methyl-2-*n*-butyl-1-pentene (dehydration from the methyl group), and a trace of 2,2-dimethyl-4-methyl-3-octene (dehydration from the neopentyl group).

3. The sluggishness of the neopentyl group in giving hydrogen for a dehydration reaction is further confirmed and emphasized.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Polymerization of Olefins. V.[1] The Isomers in Triisobutylene

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The Isomers in Triisobutylene

The preparation of "triisobutylene" was first described in 1879 by Butlerow,[3] who obtained an oil boiling at 177.5–179° by dissolving isobutylene in a cold mixture of five parts of sulfuric acid and one of water. The structures of the compounds in this oil have since been investigated.[4,5,6] Work in this Laboratory on polymerization of olefins cast doubt on some of the earlier work and made necessary a complete study of the problem.

The fractionation of the triisobutylenes was undertaken in an attempt to separate the various isomers because the structure and the ratio of these olefins are important in the work on polymerization in progress in this Laboratory since 1932. We used the highly efficient large scale fractionating columns developed during the work on the fractionation and composition of gasoline in the Petroleum Refining Laboratory.[7]

After repeated fractionations of crude triisobutylene about 90% boiled 177–179° and about 10% 183–185°. Calculations[8] show that a column of perhaps five hundred theoretical plates would be needed to separate sharply the low boiling fractions. Actually a column of 75 plates was used first. This was followed by repeated refractionation through a smaller column having 90–100 plates. Cooling curves on the various fractions indicated no pure isomers.

The degree of separation was followed during the distillations by careful determination of the index of refraction, Cottrell boiling point, and density. The Kauri-butanol number[9] was also determined. Examination of these constants for the final fractions shows that the triisobutylene had been divided by distillation into three parts. A summary of the physical constants is given in Table I. These results summarize many distillations carried out from 1933 to date.

TABLE I

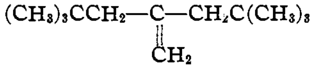
PHYSICAL CONSTANTS OF TRIISOBUTYLENE FRACTIONS

Group	A	B	C
% of total triisobutylene	75	15	10
Cottrell b. p. °C. at 760 mm.	177.7	179.0	183–185
n^{20}_D	1.4300	1.4318	1.4415
d^{20}	0.7587	0.7597	0.7765
K. b. number	28.5	28.5	36.5

The hundreds of fractions making up Group A had a constant index of refraction. Repeated fractionation of this material through a 100-plate column gave no further separation. Extraction with methyl alcohol and with aniline also did not alter the composition. Likewise equilibrium melting gave no change.

Six possible triisobutylenes have been formulated.[10] Ozonolysis of the Group A material gave trimethylacetaldehyde, methyl neopentyl ketone, formaldehyde, dineopentyl ketone, and the related acids, thus proving the fractions to contain 2,2,4,6,6-pentamethyl-3-heptene (I) and 2-neopentyl-4,4-dimethyl-1-pentene, 1,1-dineopentylethylene (II).

$$(CH_3)_3CCH{=}C(CH_3)CH_2C(CH_3)_3 \qquad (I)$$



$$(CH_3)_3CCH_2{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}CH_2C(CH_3)_3 \qquad (II)^6$$

The Group B material gave a larger yield of fragments from I than did the Group A fractions.

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(1) Whitmore and Mixon, THIS JOURNAL, **63**, 1460 (1941).

(2) Submitted in partial fulfillment for the Ph.D. degree.

(3) Butlerow, *Ber.*, **12**, 1482 (1879).

(4) Lebedev and Kobliansky, *ibid.*, **63B**, 103, 1432 (1930).

(5) McCubbin, THIS JOURNAL, **53**, 356 (1931).

(6) Bartlett, Fraser and Woodward, *ibid.*, **63**, 495 (1941).

(7) Fenske and co-workers, *Ind. Eng. Chem.*, **24**, 408 (1932); **26**, 1169 (1934); **29**, 70, 571 (1937).

(8) Rose, THIS JOURNAL, **62**, 793 (1940).

(9) Baldeschwieler, Troeller and Morgan, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 374 (1935); Beard, Ship and Spelhouse, *ibid.*, **5**, 307 (1933).

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

This indicated that the lower boiling material is probably made up of II and the lower boiling geometric isomer of I, and that the higher boiling material is largely the higher boiling geometric isomer of I with a smaller amount of II.

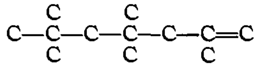
No indication of the presence of 2,4,4-trimethyl-3-*t*-butyl-2-pentene (III) was found as reported by earlier workers.[4,5] Dineopentylacetic acid and methylneopentyl-*t*-butylacetic acid separated from the higher fractions of the ozonolysis products, but these have been shown[11] to be related to I and II and not to indicate the presence of III. Thus III is *not* one of the triisobutylenes.

The identification of the fragments from the ozonolysis was made easy because most of the needed derivatives were available from earlier work in this Laboratory. The choice of a solvent for ozonolysis presented some difficulty. In most ozonolyses in this Laboratory the low boiling saturated hydrocarbon (b. p. 0–30°) supplied by the Viking Corporation of Charleston, West Virginia, has proven satisfactory, but in the present work two rather unexpected troubles developed. The dineopentylethylene (II) was ozonized very slowly and the ozonides crystallized out, tending to stop up the tube. Ozonization in carbon tetrachloride yielded decomposition products that were saturated with hydrogen chloride. The use of glacial acetic acid proved satisfactory in the preparation of the ozonides. Apparently it gave little or no isomerizing effect on the olefin mixtures.[12]

Ozonolysis of carefully selected fractions from the high boiling Group C gave a nine-carbon acid, an eleven-carbon ketone, acetone, formaldehyde, an eight-carbon tertiary alcohol, methyl neopentyl ketone, and trimethylacetic acid. The eleven-carbon ketone, on chromic acid oxidation, gave the nine-carbon acid which proved to be dimethylneopentylacetic acid. This was confirmed by converting it to 2-amino-2,4,4-trimethylpentane by the Curtius reaction using the method of Naegeli and Lendorff.[13] The amine was also synthesized. The eleven-carbon ketone failed to give the haloform reaction; however, this was shown not to rule out the methyl ketone structure by reaction with phenylmagnesium bromide, dehydrating the resulting alcohol, and ozonizing the olefins to give acetophenone. Thus the ketone was 4,4,6,6-tetramethyl-2-heptanone.

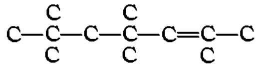
The eight-carbon alcohol on dehydration gave diisobutylene,[14] thus indicating it to be dimethylneopentylcarbinol. Synthesis of the alcohol by the addition of methyl neopentyl ketone to methylmagnesium chloride confirmed this. Such a compound could result from a side reaction such as depolymerization followed by hydration. The presence of methyl neopentyl ketone and trimethylacetic acid gave added evidence that this had occurred. It is of interest to note that in some of the runs on the same material no trace of these compounds could be detected.

The ozonolysis results show that the higher boiling triisobutylenes of Group C are 2,4,4,6,6-pentamethyl-1-heptene (IV) and 2,4,4,6,6-pentamethyl-2-heptene (V) having the carbon skeletons



$$C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{C}{=}C$$

(IV)



$$C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{C}{C}}{-}C{=}\underset{C}{C}{-}C$$

(V)

These two isomers are of special interest in their relationship to the high molecular weight isobutylene polymers.[15]

No trace of hexamethylacetone could be detected, thus eliminating III as a possible isomer in the triisobutylenes.[4,5]

We wish to thank D. E. Badertscher, N. H. Hale, K. C. Laughlin, A. R. Lux, C. S. Miner, Jr., and R. E. Meyer for help in the many distillations.

Discussion

The formation of the compounds I, II, IV and V illustrates the complexity of the polymerization process even when so simple an olefin as isobutylene and its related alcohol are involved. Many equilibria and successive and simultaneous reactions are involved. The interpretations

$$(CH_3)_2C{=}CH\boxed{H + HO_3SO}C(CH_3)_3 \longrightarrow H_2SO_4 + (CH_3)_2C{=}CH{-}C(CH_3)_3$$

and

$$CH_2{=}C(CH_3)CH_2\boxed{H + HO_3SO}C(CH_3)_3 \longrightarrow H_2SO_4 + CH_2{=}C(CH_3){-}C(CH_3)$$

often used to explain the dimers of isobutylene are no more adequate than would be

$$Na\boxed{OH + H}Cl \longrightarrow H_2O + NaCl$$

and

$$C_2H_5\boxed{OH + H}Cl \longrightarrow H_2O + C_2H_5Cl$$

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(11) Whitmore and co-workers, THIS JOURNAL, **56,** 1128, 1397 (1934).

(12) *Cf.* Laughlin and others, *ibid.*, **56,** 1395 (1934).

(13) Naegeli and Lendorff, *Helv. Chim. Acta,* **15,** 49 (1932).

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

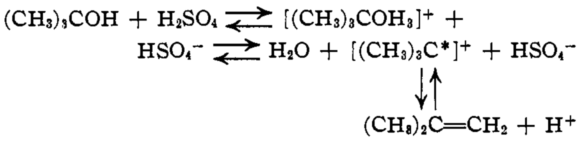
(15) Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *ibid.*, **62,** 276 (1940).

In the case of the base we know that *ionization* precedes reaction whereas with the alcohol the first step is *addition* to form an oxonium salt.

In polymerization in the presence of an acid catalyst we regard the alkyl acid sulfate or other ester-like compound or complex as serving merely as a source and reservoir for the corresponding olefin and electronically deficient alkyl group.[16]

$$(CH_3)_2C{=}CH_2 + H_2SO_4 \rightleftharpoons (CH_3)_3C{-}OSO_3H \rightleftharpoons [(CH_3)_3C^*]^+ + HSO_4^-$$

The asterisk indicates a carbon with only six electrons. It is probably incorrect to think of the electronically deficient tertiary butyl group as an *ion*. Although it is sometimes referred to as a carbonium ion, it does not resemble ordinary -onium ions such as ammonium which have complete octets of electrons and a consequent high stability. It is perhaps better to picture the equilibria as

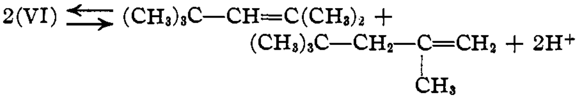


$$\begin{tikzcd}[column sep=small] (CH_3)_3COH + H_2SO_4 \arrow[r, shift left] & \arrow[l, shift left] [(CH_3)_3COH_2]^+ + HSO_4^- \arrow[r, shift left] & \arrow[l, shift left] H_2O + [(CH_3)_3C^*]^+ + HSO_4^- \arrow[d, shift left] \\ & & (CH_3)_2C{=}CH_2 + H^+ \arrow[u, shift left] \end{tikzcd}$$

The complete reversibility of all these processes in the case of the tertiary alcohols and related complexes, fragments and olefins explains the ready polymerization of such materials. Just as H$^+$ can add to isobutylene, so can the electronically deficient $(CH_3)_3C^*$ add to it to give

$$(CH_3)_3C{-}CH_2{-}C^*(CH_3)_2 \qquad \text{(VI)}$$

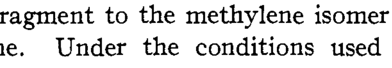
This can break down reversibly to give two molecules of isobutylene and H$^+$. The electronically deficient atom can be stabilized by the loss of a proton from an adjacent carbon to give a double bond



$$2(\text{VI}) \rightleftharpoons (CH_3)_3C{-}CH{=}C(CH_3)_2 + (CH_3)_3C{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + 2H^+$$

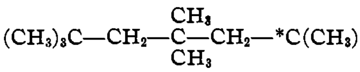
Thesea re the diisobutylenes. Again, the reversibility of the loss of the proton should be emphasized. Moreover it should be remembered that VI can be stabilized by union with an HSO_4^- ion to give an acid sulfate. In the case of a tertiary group of this kind such a process is readily reversible.

Just as the diisobutylenes can unite with H$^+$ to give VI they might be expected to unite with $(CH_3)_3C^*$. Apparently this cannot happen with the first diisobutylene, 2,4,4-trimethyl-2-pentene. Such an addition would put two tertiary butyl groups on one carbon and would give the triisobutylene isomer III which has not been found during years of search in this Laboratory nor by Bartlett.[6] Others of the multitude of possible changes are easier. Thus the second diisobutylene, 2,4,4-trimethyl-1-pentene, could add $(CH_3)_3C^*$ to form



$$(CH_3)_3C{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C^*}}{-}CH_2{-}C(CH_3)_3 \qquad \text{(VII)}$$

The fragment VII is much like VI in being stabilized by loss of a proton. If the proton comes from the adjacent methyl group the result is 1,1-dineopentylethylene (II). If it comes from one of the adjacent methylene groups the result is 2,2,4,6,6-pentamethyl-3-heptene (I). Since I and II form about 90% of the triisobutylenes it is evident that the chief trimerization reaction of isobutylene goes through the addition of a tertiary butyl fragment to the methylene isomer of diisobutylene. Under the conditions used the two diisobutylenes are in equilibrium. Another possibility is that the 8-carbon fragment VI can add to isobutylene to give



$$(CH_3)_3C{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}{}^*C(CH_3)_2 \qquad \text{(VIII)}$$

This can be stabilized by the loss of a proton from one of the adjacent methyl groups or from the adjacent methylene group to give, respectively, the 1- and 2-isomers of the 2,4,4,6,6-pentamethylheptenes, IV and V. Since these compounds form only about 10% of the triisobutylenes, there is evidently a relatively small chance of the addition of VI to isobutylene. This may be due to a variety of causes including the lessened reactivity of the larger fragment toward a double bond and its greater tendency to lose a proton to form the diisobutylenes as well as the small concentration of isobutylene available after the formation of VI and the diisobutylenes. The polymers[15] formed by more active catalysts such as boron fluoride apparently follow a chain reaction going through VIII by its addition to isobutylene. As will be shown in a later paper in this series VI can add to the methylene isomer of diisobutylene to give tetraisobutylenes.

In such a wealth of possible similar reactions the actual survival of individual compounds depends on factors not known at present. The assumption of activated complexes may be comforting although hardly clarifying.

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(16) Whitmore and co-workers, THIS JOURNAL (1932), and later.

Experimental

Materials.—The crude "triisobutylene" donated by Rohm and Haas Company was obtained as a by-product in the preparation of "diisobutylene" by the dehydration and polymerization of tertiary butyl alcohol. Most of the diisobutylene had been stripped from this leaving only the trimers and higher polymers. This crude material had $n^{20}\text{D}$ 1.4327–1.4332, was a dark straw color, and was neutral to litmus.

Description of Fractionating Columns.—The columns used in these fractionations of the triisobutylenes have been described over a period of years by Fenske and his co-workers.[7] The operating technique is beyond the aim of this paper, and only an abstract of the procedure is given. The following is only a general summary of the columns.

Aluminum Column.[17]—The column had an over-all diameter of 22.6 cm. (8.5 in.) and a packed section of 7.84 m. (26 ft.). The packing was no. 19 aluminum jack chain. The electrically heated still had a capacity of 190 liters (50 gal.). When tested under total reflux with a mixture of *n*-heptane and methylcyclohexane, the column had the equivalent of 70–75 theoretical plates and a maximum through-put of 44 liters per hour.

The 3/4 In. Brass Column.—This was made from 1.9 cm. (0.75 in.) inside diameter brass, 15.7 m. (52 ft.) long and was packed in alternate layers with 6 × 6 mm. glass rings and 6 × 6 mm. Lucero wire helices. The metal still had a capacity of 5 liters. The column had a theoretical plate value of 100. The reflux ratio was 60:1.

The Vacuum Iron Column.—This column had an inside diameter of 5.08 cm. (2 in.) and a packed section 3.96 m. (13 ft.) in length. Packing of 6-mm. six-turn no. 24 Lucero wire helices gave it a theoretical plate value of 10. The still was electrically heated and held a maximum charge of 10 liters. The take-off was constructed in such a way that the column could be operated continuously under a vacuum of 20 mm. which was obtained by a standard type water pump.

Fractional Distillation of the Triisobutylenes.—Since in preliminary distillations trouble had been encountered because of water and oxygen compounds, the crude triisobutylene was first distilled from sodium. A 190 liter (50 gal.) drum was wound with resistance wire, lagged, and fitted with a goose-neck connected to a large condenser. The drum was charged with 178 liters (46 gal.) of the crude triisobutylene and 454 g. (1 lb.) of sliced sodium. After standing overnight, another pound of sodium was added, and three hours later the drum was slowly heated and the distillation was begun. It was completed in eighteen hours and gave 10.4 liters of low boiling material, 157 liters of the triisobutylenes, and 9.4 liters of residue.

Of the distillate of triisobutylenes 138 liters was charged to the still of the aluminum column. Nitrogen was passed into the column in such a way as to exclude air. After giving the column ten hours to come to equilibrium, fractions were taken at the rate of about 1 liter per hour. The total time for the distillation was twelve days with the column running continuously. In all, 184 fractions were taken, accounting for 90% of the charge.

The amount of high boiling material in the crude triisobutylenes was determined separately. Crude triisobutylene, 83 kg., was fractionated in the iron vacuum column by first concentrating the higher boiling isomers in 10-liter runs. This was followed by fractional distillation of the combined residues. These distillations were carried out under conditions such as to avoid decomposition and polymerization by having anhydrous potassium carbonate present in the still and by operating the column at a vacuum of 20 mm. so as to avoid still temperatures above 100°. The high boiling material was about 4% as plentiful as the triisobutylenes. It boiled at about 240° at atmospheric pressure.

Refractionation of the Triisobutylenes by Parts.—The refractionation of the material of $n^{20}\text{D}$ 1.4300 in the 0.75-in. brass column did not materially change its physical properties. Chemical data shows it to be a mixture. A second distillation of the $n^{20}\text{D}$ 1.4301–1.4308 material in the 0.75-in. column gave some separation into materials with $n^{20}\text{D}$ 1.4300 and 1.4315–8, respectively. Similarly fractions having $n^{20}\text{D}$ 1.4320–1.4400 finally gave cuts with $n^{20}\text{D}$ 1.4315–20 and 1.4410–20. These refractionations indicate the presence of only two sets of close boiling isomers. Hundreds of samples from many distillations were studied as to Cottrell b. p. and $n^{20}\text{D}$.

Freezing Points.—No satisfactory cooling curves were obtained with any of the fractions. They did not freeze sharply; instead, crystals would appear and the temperature would drop slowly until a thick slush was formed and then the temperature of the mixture would decrease rapidly.

Other Methods of Separation.—Chemical data and cooling curves have shown that the $n^{20}\text{D}$ 1.4300 was not a pure substance and that it could not be separated by fractional distillation. In a study of equilibrium melting this material was frozen, then partly melted, the liquid decanted, and the remaining solid melted. Freezing points and refractive indices of the decanted liquids and the melted solids were the same, showing that no separation was obtained.

Samples of the $n^{20}\text{D}$ 1.4300 material were extracted with methyl alcohol and with aniline without any separation into materials of different properties.

Kauri-butanol Number.[9]—The standard procedure was to dissolve 100 g. of Kauri gum in 500 g. of *n*-butyl alcohol and then determine the volume of triisobutylene that could be added to 20 g. of the solution before the gum began to precipitate. The volume of the diluent added is called the Kauri-butanol number and is accurate to 0.2. The results obtained follow:

$n^{20}\text{D}$ of triisobutylene	Kauri-butanol number
1.4300	28.5
1.4303	28.7
1.4308	28.5
1.4415	36.5

It is interesting to compare these results with those obtained with the isomeric diisobutylenes.[15]

$n^{20}\text{D}$ of diisobutylene	Kauri-butanol number
1.4088	31.1
1.4158	31.6

Thus it would appear that the first three samples of tri-

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[17] Fenske, U. S. Patents 2,037,316 and 2,037,317; *Chem. Abst.*, **30**, 3997, 3684 (1936).

isobutylenes differ, if at all, only in the position of the double bond and not in the carbon skeleton, whereas the last one differs more fundamentally.

General Method of Ozonolysis.—One-half mole of the olefin mixture was dissolved in 125 cc. of solvent, and ozone passed into the solution until the ozone ceased to be absorbed by the olefin. To decompose the ozonide the solution was added from a dropping funnel to a stirred boiling mixture of 1500 cc. of water, 65 g. of zinc dust, 1 g. of hydroquinone, and a trace of silver nitrate. The decomposition products were allowed to steam distill as they formed.[14] The steam distillate was separated, the formaldehyde in an aliquot part of the water layer titrated and the remaining water layer ether extracted. The ether extract was added to the steam distilled oil, and the oil–ether solution dried for several days over anhydrous sodium sulfate. This dried product was then carefully fractionated, using a total reflux type column with a packed section 1.5 × 60 cm. having an efficiency of 12 theoretical plates.

Of several scores of ozonolyses only three will be included.

Ozonolysis of the Lower Boiling Triisobutylene Isomers in Glacial Acetic Acid.—To check on the apparent separation in the repeated distillations of the lower boiling isomers four moles of the best fractions were ozonized. Due to the danger involved in working with ozonides, this was done 0.5 mole (84 g.) at a time using 125 cc. of glacial acetic acid containing 1–2% of acetic anhydride as the solvent. The solution was held at 15–20° by means of a water-bath. The following is a summary of the results after repeated fractional distillation. The removing of the acetic acid by water extractions probably makes the values for the water soluble compounds somewhat low.

TABLE II

	B. p., °C	$n^{20}\text{D}$	$n^{20}\text{D}$ of starting material 1.4300	1.4318
			yield, moles	
Formaldehyde			0.7	0.4
Trimethylacetaldehyde	73–77	....	.6	.8
Methyl neopentyl ketone	120–4	1.4030	1.1	1.7
Trimethylacetic acid	163–5	....	0.5	0.6
Dineopentyl ketone	182	1.4200	.65	.4
High boiling oil	85–95° at 13 mm.		107 g.	55 g.
Residue and a higher boiling oil			58 g.	30 g.

These products were identified in the following way: formaldehyde by Schryver's test[18] and its dimethylcyclohexanedione derivative, m. p. 187°; trimethylacetaldehyde, by its semicarbazone, m. p. 191°, and its 2,4-dinitrophenylhydrazone, m. p. 210°; methyl neopentyl ketone, by its semicarbazone, m. p. 176°, and its 2,4-dinitrophenylhydrazone, m. p. 100°; and trimethylacetic acid by its amide, m. p. 153°. All of these derivatives were checked by mixed melting points with authentic samples. Repeated attempts to detect acetone, acetaldehyde, and other possible compounds in the boiling ranges of the products gave negative results. No derivative of dineopentyl ketone had been reported in the literature. The only one that we could prepare was the oxime, m. p. 78°, which was checked by analysis and synthesis. The high boiling oil on standing exposed to air gave the Butlerow acids.[11] On recrystallization the melting point when compared to those of known mixtures indicated that the acids consisted of 90% dineopentylacetic acid and 10% methylneopentyl-*t*-butylacetic acid. The residue and the very high boiling oil were not identified. They may be polymerization products of the mixture of carbonyl compounds.

Ozonolysis of the $n^{20}\text{D}$ 1.4300 Triisobutylene in Low Boiling Hydrocarbon.—In the same way as with the acetic acid experiments, 97 g. of the $n^{20}\text{D}$ 1.4300 material was dissolved in 300 cc. of the low boiling hydrocarbon, cooled in a salt–ice-bath and ozonized. The following products were obtained and identified as has been described: trimethylacetaldehyde, 20 g.; methyl neopentyl ketone, 22 g.; unozonized olefin, $n^{20}\text{D}$ 1.4285, 41 g.; residue, 9 g.; formaldehyde, dineopentyl ketone and trimethylacetic acid, trace. The unchanged olefin was nearly pure methylene isomer (II). This agrees with unpublished data from this Laboratory and of Bartlett[6] which indicate that in chromic acid oxidation II is much harder to oxidize than is I. Thus II can be obtained nearly pure by either method. This preparation of II and a study of its properties are in progress.

Synthesis of Dineopentyl Ketone (2,2,6,6-Tetramethyl-4-heptanone).—A solution of 11.0 g. (0.104 mole) of neopentyl chloride[19] in 100 cc. of anhydrous ether was converted to the Grignard reagent, in 86% yield. The solution of neopentylmagnesium chloride was filtered under an atmosphere of nitrogen into a separatory funnel, and during six hours was added to a solution of 11.4 g. (0.085 mole) of *t*-butylacetyl chloride in 50 cc. of ether. The product was then decomposed as usual. The ether was removed using a 1.2 × 60 cm. indented column. The crude ketone was then fractionated through a semi-micro column, packed section 37 × 0.55 cm. (12 theoretical plates). The dineopentyl ketone was obtained in 60% yield based on the Grignard reagent, $n^{20}\text{D}$ 1.4202, b. p. 63° at 11 mm., m. p. −10°.

All attempts to prepare derivatives other than the oxime failed. The oxime was prepared by heating the usual mixture in a sealed tube at 100° for twenty-four hours. On recrystallizing from 50% alcohol a m. p. of 78° was obtained. No depression resulted in the mixed melting point with a sample from the ozonolysis ketone.

Anal. Calcd. for $C_{11}H_{22}ON$: C, 71.4; H, 12.41; N, 7.57. Found: C, 71.35; H, 12.70; N, 7.66.

Ozonolysis of the Higher Triisobutylene Isomers.—Four moles of triisobutylene, $n^{22}\text{D}$ 1.4410–5, from selected fractions was ozonized in glacial acetic acid using the technique of ozonolysis and decomposition described before. Table III gives a summary of the results. The formaldehyde, methyl neopentyl ketone, and trimethylacetic acid were identified in the usual way by the derivatives listed below. Attempts to prepare derivatives of 2,4,4-trimethyl-2-pentanol failed. By qualitative tests it was shown to be a tertiary carbinol. Dehydration to the olefins and the synthesis of the alcohol were necessary for complete characterization. Since neither the eleven-carbon ketone nor the nine-carbon acid was known, identification was made by analysis, degradation, and synthesis.

Identification of 2,4,4-Trimethylpentanol-2.—Fractions from the ozonolysis were combined, dried, and refrac-

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[18] Schryver, *Proc. Roy. Soc.* (London), **B82**, 266 (1910).

[19] Whitmore and Fleming, THIS JOURNAL, **55**, 3803, 4161 (1933).

TABLE III

Product	B. p., °C.	$n^{20}_{\rm D}$	Yield, moles	Derivative
Formaldehyde			0.6	Dimetol, m. p. 187°
Acetone	56	1.3590	1.2	Dibenzal, m. p. 111°
Methyl neopentyl ketone	120–124	1.4030	0.1	Semicarbazone, m. p. 176°
2,4,4-trimethyl-2-pentanol	143–145	1.4270	.5	...
Trimethylacetic acid	160–165	....	.1	Amide, m. p. 153°
4,4,6,6-Tetramethyl-2-heptanone	75 (10 mm.)	1.4358	.9	Semicarbazone, m. p. 149°
Dimethylneopentylacetic acid	123 (15 mm.)	....	.8	Amide, m. p. 71°

tionated through a small packed column, b. p. 38° at 8 mm., $n^{20}_{\rm D}$ 1.4270. Dehydration of 28 g. of the alcohol with 20% sulfuric acid gave 19 g. of an oil which after drying distilled over a range 101–104, $n^{20}_{\rm D}$ 1.4093–8, and thus corresponds to diisobutylene. Chromic acid oxidation of this product gave acetone, trimethylacetic acid, methyl neopentyl ketone, and methylneopentylacetic acid, which are the usual oxidation products of diisobutylene.[20]

Synthesis of 2,4,4-Trimethylpentanol-2.—This compound had been obtained by Butlerow[8] in his studies on diisobutylene and was called by him "diisobutol." Since there could be a question on the accuracy of his constants, we prepared the compound by a more direct method. In the usual way methylmagnesium chloride was prepared. Titration indicated a yield of 1.2 moles of the reagent. To this was added 114 g. of methyl neopentyl ketone prepared by the oxidation of diisobutylene. The product was steam distilled out, separated, the ether stripped off, and the carbinol fractionated through a 12-plate column. The yield of pure alcohol was 101 g. or 78% based on the ketone. The constants, $n^{20}_{\rm D}$ 1.4272, b. p. 38° at 8 mm., d^{20} 0.8250 are the same as those of the ozonolysis product.

4,4,6,6-Tetramethyl-2-heptanone.—Molecular weight determinations by the lowering of the freezing point of benzene gave a value of 170, which corresponds to an eleven-carbon ketone. Attempts to obtain a haloform reaction gave negative results. The **semicarbazone** was prepared with ease. Recrystallization from 50% ethanol gave fine needles, m. p. 149°.

Anal. Calcd. for $C_{12}H_{25}ON_3$: C, 63.4; H, 11.0; N, 18.5. Found: C, 63.2; H, 10.9; N, 17.8.

Oxidation of 4,4,6,6-Tetramethylheptanone-2.—One-half mole (85 g.) of the ketone was placed in a flask equipped with a mercury-sealed stirrer and condenser, and containing 100 g. of chromic acid, 500 cc. of water, and 80 cc. of concentrated sulfuric acid. After stirring for three days on a steam-bath, the products were steam distilled out and the oil layer separated from the water.

Using phenolphthalein the acid in the water layer was just neutralized with 0.5 *N* sodium hydroxide solution and this solution of the sodium salt evaporated. A *p*-toluidide derivative prepared from this salt melted at 146–147°, indicating acetic acid and gave no depression when mixed with a known sample. A yield of 8.3 g. of the sodium salt was obtained, or 20% calculated as acetic acid.

The water insoluble oil from the oxidation was extracted with 10% sodium hydroxide solution, dried over anhydrous potassium carbonate, and then distilled through a small packed column. The entire neutral oil distilled at 197–199°. A semicarbazone melted at 149°, thus proving the compound to be the original ketone. The total ketone recovered was 37 g. or 44%.

The sodium hydroxide solution from the extraction of the neutral oil was washed with ether and then acidified. The acids were taken up in ether and the solution dried over anhydrous sodium sulfate. After evaporation of the ether, the acid weighed 17 g. or a yield of about 21% calculated as $C_9H_{18}O_2$. Fractionation under a pressure of 14–15 mm. gave about 1 g. at 60–110° with the remainder distilling at 122–128°. A neutral equivalent on this material in 95% alcohol gave 161.5, indicating the product to be a contaminated nine-carbon acid.

Several attempts to prepare an amide of this material yielded a viscous oil requiring several days to crystallize. The derivative was too soluble to be recrystallized in small amounts from the solvents tried. A derivative was therefore prepared by the method of Locquin and Freylon.[21] The acid (0.7 g.) was dissolved in 95% alcohol, neutralized with sodium hydroxide solution, and the solution evaporated. To the sodium salt was added 0.6 cc. of freshly prepared monochloroacetone, and the mixture heated for one hour at 115°. After cooling 30 cc. of ether was added, the solution filtered, and the ether evaporated. A semicarbazone prepared from this oil melted at 155° and gave no depression when mixed with the same derivative from dimethylneopentylacetic acid.

2-Phenyl-4,4,6,6-tetramethyl-2-heptanol.—4,4,6,6-Tetramethyl-2-heptanone 68.0 g. was added to an excess of phenylmagnesium bromide. Ammonium chloride and enough 1:1 sulfuric acid were added to decompose the magnesium complex, the ether solution of the alcohol separated, and the water layer extracted with ether. After drying over anhydrous sodium sulfate, the ether was evaporated, and the carbinol distilled through a small packed column. A yield of 72 g. or 73%, b. p. 139° at 5 mm., $n^{20}_{\rm D}$ 1.5066, was obtained.

The tertiary carbinol was dehydrated with iodine, and after drying the olefins were fractionated to give a product, b. p. 120–123° at 5 mm., $n^{20}_{\rm D}$ 1.5098–1.5168. These olefins were ozonized in the usual way. Distillation of the material gave a number of products. Of these acetophenone was identified; thus the original ketone was a methyl ketone. Formaldehyde was detected in the water layer in the decomposition of the ozonide.

Dimethylneopentylacetic Acid.—Fractions from the ozonolysis were dissolved in 10% sodium hydroxide solution, the solution was washed with ether, and then acidified with hydrochloric acid. The free acid was taken up in ether and dried over sodium sulfate. On slow evapora-

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[20] Butlerow, *Ann.*, **189**, 44 (1877).

[21] Locquin, *Compt. rend.*, **138**, 1274 (1904); Freylon, *Ann. chim.*, [8], **20**, 70 (1910).

tion of the ether the acid crystallized in large, soft, square crystals melting at 40–45°. After drying in a vacuum desiccator, a neutral equivalent of 159 was obtained, indicating a nine-carbon acid, which was confirmed by analysis.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.4; H, 11.39. Found: C, 68.2; H, 11.5.

The amide was prepared in the usual way by the reaction of the acid chloride with ammonia. After three recrystallizations from a water–methanol solution it gave square crystals m. p. 70–71° that tend to sublime.

Anal. Calcd. for $C_9H_{19}ON$: C, 68.8; H, 12.1; N, 8.9. Found: C, 68.9; H, 11.4; N, 8.7.

Curtius Degradation[18] of Dimethylneopentylacetic Acid.—The acid chloride was made from 6 g. of the acid by refluxing it with an excess of thionyl chloride. To this after removing the excess thionyl chloride, was added 1.5 g. of sodium azide in 50 cc. of dry toluene. The mixture was heated to gentle refluxing and stirred for forty-eight hours. In this time about 800 cc. of gas was collected (calcd. 850 cc.). After cooling, 75 cc. of 40% potassium hydroxide solution was added, the mixture was refluxed for three hours, and then steam distilled. Hydrochloric acid was added to the steam distillate, and the amine hydrochloride solution separated. After washing with ether to remove toluene, the solution was made alkaline and extracted with ether. The ether solution was dried and then used in the preparation of derivatives of the amine, 2,4,4-trimethyl-2-aminopentane.

Its phenyl urea was prepared by the addition of 0.5 cc. of phenyl isocyanate to 10 cc. of the ether solution. On evaporation of the ether the product separated as crystals. Recrystallization from ligroin gave fine needles melting at 137°.

Anal. Calcd. for $C_{15}H_{24}ON_2$: C, 72.58; H, 9.68; N, 11.28. Found: C, 72.4; H, 9.6; N, 11.1.

The acetyl derivative was prepared by adding 5 cc. of acetic anhydride to 10 cc. of the ether solution and warming the mixture on a steam-bath for five minutes. Water was added, the ether evaporated, the solution cooled, and the derivative filtered off. After recrystallizing from ligroin twice the compound melted at 98–99°.

Anal. Calcd. for $C_{10}H_{21}ON$: C, 70.2; H, 12.3; N, 8.2. Found: C, 69.5; H, 12.0; N, 7.8.

Preparation of "Diisobutylene Hydrochloride," 2,4,4-Trimethyl-2-chloropentane.—Dry hydrogen chloride was passed through 166 g. of diisobutylene in a flask cooled with ice. After no more hydrogen chloride was taken up, the oil was washed with ice water and stored over anhydrous potassium carbonate. Fractional distillation under reduced pressure to prevent decomposition gave almost a quantitative yield of the chloride, b. p. 44° at 16 mm., $n^{20}D$ 1.4307.

Preparation of 2,4,4-Trimethyl-2-aminopentane.—Fifteen grams each of silver cyanate and the diisobutylene hydrochloride were placed in a flask fitted with a mercury-sealed stirrer and a condenser. The reaction took place immediately with the generation of heat. After stirring for six hours, 60 cc. of 40% potassium hydroxide solution was added, the mixture refluxed for three hours, diluted, and steam distilled. The distillate was treated with hydrochloric acid, the solution of the amine hydrochloride washed with ether, made alkaline with 10% sodium hydroxide solution, and the amine taken up in ether. After drying over sodium sulfate, the phenyl urea, m. p. 137°, and the acetyl derivative, m. p. 99°, were prepared as before. Neither of these depressed the melting points of the derivatives obtained in the degradation of the dimethylneopentylacetic acid.

Summary

1. Repeated fractionations of triisobutylene through columns of upward of 100 theoretical plates gave a partial separation into lower and higher boiling materials in the ratio of about 9:1.

2. The lower boiling isomers of triisobutylene have been shown to be 2,2,4,6,6-pentamethyl-3-heptene (I) and 2-neopentyl-4,4-dimethyl-1-pentene, *unsym*-dineopentylethylene (II).

3. The series of fractions of n^{20} D 1.4300 in the lower boiling isomers of triisobutylene contains I and II in the ratio of 2:3, and the slightly higher boiling material of $n^{20}D$ 1.4310–5 which cannot be completely separated by the available columns is apparently mainly the higher boiling geometric isomer of I.

4. Dineopentylethylene (II) is more resistant to ozonolysis than its isomer (I).

5. The higher boiling isomers of triisobutylene consist of 2,4,4,6,6-pentamethyl-1-heptene (IV) and 2,4,4,6,6-pentamethyl-2-heptene (V) in about equal quantities.

6. No evidence has been found for the presence of 2,4,4-trimethyl-3-*t*-butyl-2-pentene as reported by other workers.

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