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

# The Dimerization of Triptene with Sulfuric Acid[1]

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In a continuation of the dimerization studies conducted in this laboratory,[4,5,6,7,8,9,10] we have carried out an investigation of the products from the reaction of triptene, 2,3,3-trimethyl-1-butene, with sulfuric acid.

The majority of the mechanisms postulated for the dimerization reaction have been based on the relatively simple products obtained from isobutylene. One large factor causing a complexity of products from higher molecular weight olefins is isomerization prior to polymerization, since the same catalysts are, in general, effective for both reactions.

Triptene, like isobutylene, is not altered by the rearrangements possible under the mild conditions employed for the dimerization reaction. The initial polymerization of triptene, therefore, should be simple. However, the complicating reactions following the polymerization, *i. e.*, rearrangement, $\beta$-fission and repolymerization should be abundant. Such was the case. The products were

| | | | |
|---|---|---|---|
| Hexenes | 0.2% | Undecenes | 10% |
| Octenes | 0.6% | Do- and tridecenes | 9% |
| Nonenes | 3 % | Tetradecenes | 56% |
| Decenes | 12 % | $C_{15}$ and above | 9% |

The major components of the above isomers have been identified and their presence explained through the application of the mechanism in current use.

## Experimental

**Materials.**—The triptene used in preliminary work was prepared by the dehydration of 2,3,3-trimethyl-2-butanol. This alcohol was prepared by the reaction of methylmagnesium bromide with pinacolone or bromomagnesium trimethylacetate.

For the large-scale dimerization, triptene furnished by General Motors Corporation was fractionated through an 80-plate helix packed column and the fractions having constant boiling points and indices of refraction combined. The fractionation was carried out with metallic sodium in the still pot to reduce peroxides to a minimum.

The catalyst was prepared by the dilution of J. T. Baker concentrated, C. P., sulfuric acid to 75%. The concentrated acid was added to the theoretical quantity of water and the final concentration checked by density measurement.

**Polymerization.**—The polymerization was carried out in an all-glass system. The polymerization flask proper was 5-l. capacity. It was fitted with a separatory funnel, mercury-sealed, air-driven stirrer, thermometer and a bulb condenser. Triptene was distilled from metallic sodium into the separatory funnel of the polymerization flask. The distillation and polymerization were carried out under an atmosphere of Linde nitrogen which was passed through alkaline pyrogallol. The polymer was separated from the sulfuric acid after about twelve hours, washed with aqueous sodium bicarbonate solution and dried over anhydrous potassium carbonate. The weight of olefin reacted was 13,011 g. This yielded 12,539 g. (96.3%) of crude dry polymer.

**Analytical Fractionation.**—The polymer was roughly fractionated through a fifty theoretical plate, helix-packed column to separate it into dimer, monomer and hydrocarbons of intermediate molecular weight. The fractions were redistilled through columns of sixty theoretical plates with the exception of the material boiling above ditriptene, the principal dimer. This higher boiling material was fractionated through a column of thirty-five theoretical plates. Two fractionation curves, in which the index of refraction is plotted against the weight distilled, are reproduced. Figure 1 shows the preliminary general fractionation, while Fig. 2 shows one of the refractionations. The other refractionations gave curves equally complicated except for the main dimer portion.

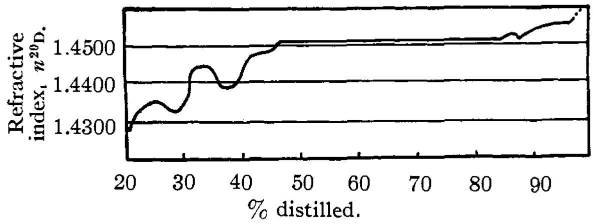

Fig. 1.—Original fractionation of polymer products (hexenes and recovered monomer not shown).

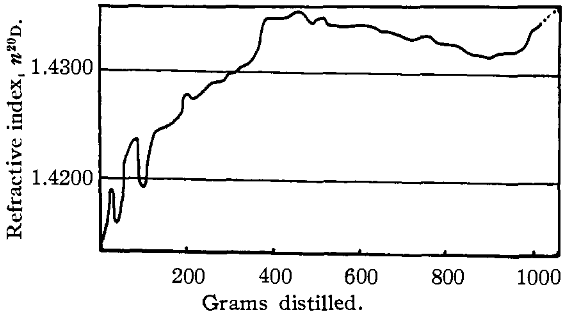

Fig. 2.—Refractionation of 20–30% (mainly decenes) from Fig. 1.

**Ozonolyses.**—Selected fractions having the same or approximately the same boiling point and index of refraction were ozonized. The method of ozonolysis was essentially that of Church.[11]

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(1) Presented in part before the American Chemical Society, September, 1944, New York City.

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(4) Whitmore and Wrenn, THIS JOURNAL, **53**, 3136 (1931).

(5) Tongberg, Pickens, Fenske and Whitmore, *ibid.*, **54**, 3706 (1932).

(6) Whitmore and Church, *ibid.*, **54**, 3710 (1932).

(7) Marschner, Ph.D. Thesis, The Pennsylvania State College (1936).

(8) Laucius, Ph.D. Thesis, The Pennsylvania State College (1940).

(9) Clarke, M.S. Thesis, The Pennsylvania State College (1942).

(10) Cook, Ph.D. Thesis, The Pennsylvania State College (1943).

(11) Church, Ph.D. Thesis, The Pennsylvania State College, 1933.

TABLE I

POLYMERIZATION PRODUCTS

| Types of isomers | B. p., °C. 760 mm. | $n^{20}D$ | Amount | Ozonolysis products | Olefins present |
|---|---|---|---|---|---|
| Hexenes | 63–72 | 1.3915–1.4007 | 0.2 | Acetaldehyde + — | 3-Methyl-2-pentene[a] |
| | | | | Acetone + — | 2-Methyl-2-pentene |
| Recovered monomer[b] | 77–79 | 1.4028–1.4030 | 16 | | |
| Octenes[c] | 100–124 | 1.4174–1.4248 | 0.5 | | |
| Nonenes[d] | 124–142 | 1.4218–1.4280 | 2.2 | | |
| Decenes | 143–160 | 1.4292–1.4350 | 10 | | |
| A | 143 | 1.4292 | 0.5 | Acetone + 2,2,3-$Me_3$-butanoic acid | 2,4,5,5-$Me_4$-2-hexene[e] |
| B | 151 | 1.4350 | 1 | Acetaldehyde + 2,2,3,3-$Me_4$-butanoic acid | 4,4,5,5-$Me_4$-2-hexene[e,f] |
| | | | | Acetaldehyde + 3,4,4-$Me_3$-2-pentanone | 3,4,5,5-$Me_4$-2-hexene[g] |
| C | 153 | 1.4341 | 1 | Acetaldehyde + 3,4,4-$Me_3$-2-pentanone | 3,4,5,5-$Me_4$-2-hexene |
| | | | | $Me_3$-acetaldehyde + pinacolone | 2,2,3,5,5-$Me_5$-3-hexene[e,h] |
| D | 155 | 1.4317 | 1.5 | $Me_3$-acetaldehyde + pinacolone | 2,2,3,5,5-$Me_5$-3-hexene[h] |
| E | 163 | 1.4320–2 | 0.3 | Acetaldehyde + 3,3,4-$Me_3$-2-pentanone | 3,4,4,5-$Me_4$-2-hexene[i] |
| | | | | Acetaldehyde + 4,4-$Me_2$-2-hexanone | 3,5,5-$Me_3$-2-heptene |
| Undecenes | 155–175 | 1.4320–1.4464 | 8 | | |
| A | See C and D above | | | | |
| B | 175 | 1.4461–4 | 2 | Acetone + 2,2,3,3-$Me_4$-butanoic acid | 2,4,4,5,5-$Me_5$-2-hexene[e] |
| Do- and tridecenes | 175–210 | 1.4400–1.4500 | 7 | | |
| A | 178 | 1.4459–61 | 1.2 | Pinacolone + 2,2-$Me_2$-butanal | 2,2,3,5,5-$Me_5$-3-heptene[e] |
| B | 178 | 1.4469–70 | 0.4 | Pinacolone + 2,2-$Me_2$-butanal | 2,2,3,5,5-$Me_5$-3-heptene[e] |
| Tetradecenes | 215–230 | 1.4510–1.4530 | 50 | | |
| A | 216.3 | 1.4511 | 36 | Pinacolone + 2,2,3,3-$Me_4$-butanoic acid | 2,2,3,5,5,6,6-$Me_7$-3-heptene |
| Higher boiling material | 225 | 1.4530 | 6 | | |

[a] There were undoubtedly more hexenes formed during the reaction, but they would have reacted with the triptene to give tridecenes. The hexenes are fission products and under the conditions used would be expected to be mainly tertiary. So although only a fragment of each one was identified, there is little doubt that acetaldehyde came from 3-methyl-2-pentene, and acetone from 2-methyl-2-pentene. [b] The saturated hydrocarbon, triptane, is probably present also. There is an alkane present boiling slightly above triptene which causes a drop of 0.0070 unit in the refractive index curve. [c] A small amount of triptanol distilled over with the octenes making it impossible to determine from the physical properties their probable composition. [d] None of the nonenes were identified but physical properties indicated the presence of 2-isopropyl-3,3-dimethyl-1-butene, 2,3,3,4-tetramethyl-1-pentene and 2,3,4,4-tetramethyl-1-pentene. [e] This compound has not been previously reported. [f] The corresponding 1-isomer, synthesized in this Laboratory, boils at 153°, $n^{20}D$ 1.4368. [g] The properties of 3,4,5,5-tetramethyl-2-hexene are: b. p. 152°, $n^{20}D$ 1.4361–71 (unpublished work, this Laboratory). [h] The low boiling point of this undecene is probably due to the isomer being the *trans*-form. [i] The properties of 3,4,4,5-tetramethyl-2-hexene are: low form, b. p. 159°, $n^{20}D$ 1.4395; high form, b. p. 160°, $n^{20}D$ 1.4430; 3,5,5-trimethyl-2-hexene, low form, b. p. 160.5°, $n^{20}D$ 1.4358, high form b. p. 162°, $n^{20}D$ 1.4388. (unpublished work, this Laboratory). The low refractive index of the polymer mixture containing these isomers must be due to the presence of considerable amounts of other decenes or undecenes with lower refractive indices.

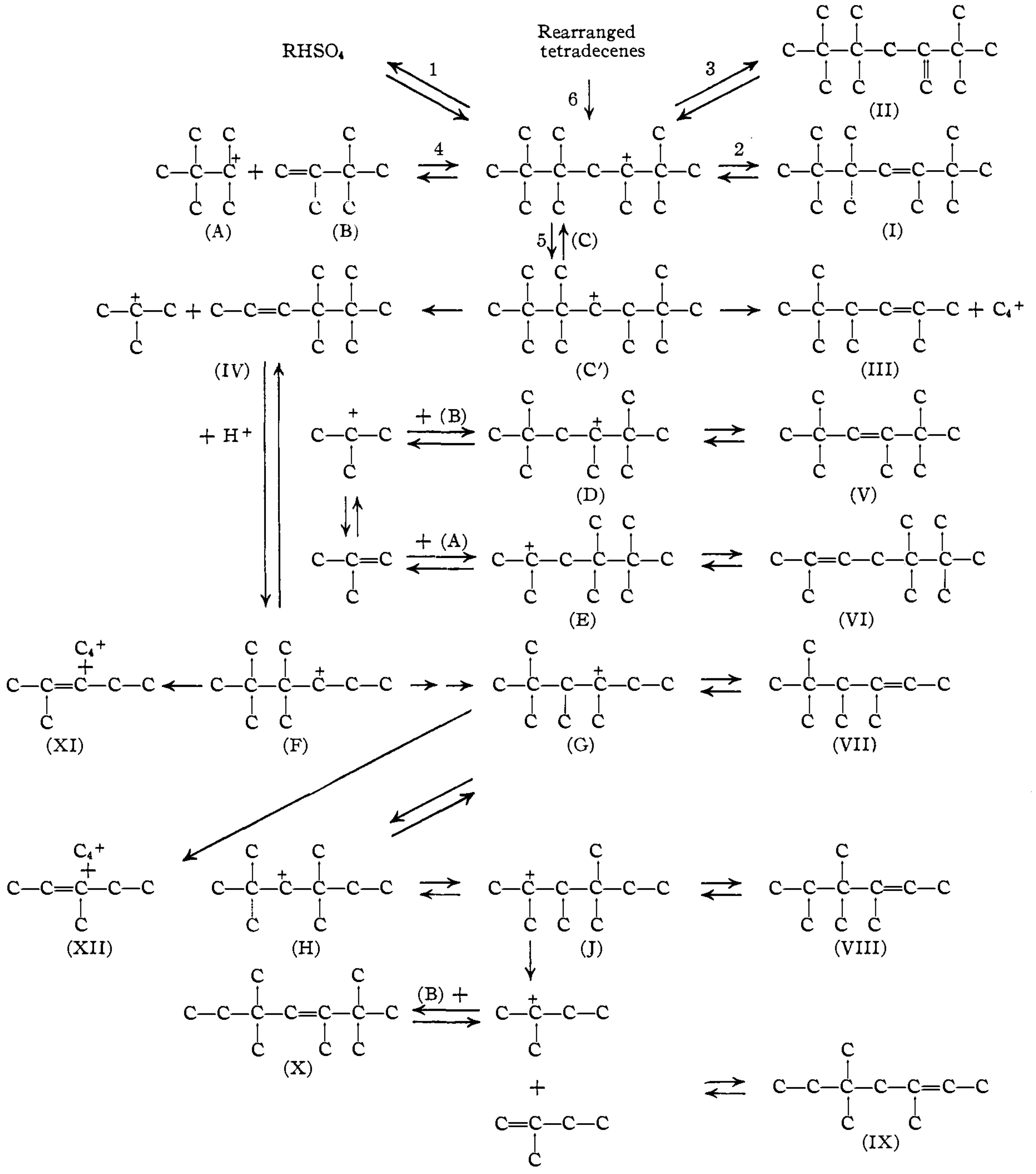
GENERAL REMARKS. This identification is of necessity only partial. The major compounds have been identified, but there are many others occurring in lesser amounts which complicate the separation problem. There is at least another tetradecene present as well as olefins of higher molecular weight. The percentages in this table are calculated on the basis of all products, including recovered monomer; the precentages in the third paragraph of the paper are calculated on the basis of all products other than recovered monomer.

The aldehydes, ketones and acids were identified by preparation of derivatives and taking melting and mixed melting points. In the case of aldehydes and ketones 2,4-dinitrophenylhydrazones were prepared with the semicarbazone serving as a check where necessary. In the case of solid acids, the melting point was taken on the free acid. The *p*-phenylphenacyl ester was prepared from all acids isolated. The data on the ozonolyses are given in Table I.

**Discussion of Results.**—The principal product from this reaction is 2,2,3,5,5,6,6-heptamethyl-3-heptene which occurs in about 40% yield varying with the conditions under which the material is polymerized. The majority of the minor products are formed from a carbonium ion related to this dimer.

A proton adds to the polarized π electrons of a triptene molecule (B) giving the triptyl carbonium ion (A) which adds to another triptene molecule (Chart I). This reaction yields the ditriptyl carbonium ion (C) which may undergo at least six different reactions. (1) By combination with the

CHART I



acid catalyst (C) forms the unstable ditriptyl bisulfate which can revert to the ditriptyl carbonium ion, thus serving as a reservoir for the latter. (2) By the attraction of a pair of electrons from the methylene carbon atom without the attached proton, (C) forms ditriptene (I), the principal product. (3) By a similar change involving an electron pair from a methyl hydrogen (C) would produce an isomeric ditriptene. This isomer is probably present, but in small concentrations. It would be difficult to detect since the ketone which would be produced by ozonolysis would form a derivative with great difficulty or not at all.[12]

The other three reactions of (C) lead to prod-

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(12) From the reaction of triptylacetyl chloride and *t*-butylmagnesium chloride was obtained two products (1) b. p. 220–225°, $n^{20}\text{D}$ 1.4460–1.4465 and (2) b. p. 240–250°, $n^{20}\text{D}$ 1.4610–1.4600, m. p. 79–85°. The lower boiling product is probably 2,2,3,3,5,5-hexamethyl-3-pentanone and the higher boiling material, the corresponding alcohol. No derivative could be obtained from either of these products.

ucts which are still carbonium ions and must undergo further change to stabilize the electronically deficient carbon. (4) By the shift of a pair of electrons belonging to the triptyl radical without that radical, β-fission or depolymerization occurs yielding the monomer. (5) By the attraction of an electron pair from the methylene carbon with the attached proton, (C) changes to a secondary carbonium ion (C′) which can undergo irreversible β-fission. Fission in one direction yields 2,4,5,5-tetramethyl-2-hexene (III), and in the other direction 4,4,5,5-tetramethyl-2-hexene (IV). Both fissions also yield *t*-butyl carbonium ions.[13]

Compound III appeared to be stable. It might conceivably undergo carbonium ion changes just as (C) changed to (C′), etc. No products corresponding to these transformations were identified but several other unidentified decenes appeared to be present from the distillation data.

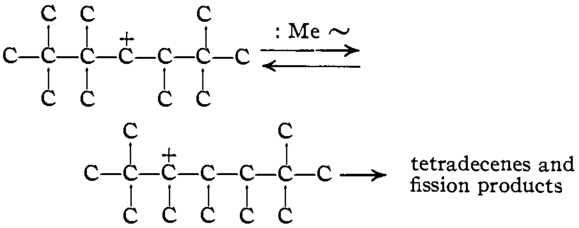
Olefin IV should and did change as shown in (Chart I) to the carbonium ion in which the electron deficiency is adjacent to a neopentyl carbon. Rearrangement to the series of diamylenes followed since structures VII, VIII and IX were isolated. Other diamylenes were undoubtedly present also.[14]

There are two reactions possible from the codimerization of the isobutylene and triptene. One is the addition of a *t*-butyl carbonium ion to a triptene molecule, the second, the addition of a triptyl carbonium ion to an isobutylene molecule. Undecenes of both reactions (V) and (VI) were found.

(6) The last plausible reaction of the ditriptyl carbonium (C) is the rearrangement of a methyl group with its attached pair of electrons, and subsequent loss of a proton to give a rearranged ditriptene.

This compound has not been identified and may or may not be formed. There was however, some material boiling about five degrees above ditriptene which is probably one of the isomeric tetradecenes. Ozonolysis produced formaldehyde and a high boiling ketone which did not give an iodoform test. Hydrogenation of two selected series of fractions boiling slightly above ditriptene yielded material whose refractive index did not correspond with that of pure hydrogenated ditriptene, 2,2,3,3,5,6,6-heptamethylheptane. Thus there are tetradecenes present whose carbon structure is not the same as ditriptene.

Other tetradecenes were undoubtedly formed by the rearrangement of (C′)



Several products may undergo fission in addition to those already mentioned. The majority of these yield isobutylene by splitting off a *t*-butyl carbonium ion. A second principal fission product would be isoamylenes from fission of the diisoamylenes. It has been shown that from the depolymerization of 3,4,5,5-tetramethyl-2-hexene (VII), trimethylethylene is obtained in yields up to 45%.[15] Thus it is not surprising that (X), a copolymer of trimethylethylene and triptene, was found. Other dodecenes undoubtedly formed also.

An olefin whose presence is more difficult to explain is 3,5,5-trimethyl-2-heptene (IX). This is a diisoamylene but does not belong to the series which are formed from 4,4,5,5-tetramethyl-2-hexene (IV). The presence of this diisoamylene can only be explained by assuming a rapid repolymerization of the fragments of depolymerization of one of the diisoamylenes. To arrive at this conclusion one must realize that the two series of diisoamylenes are not interconvertible under the usual mild isomerization conditions,[14] and that after fission for a short period of time the products are of necessity in the same vicinity and in an active state.

Other carbonium ions which would fission to different products are (E), (F) and (G). Products of (F), 2-methyl-2-hexene (XI), and (G), 3-methyl-3-hexene XII, were identified. The *t*-butylcarbonium ions produced at the same time would appear as undecenes (VI, VII). These hexenes would react with triptene to form a variety of tridecenes. The number of possible compounds formed by these reactions, their complexity and low yield have prevented identification.

## Summary

1. The polymerization of triptene with 75% sulfuric acid give 56% tetradecenes (dimers) and 44% side reaction products, resulting from β-fission and repolymerization.

2. Approximately 40% of the dimers was 2,2,3,5,5,6,6-heptamethyl-3-heptene, the other 17% being rearranged isomers. The 44% side products was made up of 0.6% octenes, 3% nonenes, 12% decenes, 10% undecenes, 9% do- and tridecenes and 9% of $C_{15}$ and higher boiling material.

3. The following products have been identified in the β-fission and repolymerization products: 2,2,3,5,5-pentamethyl-3-hexene, 2,4,4,5,5-pentamethyl-2-hexene, 4,4,5,5-tetramethyl-2-hexene, 2,4,5,5-tetramethyl-2-hexene, 3,4,4,5-tetrameth-

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[13] These fissions do not occur if the pure dimer (I) is treated with the same strength acid used for the polymerization. Pure ditriptene was stirred for four and one-half hours with 75% sulfuric acid. The recovery after washing and drying was 98%. Fractionation yielded 0.3% having an $n^{20}D$ of 1.4470 and 1.4% having an $n^{20}D$ of 1.4510–1.4511. This result must be attributed to the fact that the dimer does not readily revert to a carbonium ion, although it must pass through a carbonium ion stage in its formation from the monomer.

[14] Stehman, Ph.D. Thesis, The Pennsylvania State College, 1947.

[15] Whitmore and Mosher, THIS JOURNAL, 68, 281 (1946).

yl-2-hexene, 3,4,5,5-tetramethyl-2-hexene, 3,5,5-trimethyl-2-heptene and 2,2,3,5,5-pentamethyl-3-heptene.

4. The mechanism for the formation of these products is discussed.

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

# Some Reactions of *t*-Butylethylene[1]

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Several reactions of *t*-butylethylene have been investigated to throw further light on the behavior of compounds containing the neopentyl system.

Addition of chlorine was found to produce principally unrearranged dichlorides which yielded on dehydrochlorination both the 1- and 2-chloro-3,3-dimethylbutenes. Contrary to expectations gained from a study of pinacolyl alcohol, hydrogen chloride added to *t*-butylethylene to give considerable amounts of pinacolyl chloride. The presence of benzoyl peroxide caused an increase in the yield of pinacolyl chloride, and produced a peroxide effect in those reactions which contained low ratios of hydrogen chloride to olefin, giving 1-chloro-3,3-dimethylbutane. Hydrogen iodide added to *t*-butylethylene almost completely without rearrangement, giving 90% pinacolyl iodide.

## Experimental

Distillations were made through columns of the adiabatic, total reflux, variable take-off type, packed with (A) $^{3}/_{32}''$ glass helices, packed section 1.5 × 70 cm., 30 theoretical plates, (B) $^{3}/_{32}''$ glass helices, 1.4 × 40 cm., 20 theoretical plates, (C) $^{1}/_{16}''$ glass helices, 0.8 × 28 cm., 30 theoretical plates, (D) $^{1}/_{16}''$ glass helices, 1.5 × 145 cm., 80 theoretical plates.

**Reaction of Chlorine with *t*-Butylethylene.**—The olefin mixtures from the dehydration of 3,3-dimethyl-2-butanol with alumina as described by Cramer and Glasebrook[4] were fractionated through Column D to produce a *t*-butylethylene fraction with constant boiling point and refractive index, b. p. 41°, $n^{20}\mathrm{D}$ 1.3760. For the hydrogen chloride addition reactions the olefin was given a subsequent distillation under nitrogen and kept in sealed ampules until needed.

Chlorine was bubbled into a 2-mole (168-g.) portion of *t*-butylethylene and a 111 g. (78% theoretical) gain in weight noted over an eight-hour period. The mixture was stirred, protected from light, and maintained at 0–5° during the reaction. Preliminary distillation under reduced pressure through column B gave an olefin fraction, a dichloride fraction, and a higher chloride fraction. Fractionation of these products by parts through column C gave 31 g. (16%) recovered *t*-butylethylene, b. p. 41°, $n^{20}\mathrm{D}$ 1.3758–1.3761, 20 g. (6%) of dichloride, b. p. 46–52 (11 mm.), $n^{20}\mathrm{D}$ 1.4553–1.4622 (believed to be mainly unsaturated dichlorides), 163 g. (53%) 1,2-dichloro-3,3-dimethylbutane (I), b. p. 52° (11 mm.), $n^{20}\mathrm{D}$ 1.4553, and 42 g. of a mixture of higher chlorides, b. p. 55–100° (10 mm.), $n^{20}\mathrm{D}$ 1.4644–1.5024.

**Reaction of *t*-Butylethylene with Sulfuryl Chloride.**—A solution of 7 moles (588 g.) of *t*-butylethylene and 3 g. of dibenzoyl peroxide was heated to reflux and 6.8 moles (920 g.) of sulfuryl chloride added over a four-hour period. Heating was continued an additional four hours, the pot temperature finally reaching 98°. The 905 g. of product was given a preliminary fractionation through Column A to yield 640 g. (61%) crude (I) and 210 g. of higher chlorides. Fractionation of the crude (I) through column A gave 575 g. of the pure dichloride, b. p. 52° (11 mm.), $n^{20}\mathrm{D}$ 1.4551, $d^{20}_{4}$ 1.071.

**Dehydrochlorination of 1,2-Dichloro-3,3-dimethylbutane.**—To 3.76 moles (584 g.) of (I) was added 1040 ml. of 3.97 *N* ethanolic potassium hydroxide representing a 10% excess for the removal of one hydrogen chloride per molecule. The mixture was stirred and heated to reflux for three hours. After cooling 2500 ml. of water was added. The organic layer was removed, washed with water, and steam distilled. Titration of the water layer from the reaction indicated 87% dehydrochlorination for the removal of one hydrogen chloride per molecule of dichloride. Fractionation of the organic layer from the steam distillation gave an unsaturated monochloride fraction, 378 g. (85% conversion) and a recovered dichloride fraction, 53 g. (94% material balance). The monochloride fraction was refractionated through column D to yield 2-chloro-3,3-dimethyl-1-butene (II), b. p. 95.5° (730 mm.), $n^{20}\mathrm{D}$ 1.4247, $d^{20}_{4}$ 0.8888 and 1-chloro-3,3-dimethyl-1-butene (III), b. p. 105° (730 mm.), $n^{20}\mathrm{D}$ 1.4276, $d^{20}_{4}$ 0.8835 in a ratio of 1.7:1. No evidence of the *cis–trans* pair of (III) was found.

**Ozonolysis of the Unsaturated Monochlorides.**—A 10-ml. portion of (II) was dissolved in 150 ml. of pentane and ozonized at ice temperature over an eleven-hour period. Ozone absorption was definitely sluggish. Decomposition of the ozonide with boiling water and zinc dust gave a steam distillate, the water layer of which yielded the 2,4-dinitrophenylhydrazone of formaldehyde, m. p. and a mixed m. p. 161–162°. The pentane layer yielded a low melting solid which was purified through conversion to and regeneration from the potassium salt. It melted at about 28° and was not depressed by an authentic sample of pivalic acid. These results indicate the low boiling isomer to be 2-chloro-3,3-dimethyl-1-butene and establish the unrearranged structure of the parent dichloride.

A 10-ml. sample of the high boiling flat was ozonized in a similar manner except that ozone absorption was rapid. Decomposition of the ozonide yielded the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. 210–211°. The cold trap from the ozonolysis exhaust gases gave a copious quantity of hydrogen chloride upon warming as evidenced by their reaction with moist litmus and silver nitrate solution. These facts indicate the high boiling isomer to be 1-chloro-3,3-dimethyl-1-butene and affirm the structure of (I).

**Reactivities of the Unsaturated Monochlorides.**—A series of sealed glass tubes were prepared each containing 5 ml. of 1.276 *N* ethanolic potassium hydroxide along with 2 ml. of the desired halide. The tubes were placed in a steam-bath and one tube of each isomer removed at appropriate times. Whereas (III) was less than 5% reacted at the end of forty-six hours, (II) showed greater than 95% reaction.

Both ozone and permanganate in acetone reacted more rapidly with (III) than with (II). Attempts to form

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[1] Presented before the Organic Division of the American Chemical Society, Atlantic City, September, 1949.

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[3] Deceased.

[4] Cramer and Glasebrook, THIS JOURNAL, **61**, 230 (1939).