawn and analyzed for peroxides. The results of these analyses are given in figures 3 and 4. The great difference in rates of peroxide formation in the two compounds may be seen in the comparison given in figure 3.

3-Methyl-2-Pentene (cis and trans)

The two geometric isomers of 3-methyl-2-pentene were prepared by dehydration of 3-methyl-3-pentanol, which was formed by action of ethylmagnesium chloride on 2-butanone.

To 53.8 moles of ethylmagnesium chloride was added 55.8 moles of 2-butanone in 5 liters of ether. The yield of carbinol (b.p. 75° to 80° C at 142 mm Hg) was 40 percent of the theoretical. The carbinol was dehydrated with β-naphthalene sulfonic acid to yield a mixture of olefins. A charge of 2240 ml of the washed, dried olefin mixture was fractionated in Column 2, which gave 240 ml of the lower-boiling (cis?) and 960 ml of the higher-boiling (trans?) isomers. Physical constants were measured on the best samples of each isomer. Analysis of the distillation curve showed that the original mixture contained 26 percent (by volume) of the lower-boiling and 74 percent of the higher-boiling forms.

The identification of these two olefins as cis and trans 3-methyl-2-pentene, rather than the isomers 3-methyl-2-pentene and 2-ethyl-1-butene, is based primarily on mass spectrometer studies. The two patterns formed by analysis of the compounds obtained are very nearly identical. No third component was isolated from the distillation, although it is probable that one was present in small quantity.

Investigation of Diisobutylene

It was necessary to isolate large quantities of the two diisobutylenes, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, in order to provide samples for engine studies and for the syntheses of 4,4-

dimethyl-2-pentanone and trimethylacetic acid by oxidation. For this purpose, a considerable quantity (450 liters) of the commercial mixture was systematically fractionated.

The original material was separated into five "cuts" or concentrates by fractionation in Column 11. Because of the limited pot capacity, it was necessary to perform this operation in batches. Corresponding cuts from each batch were combined. The data on these distillations are summarized in table 4.

Cut A (forerun) comprised an azeotrope containing a small quantity of 2,4-4-trimethyl-1-pentene with butyl alcohol, along with other polar compounds. This cut was not extensively investigated.

Cut C (58 liters), the intermediate between cuts B and D, was refractionated in Column 11 to yield 34 liters of 2,4,4-trimethyl-1-pentene which was combined with cut B, 14 liters of intermediate which was not further investigated, and 9 liters of residue which was added to cut D. The augmented cuts B and D were then designated as B-1, and D-1, respectively.

Cut B-1 (298 liters) was found to be about 96.7 percent pure 2,4,4-trimethyl-1-pentene; its freezing point was -96.5° C. A 170-liter portion from the middle of this cut was refractionated in three runs and 72 liters of purified 2,4,4-trimethyl-1-pentene was obtained, comprising fractions with freezing points in the range -93.59° C to -93.55° C. Physical constants were measured on one of the fractions of -93.55° C material. These constants agree with those reported by Tongberg, Pickens, Fenske, and Whitmore (reference 36). This compound has been identified by ozonolysis by Whitmore and Church (reference 26).

Cut D-1 (95 liters), a concentrate of 2,4,4-trimethyl-2-pentene, was refractionated in two runs. From these distillations, there was obtained 49.3 liters of high purity 2,4,4-trimethyl-2-pentene, composed of fractions with freezing points from -106.62° to -106.58° C. A portion was refractionated in Column 1 for isolation of a sample for physical-constants measurements. This compound was also characterized by Tongberg and others (reference 36), and identified by Whitmore and Church (reference 26).

The residue from distillation of cut D-1 was fractionated in Column 1. From this distillation there were obtained two concentrates, designated as D-2 and D-3.

Cut D-2 (745 ml, b.p. 106.8° C, n_D^{20} = 1.4149 to 1.4152, d^{20} = 0.7265) was probably an impure sample of 2,3,4-trimethyl-1-pentene. Kuykendall (reference 37) obtained the following properties for this compound: b.p. 106.7° to 107.7° C, n_D^{20} = 1.4146, d^{20} = 0.726.

Cut D-3 (804 ml, b.p. 108.0° C, n_D^{20} = 1.4162 to 1.4171, d^{20} = 0.733) was a complex mixture in which 2,3,3-trimethyl-1-pentene was the probable major component. This partial identification is made by a comparison of the physical properties of cut D-3 with those of the 2,3,3-trimethyl-1-pentene isolated from Shell Hot-Acid Polymer. (See next section.) Since only small quantities of these cuts (D-2 and D-3) were available, no extensive investigation was made on them.

Cut E was combined with the residue from the preliminary fractionations. The combined material (27 liters) was fractionated in Column 11, and yielded 3.8 liters of 3,4,4-trimethyl-2-pentene (cis and trans) (b.p. 112.0° to 112.6° C, n_D^{20} = 1.4235, d^{20} = 0.739) and 4.5 liters of 2,3,4-trimethyl-2-pentene (b.p. 116.1° to 116.2° C, n_D^{20} = 1.4275, d^{20} = 0.7428). These two compounds were identified by comparison of their physical properties with those of pure 3,4,4-trimethyl-2-pentene and 2,3,4-trimethyl-2-pentene. The pure compounds were obtained by the distillation analysis of Shell Hot-Acid Polymer and by dimethyl-zinc synthesis. Part of this sample of 3,4,4-trimethyl-2-pentene was oxidized to pinacolone. The entire sample of 2,3,4-trimethyl-2-pentene was hydrogenated to 2,3,4-trimethylpentane (b.p. 113.41° C, n_D^{20} = 1.4038 to 1.4040).

An approximate analysis of the original diisobutylene (gas-free basis) was made by examination of the distillation curves. This mixture was found to contain:

2,4,4-trimethyl-1-pentene	70.0 percent (by volume)
2,4,4-trimethyl-2-pentene	18.7
3,4,4-trimethyl-2-pentene	4.6
2,3,4-trimethyl-2-pentene	3.7
2,3,4-trimethyl-1-pentene } 2,3,3-trimethyl-1-pentene }	1.0
Other octene(s)	
Polar compounds	2.0

Investigation of Hot-Acid Polymer (Shell Oil Company)

(Unfinished project)

The investigation of Hot-Acid Polymer was undertaken to isolate and purify some of the major constituents. The general method of operation was the same as that used in the investigation of diisobutylenes, but for this work more efficient, higher-capacity stills (12, 13, 14, and 16) were available.

A total of 1041 liters of crude polymer was subjected to preliminary fractionation in five batches. Corresponding cuts from the several

batches were combined. In this way, the polymer was divided into five portions. The data on these fractionations are given in table 5.

Cut A, which contained butanol-2 was not further investigated. Likewise, the residue has not been studied.

By refractionation of cut B, there were isolated the following materials:

Cut B-1 - 103 liters, 2,4,4-trimethyl-1-pentene, b.p. 101.1° to 101.3° C/755 mm Hg, n_D^{20} = 1.4084 to 1.4086

Cut B-2 - 9.5 liters, a mixture of close-boiling olefins, b.p. 107.0° to 107.1° C/756 mm Hg, n_D^{20} = 1.4144 to 1.4146

Cut B-3 - 8.0 liters, 2,3,3-trimethyl-1-pentene, b.p. 108.0° to 108.1° C/753 mm Hg, n_D^{20} = 1.4173 to 1.4175

A considerable amount of material between B-1 and B-2 has not yet been investigated. This intermediate contains 2,4,4-trimethyl-2-pentene, associated with at least two other compounds with boiling points near 105° C.

Cut B-2 was refractionated. The presence of several compounds is indicated by the distillation data. A sample of B-2 was hydrogenated. Analysis of the product showed the presence of about 30 percent 2,2,3- and 70 percent 2,3,4-trimethylpentanes.

Cut B-3 was refractionated for isolation of a sample suitable for physical-constants measurements. A sample of this material was oxidized to methyl t-amyl ketone (b.p. 130.8° to 131.2° C, n_D^{20} = 1.4201), of which the 2,4-dinitrophenylhydrozone melted at 111° to 112° C. Hydrogenation of a sample yielded 2,3,3-trimethylpentane (b.p. 114.5° C, n_D^{20} = 1.4073).

Purification by refractionation of cut C gave 100 liters of purified 3,4,4-trimethyl-2-pentene (b.p. 111.7° to 111.9°C/751 mm Hg; n_D^{20} = 1.4231 to 1.4233). The best sample from this fraction was used to determine the physical constants. The presence of cis and trans isomers, which were only partially separated by the fractionation, causes the wide boiling range. It is thought that the sample reserved for physical-constants measurements contained more of the higher-boiling (trans?) isomer than of the lower-boiling compound. (Oxidation of this compound by sodium dichromate produced pinacolone in 30 percent yield.)

Redistillation of 120 liters of cut D gave 45 liters of 2,3,4-trimethyl-2-pentene (b.p. 116.0° C/754 mm Hg, n_D^{20} = 1.4271 to 1.4272).

National Bureau of Standards,
Washington, D. C., July 15, 1946

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TABLE 1.- DISTILLATION COLUMNS

Still	Type	Size (cm)	Packing	Pot capacity (ml)
1	Total reflux, intermittent take-off	600 by 4.0	3/16-inch pyrex helices	5000
2	-------do--------	(see text)		5000
3	Total reflux, variable take-off	150 by 2.0	3/16-inch glass helices	200 to 5000
4	-------do--------	150 by 2.0	3/32-inch stainless-steel helices from 0.010-inch wire	Do.
5	-------do--------	150 by 2.2	----------do----------	Do.
6	-------do--------	150 by 2.2	3/16-inch glass helices	Do.
7	-------do--------	125 by 2.2	----------do----------	Do.
8	-------do--------	70 by 1.1	1/16-inch nichrome helices from 0.010-inch wire	Do. Do.
9	-------do--------	40 by 1.0	3/64-inch stainless-steel helices from 0.0065-inch wire	250
10	-------do--------	243 by 5.1	Sash chain	40,000
11	-------do--------	600 by 5.1	90 centimeter 1/2-inch carbon raschig rings, then 510 centimeter 3/32-inch stainless-steel helices from 0.010-inch wire	75,000
12 & 13	-------do--------	1600 by 10.2	3/8-inch porcelain raschig rings	227,000
14	-------do--------	1600 by 5.1	50 centimeter 3/8-inch porcelain raschig rings, followed by 1550 centimeter 3/32-inch stainless-steel helices from 0.010 inch wire	227,000
16	-------do--------	1600 by 2.7	----------do----------	113,000
17	Podbielniak Hypercal	127 by 0.8	Heli-grid	250 to 5000
18	-------do--------	127 by 2.5	----------do----------	250 to 5000
19 & 20	-------do--------	250 by 2.5	----------do----------	250 to 5000
21	Dephlegmator controlled take-off	120 by 3.5	3/16-inch glass helices	22,000
22 to 25	Total reflux, variable take-off	183 by 2.5	3/32-inch stainless-steel helices from 0.010-inch wire	500 to 5000
26 to 27	-------do--------	183 by 2.5	3/16-inch glass helices	500 to 5000

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TABLE 2 .- PHYSICAL PROPERTIES OF COMPOUND PREPARED

[Values are believed to be precise to within a few units in the last place given.]

Compound	Freezing point in air (°C)	Boiling point at 760 mm Hg (°C)	dtB/dP at 760 mm Hg (°C/mm Hg)	ΔT: 20-80% (°C)	Density at 20°C (g/ml)	Density at 25°C (g/ml)	dD/dt 20-25°C (g/ml/°C)	Refractive index, n_D at 20°C	Refractive index, n_D at 25°C	dn/dt 20-25°C (n_D/°C)	Date first preparation completed
n-Pentane	-129.75	36.075	0.0388	0.006	0.62619	0.62133	-0.00097	1.35746	1.35480	-0.00053	January 1941
2-Methylbutane	-159.9	27.853	0.0386	0.006	0.61963	0.61455	-0.00102	1.35357	1.35067	-0.00058	December 1939
2,2-Dimethylpropane	-16.60	9.503	[d] 0.0361	0.017	------	------	------	------	------	------	April 1942
2-Methylpentane	-153.73	60.266	0.0418	0.002	0.65285	0.64648	-0.00088	1.37141	1.36856	-0.00055	January 1944
3-Methylpentane	[a] nf	63.265	0.0426	0.005	0.66438	0.65972	-0.00093	1.37646	1.37376	-0.00054	November 1940
2,2-Dimethylbutane	[b] -100.06	49.733	[b] 0.0407	0.004	0.64923	0.64422	-0.00100	1.36873	1.36585	-0.00058	May 1941
2,3-Dimethylpentane	nf	89.787	0.0450	0.002	0.69510	0.69090	-0.00084	1.39193	1.38950	-0.00049	August 1941
2,4-Dimethylpentane	-119.86	80.508	0.0431	0.003	0.67315	0.66879	-0.00087	1.38165	1.37903	-0.00053	May 1941
3-Methyl-3-ethylpentane	-114.94(MP)	115.653	0.0477	0.004	0.71931	0.71523	-0.00082	1.40403	1.40173	-0.00046	January 1941
2,2,3-Trimethylpentane	[c] -112.32	109.847	0.0487	0.002	0.71608	0.71201	-0.00081	1.40280	1.40052	-0.00046	August 1941
2,3,3-Trimethylpentane	-101.6	114.767	0.0491	0.004	0.72621	0.72229	-0.00079	1.40757	1.40521	-0.00047	October 1940
2,2,4-Trimethylhexane	-123.4(MP)	126.54	0.0503	0.011	0.71555	0.71178	-0.00076	1.40328	1.40095	-0.00047	October 1942
2,2,5-Trimethylhexane	-105.89(MP)	124.092	0.0485	0.005	0.70711	0.70313	-0.00080	1.39956	1.39724	-0.00047	July 1941
2,3,5-Trimethylhexane	-127.9	131.37	0.0492	0.021	0.72191	0.71792	-0.00080	1.40601	1.40365	-0.00047	June 1941
2,3-Dimethyl-3-ethylpentane	-99.30	133.834	0.0506	0.002	0.73478	0.73100	-0.00076	1.41227	1.41014	-0.00043	September 1941
2,4-Dimethyl-3-ethylpentane	-122.4	136.717	0.0504	0.009	0.73793	0.73415	-0.00076	1.41371	1.41146	-0.00045	November 1940
2,2,3,3-Tetramethylpentane	-10.04	140.264	0.0512	0.009	0.75676	0.75300	-0.00075	[e] 1.42365	[c] 1.42146	-0.00044	June 1941
2,2,3,4-Tetramethylpentane	-122.2	133.010	0.0501	0.007	0.73915	0.73537	-0.00076	1.41462	1.41242	-0.00044	July 1941
2,3,3,4-Tetramethylpentane	-102.14	141.544	0.0514	0.002	0.75489	0.75112	-0.00075	1.42222	1.42005	-0.00043	November 1941
2,2,3,3-Tetramethylhexane	-54.03	160.310	0.0538	0.005	0.76450	0.76080	-0.00074	1.42812	1.42606	-0.00041	November 1945
2,2,4,5-Tetramethylhexane	nf	147.875	0.0512	0.011	0.73542	0.73165	-0.00075	1.41321	1.41093	-0.00046	October 1945
2,2,5,5-Tetramethylhexane	-12.64	137.457	0.0500	0.004	0.71875	0.71480	-0.00079	1.40550	1.40315	-0.00047	August 1945
3,3,4,4-Tetramethylhexane	nd	170.0	0.046	0.57	0.7824	0.7789	-0.0007	1.4368	1.4346	-0.0004	August 1945
2,4-Dimethyl-3-isopropylpentane	-81.75	157.042	0.0544	0.012	0.75826	0.75460	-0.00073	1.42465	1.42246	-0.00044	March 1945
2,2,3,3,4-Pentamethylpentane	-36.49	166.05	0.0552	0.039	0.78009	0.77675	-0.00067	1.43606	1.43412	-0.00039	February 1942
2,2,3,4,4-Pentamethylpentane	-38.81	159.29	0.0537	0.052	0.76702	0.76362	-0.00068	1.43069	1.42868	-0.00040	October 1944
3-Methyl-2-pentene (L.B.I.)	-135.4	67.8	0.039	0.16	0.6942	0.6898	-0.00088	1.4016	1.3989	-0.00054	September 1942
3-Methyl-2-pentene (H.B.I.)	-138.5	70.5	0.037	0.17	0.6986	0.6942	-0.00088	1.4045	1.4018	-0.00054	September 1942
2,3-Dimethyl-1-butene	nf	55.641	0.0429	0.002	0.67792	0.67312	-0.00096	1.39044	1.38745	-0.00060	February 1944
2,3-Dimethyl-2-butene	-74.30	73.206	0.0424	0.006	0.70795	0.70336	-0.00092	1.41221	1.40944	-0.00055	October 1943
2,3,3-Trimethyl-1-pentene	nf	108.4	0.05	0.27	0.7352	0.7308	-0.00088	1.4174	1.4151	-0.00047	April 1945
2,4,4-Trimethyl-1-pentene	-93.56	101.437	0.0459	0.003	0.71500	0.71076	-0.00085	1.40856	1.40601	-0.00051	June 1943
2,3,4-Trimethyl-2-pentene	-113.38	116.26	0.0493	0.082	0.74342	0.73914	-0.00086	1.42736	1.42500	-0.00047	July 1943
2,4,4-Trimethyl-2-pentene	-106.51	104.914	0.0470	0.007	0.72124	0.71700	-0.00085	1.41602	1.41350	-0.00050	July 1943
3,4,4-Trimethyl-2-pentene (CT)	nf	112.3	0.05	0.42	0.7392	0.7350	-0.00083	1.4235	1.4210	-0.00050	July 1942
2,3,5-Trimethyl-2-hexene	------	73 (100 mm) 58 (50 mm)	-----	----	------	------	------	1.4299	------	------	October 1940
2,3,3,4-Tetramethyl-1-pentene	-------	133.2	0.051	0.30	0.7587	0.7549	-0.00076	1.4306	1.4283	-0.00046	November 1941
4-Methyl-3-isopropyl-2-pentene	nf	138.0 96 (200 mm)	0.046	0.88	0.7627	0.7591	-0.00072	1.4353	1.4328	-0.00049	August 1940
2,4-Dimethyl-3-ethyl-2-pentene	-83.5	129.97 88 (200 mm)	0.0459	0.073	0.74392	0.73997	-0.00079	1.42346	1.42112	-0.00047	August 1940
4,4-Dimethyl-3-ethyl-2-pentene (CT)	nf	134.03 84 (150 mm)	0.0466	0.060	0.7561	0.7521	-0.00079	1.4309	1.4285	-0.00049	August 1941
3,3-Dimethyl-2-isopropyl-1-butene	-78.2	122.21	0.0502	0.037	0.73614	0.73228	-0.00077	1.41669	1.41431	-0.00048	October 1941
2,3,5,5-Tetramethyl-1-hexene	nf	142.8	0.049	0.185	0.7448	0.7407	-0.00082	1.4226	1.4203	-0.00046	July 1945
2,3,5,5-Tetramethyl-2-hexene	nf	156.2	0.049	0.34	0.7659	0.7622	-0.00074	1.4374	1.4351	-0.00048	July 1945
2,2,5,5-Tetramethyl-3-hexene (CT)	-4.75	125.013	0.0480	0.010	0.71673	0.71223	-0.00090	1.41148	1.40890	-0.00052	July 1945
2,3,3,4,4-Pentamethyl-1-pentene	+38.66	158.75	0.054	0.039							September 1944
2,4-Dimethyl-3-isopropyl-2-pentene	-55.3	152.4	0.051	0.34	0.7680	0.7637	-0.00084	1.4377	1.4353	-0.00047	February 1945
3,3-Dimethyl-2-t-butyl-1-butene	-62.9	150.3	0.052	0.22	0.7710	0.7671	-0.00077	1.4359	1.4339	-0.00040	April 1944
2,3-Dimethyl-1,3-butadiene	-----	68.5-71.5	-----	----	0.7267	-----	------	1.4388	-----	------	May 1940
3-Methyl-3-pentanol	-23.6	122.4 80 (150 mm)	0.039	0.30	0.8286	0.8243	-0.00086	1.4186	1.4163	-0.00046	August 1941
2,3-Dimethyl-2-butanol	-10.4	118.4 76 (150 mm)	0.037	0.042	0.8236	0.8193	-0.00086	1.4170	1.4148	-0.00044	October 1943
3,5,5-Trimethyl-3-hexanol	----	71 (25 mm)	----	----	0.8350	------	------	1.4352	-----	------	July 1941
2,4-Dimethyl-3-ethyl-3-pentanol	-16.0	177.9 96 (50 mm)	0.048	0.70	0.8588	0.8543	-0.00089	1.4439	1.4416	-0.00045	July 1940
2,2-Dimethyl-3-ethyl-3-pentanol	-19.0	174 94 (50 mm)	0.05	1.55	0.8572	0.8526	-0.00091	1.4429	1.4405	-0.00047	July 1941
2,2,3,4-Tetramethyl-3-pentanol	+12.8	173.4 94 (50 mm)	0.047	0.83	0.8565	0.8523	-0.00085	1.4405	1.4428	-0.00047	July 1941
2,4-Dimethyl-3-isopropyl-3-pentanol	-14.7	194.5 109 (50 mm)	0.051	0.77	0.8632	0.8591 [e]	-0.00083	1.4480	1.4458	-0.00043	December 1944
2,2,3,4,4-Pentamethyl-3-pentanol	+42.1	194.4	0.059	0.38							February 1944
2,2,4-Trimethyl-3-pentanone	-29.02	136.190	0.0485	0.007	0.80654	0.80229	-0.00085	1.40596	1.40389	-0.00042	June 1941
2,2,4,4-Tetramethyl-3-pentanone	-25.24	153.521	0.0521	0.010	0.82409	0.82027	-0.00076	1.41927	1.41712	-0.00043	January 1944
Ethyl Trimethylacetate	-89.55	118.35	0.0458	0.061	0.85467	0.84952	-0.00103	1.39061	1.38821	-0.00048	June 1941
3-Chloro-2,2,3-Trimethylpentane	-17.9	87 (62 mm)	-----	----	0.9066	------	------	1.4441	------	------	July 1942
2-Chloro-2,3,3-Trimethylpentane	+10.6	82 (57 mm)			0.9105	0.9065	-0.00080	1.4457	1.4436	-0.00042	June 1945
2-Chloro-2,3,4-Trimethylpentane) 3-Chloro-2,3,4-Trimethylpentane)	---	82.86 (60 mm)	-----	----	0.888	------	------	1.438	------	------	August 1942
1-Chloro-2,3-Dimethyl-2-butene	---	32 (45 mm)	-----	----	-----	------	------	------	------	------	May 1940

[a] Symbols: nf, material became very viscous or glassy without freezing to a crystalline solid; nd, material considered too impure to warrant determination of freezing point; MP, melting point; L.B.I., lower-boiling geometric isomer; H.B.I., higher-boiling geometric isomer; CT, mixture of geometric isomers.

[b] See reference 5.

[c] See reference 4.

[d] Calculated from data given in reference 13.

[e] The refractive indices of 2,2,3,3-tetramethylpentane were determined by Mr. Leroy Tilton on the Optical Instruments Section of this Bureau.

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TABLE 3.- HYDROCARBONS ISOLATED FROM "BUTENE ALKYLATE"

Hydrocarbon	Boiling point at 760 mm Hg (°C, Cottrell)	Refractive index, n_D^{20}	Volume isolated (ml)	Volume (percent) of total Butene Alkylate[1]
Isopentane	27.9	1.3531 to 1.3533	728	0.97
2,3-Dimethylbutane	57.9	1.3749 to 1.3752	2,213	2.97
2-Methylpentane	60.2	1.3714 to 1.3716	224	.30
3-Methylpentane	63.2	1.3761 to 1.3763	224	.30
2,4-Dimethylpentane	80.5	1.3815 to 1.3820	2,610	3.44
2,3-Dimethylpentane	89.9	1.3912 to 1.3920	1,034	1.37
2,2,4-Trimethylpentane	99.3	1.3912 to 1.3915	11,727	15.48

[1]The data in this column represent the amount isolated having the properties shown. It does not constitute an exact analysis of the crude.

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TABLE 4.- DIVISION OF DIISOBUTYLENE BY PRELIMINARY FRACTIONATION

Cut	Volume (liters)	Volume percent of total	Boiling range[1] (°C)	Refractive index, n_D^{20}	Major constituents
A	14	3.1	Below 101.5	1.392 to 1.4082	2,4,4-Trimethyl-1-pentene, butyl alcohol, other polar compounds
B	264	57.8	101.5 to 102	1.4084 to 1.4088	2,4,4-Trimethyl-1-pentene
C	58	12.6	102 to 104	1.4094 to 1.4127	Intermediate, mixture of 2,4,4-trimethyl-1- and 2-pentenes
D	85	18.7	104 to 107	1.4150 to 1.4160	2,4,4-Trimethyl-2-pentene, and small quantities of 2,3,4- and 2,3,3-trimethyl-1-pentenes, and other octenes
E	27 (includes residue)	6.0 (includes residue)	107 to 117	1.4207 to 1.4238	2,3,4-Trimethyl- and 3,4,4-trimethyl-2-pentenes
Gas and loss		1.8			

[1]Cottrell boiling-point measurements on first and last fractions.

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TABLE 5.- DIVISION OF HOT ACID POLYMER BY PRELIMINARY FRACTIONATION

Cut	Volume (liters)	Volume percent of total	Boiling range[1] (°C)	Refractive index, n_D^{20}	Remarks
A	38	3.7	< 101	< 1.408	Forerun
B	200	24.9	101.0 to 101.7	1.408 to 1.420	2,4,4-Trimethyl-1-pentene 2,3,4-Trimethyl-1-pentene 2,3,3-Trimethyl-1-pentene
C	246	23.6	110.1 to 112.0	1.421 to 1.423	3,4,4-Trimethyl-2-pentene
D	169	16.2	113.0 to 116.0	1.425 to 1.426	2,3,4-Trimethyl-2-pentene
E	208	20.0	> 116	----------	Residue
Gas and loss[2]		11.6			

[1]Cottrell boiling-point measurements on first and last fractions.
[2]A preliminary distillation of 2 liters indicated over 10 percent gas.

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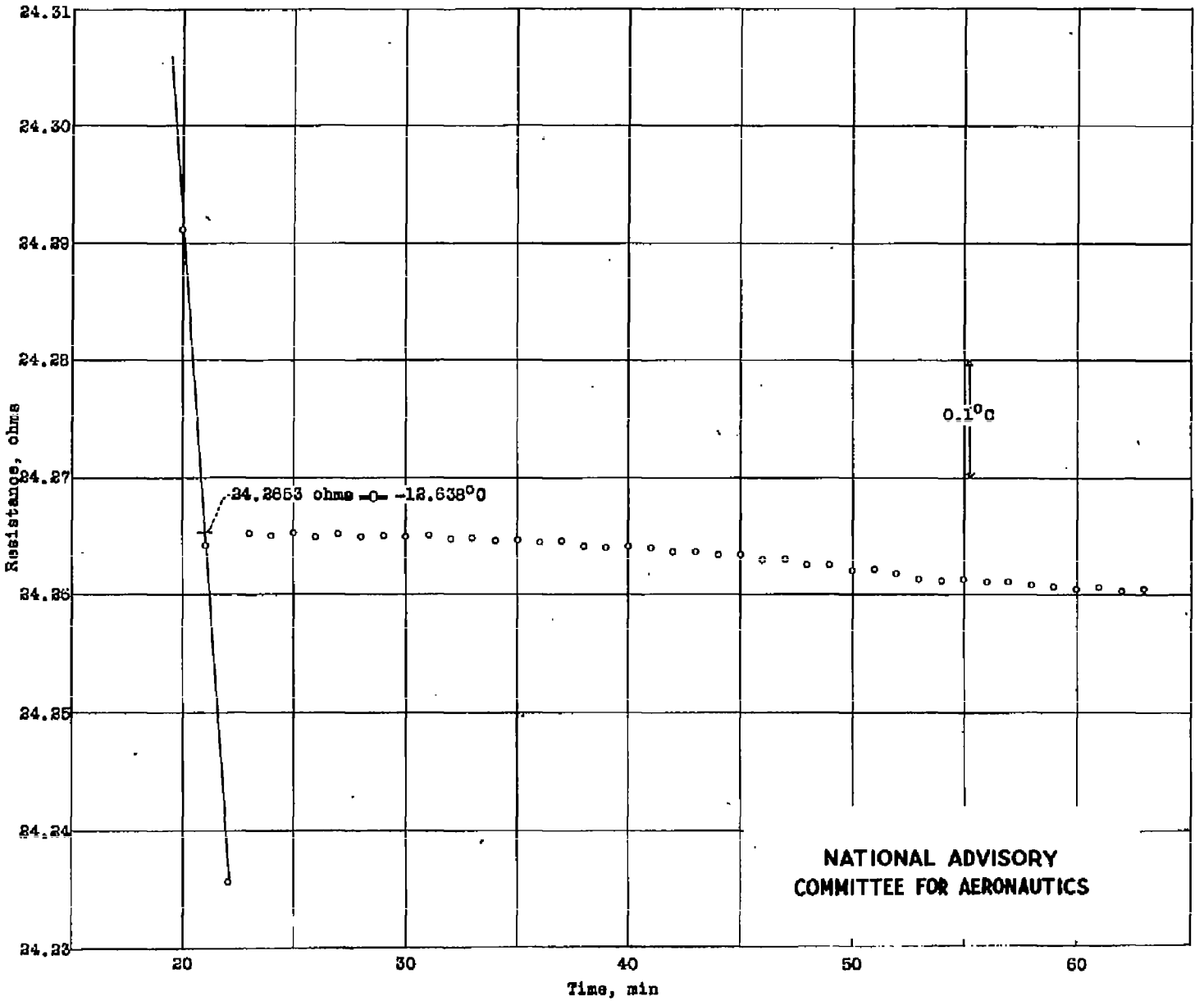

Figure 1.- Freezing point of 2,2,5,5-tetramethylhexane.

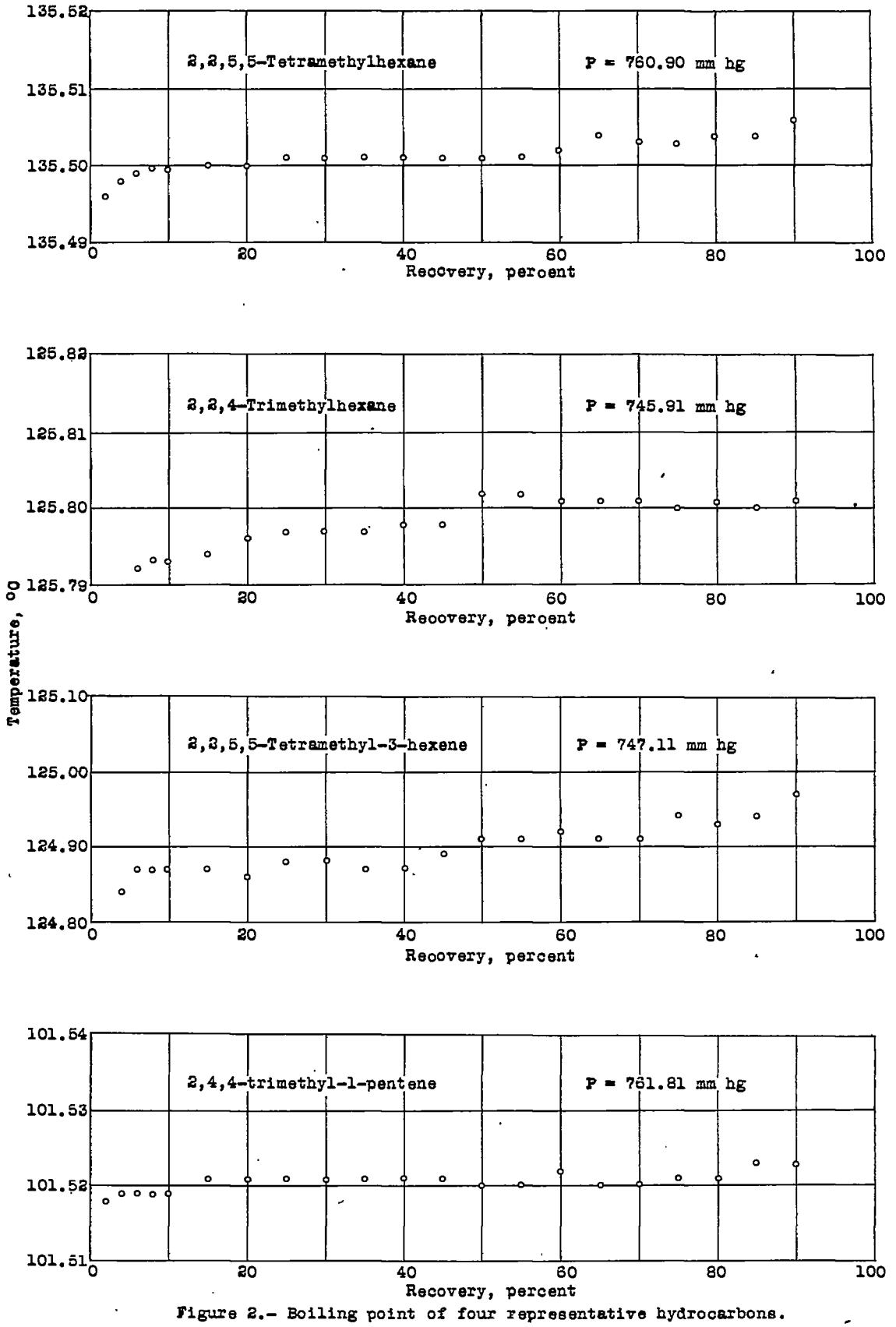

Figure 2.- Boiling point of four representative hydrocarbons.

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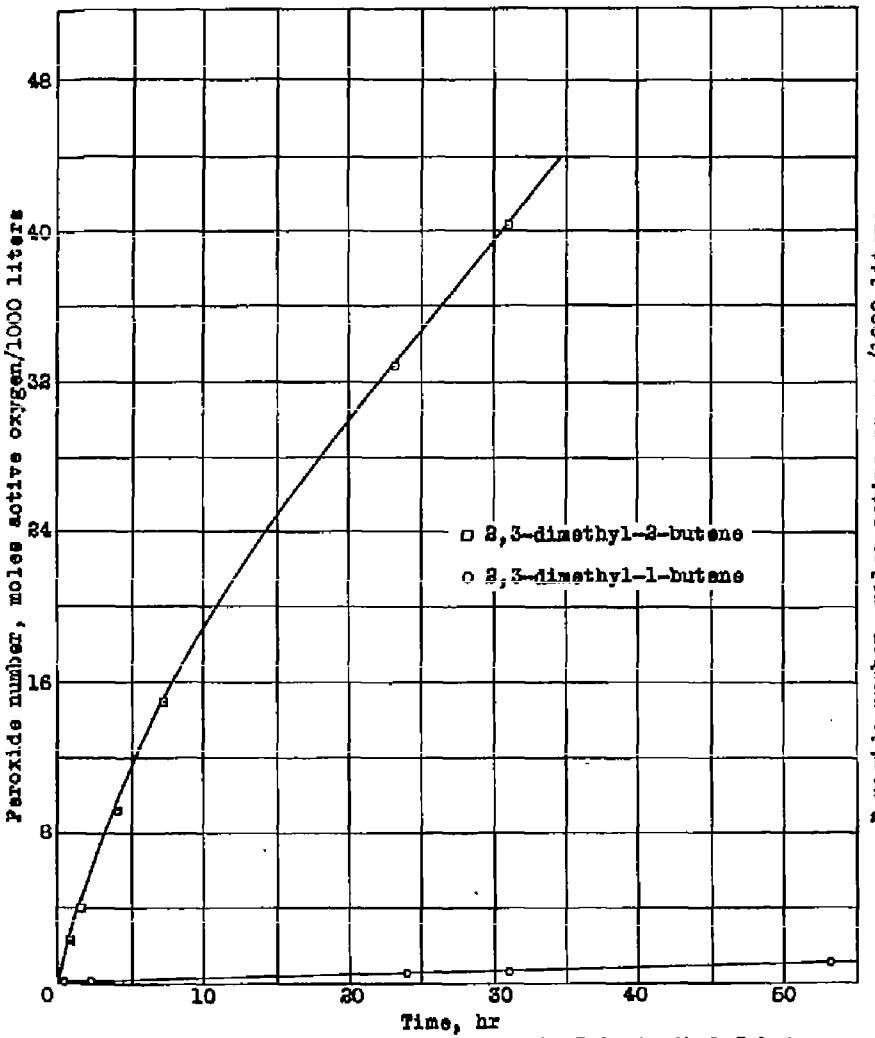

Figure 3.- Rates of peroxide formation in 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene.

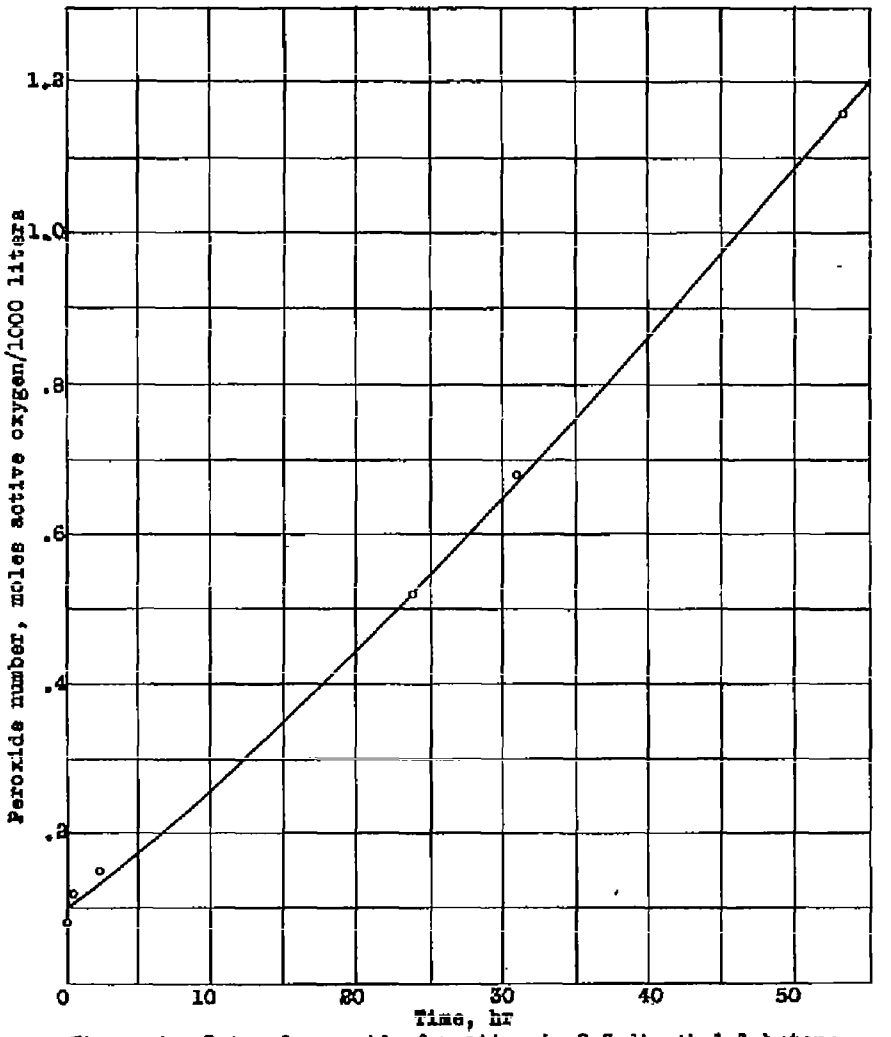

Figure 4.- Rate of peroxide formation in 2,3-dimethyl-1-butene.

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ABSTRACT

Description is given of methods of preparation and purification of numerous pentenes, hexanes, heptenes, octanes, nonanes, decanes, octenes, hexenes, nonenes, and decenes, a variety of alcohols, ketones and esters, and alkyl halides. Physical constants measured included freezing point, boiling point and its variation with pressure, refractive index and density, and their variations with temperature.

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