and twice more from aqueous methanol to give white plates, m.p. 121.3–122.6°.

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.97; H, 7.86.

p,p'-Octamethylenediphenylmethane (XIIa).—Acyloin XIa (1.9 g.) was reduced by the method outlined for XIc → XIIc, 1.6 g. of crude product remaining when the extraction solvent was evaporated. Recrystallization of this material from methanol gave 0.90 g. of hard white crystals, m.p.

118.8–121.5°. Two additional recrystallizations of this material from methanol gave 0.40 g. of XIIa, m.p. 120.3–121.5°. The mother liquors yielded an additional 0.75 g. of XIIa by chromatographic purification on alumina, m.p. 119.5–121.0°. The total yield amounted to 1.21 g. (67% yield).

Anal. Calcd. for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.64; H, 9.16.

LOS ANGELES, CALIFORNIA

Studies in the Terpene Series. XX.[1] The Thermal Isomerization of Pinane at Atmospheric Pressure

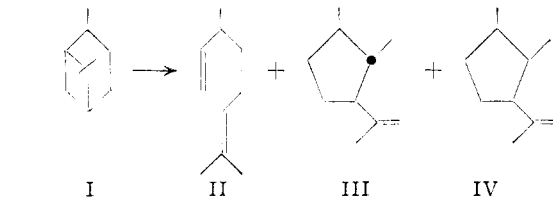BY HERMAN PINES, N. E. HOFFMAN[2] AND V. N. IPATIEFF[3]

RECEIVED MARCH 17, 1954

At 500° and atmospheric pressure pinane isomerizes to a diolefin, 3,7-dimethyl-1,6-octadiene, and two cyclic monoölefins, 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane and 1-*cis*-2-dimethyl-*cis*-3-isopropenylcyclopentane. The diolefin at 500° and atmospheric pressure cyclizes to the two monoölefins produced in the pinane reaction. A free radical mechanism is proposed for the reaction.

The thermal isomerization of pinane at high pressure has been investigated,[4] and it was found that the products of the reaction were 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane and a bicyclic dihydroterpene of unknown structure, among others.[5] Rummelsburg studied the atmospheric pressure thermal isomerization of pinane but without proving the structures of the products, he suggested that the monocyclic dihydroterpenes consisted mostly of menthenes.[6] The present study was undertaken to determine the structures of the products of the atmospheric thermal reaction of pinane and to compare these products with those produced by the high pressure thermal reaction of pinane.

Results

At 500° and atmospheric pressure pinane (I) isomerizes to a diolefin, 3,7-dimethyl-1,6-octadiene (II), a low boiling cyclic monoölefin, 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane (III), and a high boiling cyclic monoölefin, 1-*cis*-2-dimethyl-*cis*-3-isopropenylcyclopentane (IV). Under the flow conditions used, the distribution was 13% II, 57% III, 19% IV and 11% high and low boiling products. No unreacted pinane could be detected.

Furthermore, under conditions used for the pinane reaction, the diolefin II cyclizes to the monoölefins III and IV. The formation of 1,2-dimethyl-3-isopropenylcyclopentane rather than 1,2-dimethyl-3-isopropylidenecyclopentane is interesting in view of the observation that an *exo* double bond stabilizes a 5-membered ring.[7]

The method used in investigating the reaction was the following. The products of the reaction were fractionally distilled into many small cuts, and samples of these cuts were hydrogenated quantitatively to determine the degree of unsaturation of each. The distillation curve is in Fig. 1 and the results of the hydrogenations are in Table I. From hydrogenation and elemental analyses it was found that all the products were isomers of pinane of two types, monoölefin and diolefin. The first cuts from distillation contained a mixture of diolefin and low boiling cyclic monoölefin; the final cuts were pure high boiling cyclic monoölefin. Chromatographic separation over silica gel[8] was used successfully to obtain the pure diolefin. The distillation and hydrogenation data were used in the quantitative analysis of the products. The refractive indices of the distillation cuts checked well with the analy-

I   II   III   IV

(1) For the previous paper of this series, see H. Pines, A. Rudin, G. Bo and V. N. Ipatieff, THIS JOURNAL, **76**, 2740 (1954).

(2) Universal Oil Products Company Predoctoral Fellow, 1950–1953.

(3) Deceased, November 29, 1952.

(4) V. N. Ipatieff, W. D. Huntsman and H. Pines, THIS JOURNAL, **75**, 6222 (1953).

(5) During the present study it was shown that a third pinane isomer is produced in the high pressure reaction which on hydrogenation gives 1-*cis*-2-dimethyl-*cis*-3-isopropylcyclopentane.

(6) A. L. Rummelsburg, THIS JOURNAL, **66**, 1718 (1944).

TABLE I

QUANTITATIVE HYDROGENATIONS OF PRODUCTS FROM THE 500° ISOMERIZATION OF PINANE

Distilled, %	H number[a]	B.p., °C.	n^{20}D
7	1.40	157.0	1.4452
16	1.26	158.7	1.4441
38	1.25	160.4	1.4462
50	1.18	161.1	1.4475
61	1.10	161.3	1.4485
90	0.99	170.3	1.4547
95	0.98	171.2	1.4555

[a] Defined as moles of hydrogen absorbed per mole of pinane isomer.

(7) H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

(8) B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

sis assuming linearity of refractive index and composition.

Structure Proof of the Diolefin Isomer (II).— The 500° reaction produced such a small amount of diolfin it was necessary to run the reaction at 450° where the diolefin was produced in larger quantities (approximately 40% of the reaction products). These two diolefins differed only in that the 500° reaction diolefin contained 2 to 5% conjugated diolefin[9] having the 2,6-dimethyloctane skeleton while the 450° reaction diolefin contained no conjugated impurity. This 450° reaction diolefin was used in structure proof experiments.

The carbon skeleton of the diolefin was shown by its hydrogenation to 2,6-dimethyloctane. An infrared comparison of the hydrogenated diolefin to 2,6-dimethyloctane prepared by the hydrogenation of allo-ocimene showed the two were the same.

The infrared spectrogram of the diolefin showed the presence of a vinyl group from bands at 10.04 and 10.95 μ.[10] The other type of double bond present in the molecule was not clearly shown in the infrared spectrogram. Ozonolysis of the diolefin using hydrogen peroxide in aqueous acetic acid for hydrolysis of the ozonide gave three products: carbon dioxide showing the presence of a vinyl group, diacetone peroxide showing the presence of an isopropylidene group, and α-methylglutaric acid. This latter acid was optically active, as was the starting compound II. Later in this paper the optical activity of these compounds will be discussed. The hydrogenation and degradation experiments showed the structure of the diolefin was 3,7-dimethyl-1,6-octadiene (II). The following scheme outlines the methods used in structure proof

CO$_2$ + (CH$_3$)$_2$C$\underset{O_2}{\overset{O_2}{\diagup\hspace{-0.3em}\diagdown}}$C(CH$_3$)$_2$ + HO$_2$CCHCH$_3$CH$_2$CH$_2$CO$_2$H
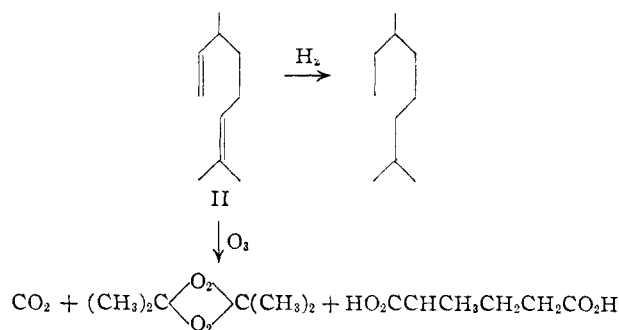
Structure of the Low Boiling Monoölefin Isomer (III).[11]—The low boiling monoölefin's infrared spectrogram was practically identical to that of 1-trans-2-dimethyl-cis-3-isopropenylcyclopentane.[4] Hydrogenation of the low boiling monoölefin isomer gave a hydrocarbon whose infrared spectrogram was identical to that of 1-trans-2-dimethyl-cis-3-isopropylcyclopentane.[4] Since the minor impurity bands in the infrared spectrum of the low boiling monoölefin were those of the diolefin II, there was no doubt that its structure was 1-trans-2-dimethyl-cis-3-isopropenylcyclopentane.

(9) The percentages are the concentrations calculated using the ultraviolet extinction coefficients of isoprene and myrcene at their maxima and assuming these coefficients are the extremes of the range of possible coefficients for the conjugated impurity.

(10) H. L. McMurry and V. Thorton, *Anal. Chem.*, **24**, 318 (1952).

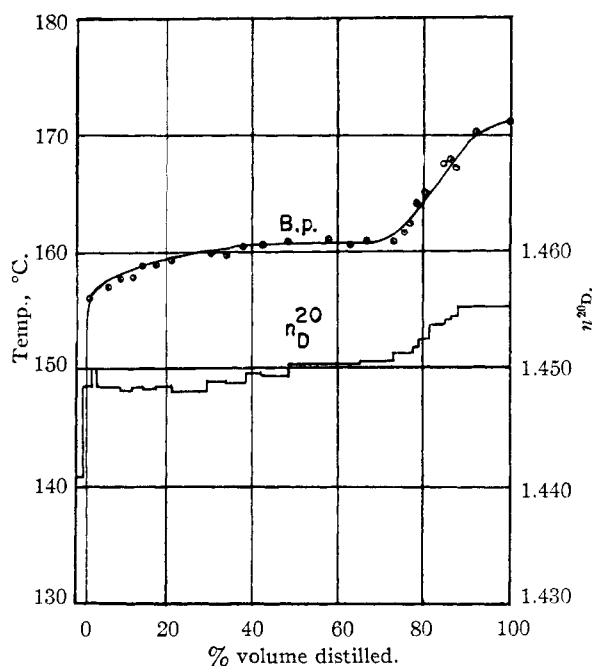(11) The structure of this product was established by W. D. Huntsman in this Laboratory.

Fig. 1.—Distillation pinane products 500° reaction.

Structure Proof of the High Boiling Monoölefin Isomer (IV).—The infrared spectrum of the high-boiling monoölefin isomer had an $R_1R_2C=CH_2$ olefin band at 11.25 μ.[9] This monoölefin was hydrogenated to hydrocarbon V which did not have a six-membered ring because it failed to undergo dehydrogenation at 260 and 320° over platinized alumina catalyst.[12]

TABLE II

CHARACTERISTIC INFRARED BANDS OF COMPOUNDS II, IV, V AND 2,6-DIMETHYLOCTANE

λ

Compound II	6.07, 6.88, 7.25, 7.70, 8.13, 8.36, 8.73, 8.94, 10.04, 10.95, 11.25, 11.97, 13.47, 14.65
Compound IV	6.08, 6.92, 7.26, 7.44, 7.92, 8.07, 8.67, 8.81, 9.22, 9.44, 9.75, 10.13, 10.42, 10.56, 11.25, 12.10
Compound V	6.80, 7.21, 7.39, 7.60, 7.80, 7.92, 8.12, 8.28, 8.46, 8.94, 9.16, 9.56, 9.69, 10.10, 10.20, 10.35, 10.64, 10.81, 11.24, 11.47, 12.13, 12.87
2,6-Dimethyl-octane	6.79, 7.20, 7.42, 7.55, 7.76, 8.02, 8.23, 8.49, 9.03, 9.34, 9.82, 10.26, 10.65, 10.86, 11.82, 12.96, 13.60

Ozonolysis of the monoölefin IV using zinc in aqueous acetic acid for hydrolysis of the ozonide gave formaldehyde and a slightly impure ketone VI. A positive iodoform test showed that a methyl ketone was produced. Hypobromite oxidation of the methyl ketone gave a carboxylic acid VII.[13]

(12) V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **68**, 1709 (1946); V. N. Ipatieff, H. Pines and M. Savoy, *ibid.*, **69**, 1948 (1947).

(13) The stereo-relationships within the ketone were not destroyed by this step because, although strongly basic conditions were used, a carbanion formed on the carbon alpha to the carbonyl group would attack bromine at a rate much greater than it would attack water and the α-bromo acid thus produced would be separated easily by distillation. See L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 104.

Lithium aluminum hydride reduction of the acid gave an alcohol VIII.

Hydrogenolysis of this alcohol VIII in the presence of nickel–Kieselguhr catalyst gave a mixture of C_7-cycloalkanes, chiefly 1-cis-2-dimethylcyclopentane, 1-trans-2-dimethylcyclopentane and methylcyclohexane. The predominance of the 1,2-dimethylcyclopentane isomers indicated the isopropenyl group of the monoölefin (IV) was attached to a 1,2-dimethylcyclopentane nucleus. The location of the isopropenyl group was shown by reduction of the hydroxymethyl group of alcohol VIII to a methyl group. Lithium aluminum hydride reduction of the p-toluenesulfonate ester IX of the alcohol VIII gave slightly impure 1-cis-2,cis-3-trimethylcyclopentane (X).

This series of reactions shown below proved the structure of the high-boiling monoölefin isomer of pinane was 1-cis-2-dimethyl-cis-3-isopropenylcyclopentane.

Cyclization of 3,7-Dimethyl-1,6-octadiene.

The thermal reaction of 3,7-dimethyl-1,6-octadiene (II) under the conditions used for the thermal isomerization of pinane gave only monoölefins III and IV and unreacted II. Quantitative hydrogenation and distillation analysis showed 30% of the distilled liquid was diolefin and 70% was monoölefin with isomer III predominating over isomer IV.

Discussion

Stereochemistry.—The pinane used for the thermal reaction was optically active and all three structural isomers produced by the reaction were optically active. However, some epimerization or racemization of pinane or the diolefin II occurred during the reaction since the rotation of diolefin II from the 500° reaction was different from the rotation of diolefin II from the 450° reaction.

Since inversion of the asymmetric carbon atom of diolefin II during cyclization is unlikely, the thermal reaction of pinane leads to a series of compounds whose configuration is known with relation to α-methylglutaric acid. Fredga has reported that the configuration of (+)-α-methylglutaric acid is

D with reference to glyceraldehyde when CHO is analogous to CO_2H, H to H, CH_3 to CH_2OH, and $(CH_2)_2CO_2H$ to OH.[14] On this basis these configurations hold

Although it is not known whether the pinane used in the thermal reaction was cis or trans or a mixture of both, the configuration of the asymmetric carbon atom of the pinane used was predominantly D according to the above convention providing it did not epimerize prior to reaction.

Mechanism.—The products of the pinane reaction can be most easily explained by the free radical mechanism

(14) A. Fredga, Arkiv Kemi, Mineral. Geol., 24A, No. 32, 10 (1947). His criterion for assignment of configuration was the following: if the mixed melting point curve of two different optically pure compounds having similar groups attached to the asymmetric center showed formation of a quasi-racemic compound, the two compounds in question were opposite in configuration. In particular, a mixed melting point curve of l-(−)-α,γ-dimethylglutaric acid and (+)-α-methylglutaric acid showed the formation of a quasi-racemic compound, and, therefore, (+)-α-methylglutaric acid was assigned the D-configuration.

In the first step the scission of the 1,7- or 5,7-bond is predictable from the fact that a stable tertiary biradical is formed. The preference of the 1,7-bond scission over the 5,7 must result from the 2-methyl group influence. Step 2, the scission of the 5,6-bond to give a diolefin, is in accord with the fact that cyclobutane gives ethylene on pyrolysis.[15] These two steps are fundamentally those proposed by Burwell, who used the 1,4-biradical mechanism to explain the isomerization of α- and β-pinene.[16]

The cyclization of the diolefin probably occurs by a free radical initiator produced in the system as shown in step 3. The least substituted carbon of the double bond is usually attacked. Step 4, the intramolecular addition of a free radical to the least substituted carbon of the double bond, and 5, the intermolecular abstraction of a hydrogen atom, complete the chain-initiating reaction. Steps 6 and 7, similar to 4 and 5, complete the chain-propagating reaction.

The above mechanism is in agreement with the experimental fact that all the products of the reaction are optically active; no radical nor double bond is formed at the optical center in the mechanism steps.

Experimental

Preparation of Pinane.—The pinane used was prepared by hydrogenating α-pinene, b.p. 155.5–157.0°, n^{20}D 1.4662, $[\alpha]^{29}$D +31.4°, in the presence of nickel–Kieselguhr catalyst[17] at 60–70° and an initial pressure of 70 atm. The pinane was fractionated on a Podbielniak Hypercal column and possessed the following properties: b.p. 167.5–168.0°, n^{20}D 1.4620, d^{20}_4 0.8580, $[\alpha]^{21}$D +10.28°.

Apparatus.—The apparatus consisted of a Pyrex reaction tube heated by a thermostatically controlled vertical furnace. The pinane was fed into the reaction tube, containing 120 ml. of $^1/_8$ in. copper punchings, by a liquid feed pump. The lower end of the tube was connected to a liquid receiver, which in turn was attached to ice and Dry Ice–acetone traps and finally to a gas-collecting bottle filled with saturated brine solution.

Procedure.—During the reaction the temperature was maintained at 498–505°, and the liquid flow rate was 50–60 ml./hr. The reaction of 805 g. of pinane gave 795 g. of liquid product, 3.2 l. of gas not condensable at −78°, and no condensable gas. The liquid product was fractionated on a Podbielniak Hypercal distilling column, and the residue from the distillation was further fractionated on a Piros Glover spinning band column (H. S. Martin and Company, Evanston, Ill.). The final residue of high-boiling liquid amounted to 48 g. Permanganate tests[18] showed all the distilled fractions contained unsaturated hydrocarbons.

Analysis for Unsaturation.—The quantitative hydrogenations were conducted at room temperature using glacial acetic acid as a solvent and platinum oxide as a catalyst. The amount of liquid sample used absorbed 200–250 ml. of hydrogen, thus minimizing errors.

Structure Proof of the Diolefin Pinane Isomer (II).—Chromatographic separation of diolefin-rich fractions from the thermal reaction by the method of Mair and Forziati[7] using 100–200 mesh high grade silica gel (Davison Chemical Corp., Baltimore, Md., Grade 923) and absolute alcohol as an eluant gave pure diolefin in about 50% yield of the amount of diolefin in the charge. The appearance of no new bands in the infrared spectrogram of the diolefin after separation showed that the diolefin did not isomerize on the silica gel. The 500° reaction gave a diolefin having the following

(15) C. T. Genaux and W. D. Walters, This Journal, **73**, 4497 (1951); C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6196 (1953).

(16) R. L. Burwell, Jr., *ibid.*, **73**, 4461 (1951).

(17) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(18) V. N. Ipatieff, W. W. Thompson and H. Pines, This Journal, **70**, 1658 (1948).

properties: b.p. 158–159°, n^{20}D 1.4386, $[\alpha]^{28.5}$D +5.42°, H number 2.02. A conjugated impurity, 2–5%, was detected by its absorption in the ultraviolet. The reaction of pinane at 448–452° and a liquid flow rate of 18–22 ml./hr. gave a diolefin having the following properties after chromatographic separation: b.p. 158–159°, n^{20}D 1.4370, d^{20}_4 0.7573, $[\alpha]^{22}$D +4.04°; MRD calcd. 47.44, found 47.77. This diolefin did not absorb in the ultraviolet. Comparison of the infrared spectrograms of the 450° and 500° reaction diolefins showed the two were practically identical.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.96; H, 13.23.

A. Hydrogenation.—Hydrogenation of 2.1 g. of the diolefin from the 500° reaction in glacial acetic acid with platinum oxide catalyst at room temperature and atmospheric pressure gave 1 g. of 2,6-dimethyloctane having the following properties: b.p. 160.0–160.5°, n^{20}D 1.4133, d^{20}_4 0.730; MRD calcd. 48.4, found 48.6. Comparison of the infrared spectrogram of this liquid with that of a sample of pure 2,6-dimethyloctane showed the liquids were the same.

B. Ozonolysis.—In all ozonolysis experiments the diolefin from the 450° reaction was used. A solution of 7.5 g. of diolefin isomer II in 75 ml. of methylene chloride was ozonized at −78° by passing through it a stream of oxygen containing 3–4% ozone at a rate of approximately 30 l./hr. The procedure of Henne and Hill[19] was used for oxidative hydrolysis except that no sulfuric acid was added. Evolution of carbon dioxide during hydrolysis was detected by precipitation of barium carbonate from a saturated barium hydroxide solution. During addition and reflux of the ozonide 0.40 g., 10% yield, of diacetone peroxide separated from the hydrolysis solution. The diacetone was identified by its water insolubility, its explosiveness when struck, and its melting point, 130.5–131.5°.

The aqueous hydrolysis solution from two runs was concentrated by atmospheric distillation then vacuum distillation. No pure compound was found in either the aqueous or organic distillate. From the residual oil from vacuum distillation was isolated 5.8 g., 37% yield, of α-methylglutaric acid, m.p. 73–76° after three recrystallizations from benzene; neut. equiv. calcd. 73, found 74, $[\alpha]^{24}$D +8.47° in ethanol (34 g./100 ml. of solution).

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.20; H, 6.92.

Its p-bromophenacyl ester, when recrystallized from water–ethanol solution, melted at 101–103°.

Anal. Calcd. for $C_{22}H_{20}O_6Br_2$: C, 48.91; H, 3.73. Found: C, 49.17; H, 3.81.

Structure Proof of the Low-boiling Monoölefin Pinane Isomer (III).—A sample of the fractionated reaction products having the following properties: b.p. 161.1–161.4°, n^{20}D 1.4475, $[\alpha]^{24}$D +2.24°, d^{20}_4 0.8150; MRD calcd. 45.71, found 45.44, had an infrared spectrogram that was practically identical to that of 1-*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane.[4] Hydrogenation of 8.0 g. of the fractionated product, b.p. 161.1°, n^{20}D 1.4485, in 15 ml. of pentane in the presence of 1.0 g. of nickel–Kieselguhr catalyst at 50° and 70 atm. initial pressure gave 6.3 g. of liquid, b.p. 157–160°, n^{20}D 0.7872, $[\alpha]^{24}$D +1.02; MRD calcd. 46.20, found 46.15. This hydrogenated liquid's infrared spectrogram was identical to that of 1-*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane.[4]

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.33; H, 14.64.

Structure Proof of the High-boiling Monoölefin Pinane Isomer IV. A. Properties.—The liquid boiling from 169–171° was considered an approximately pure compound. It possessed the following properties: n^{20}D 1.4545–1.4560, d^{20}_4 0.8243 (n^{20}D 1.4545), $[\alpha]^{21.5}$D −1.39°, H number 0.98–0.99; MRD calcd. 45.71, found 45.43.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.70; H, 13.17.

B. Hydrogenation.—A 13.2-g. sample of liquid, b.p. 170.3–170.4°, n^{20}D 1.4547, was hydrogenated in 15 ml. of pentane in the presence of nickel–Kieselguhr catalyst at 50° and 80 atm. initial pressure. Distillation gave 9.4 g. of hydrocarbon V, b.p. 162.0–163.5°, n^{20}D 1.4428, d^{20}_4 0.8040, $[\alpha]^{24}$D −0.24°; MRD calcd. 46.20, found 46.21. The

(19) A. L. Henne and P. Hill, *ibid.*, **65**, 752 (1943).

hydrogenated liquid gave a negative test for aromatics with sulfuric acid–formaldehyde reagent.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.40; H, 14.40.

C. Hydrogenation.—An attempt to dehydrogenate hydrocarbon V over 5% platinum alumina catalyst[20] at an hourly liquid space velocity (ml. compound/ml. catalyst/ hr.) of 0.2 at 260 and 320° failed. At both temperatures the gas evolved amounted to the hydrogen adsorbed on the catalyst in pretreatment. The refractive index of the liquid before and after passing differed by only 0.0012.

D. Methyl *cis*-2-*cis*-3-Dimethylcyclopentyl Ketone (VI). —The ozonolysis procedure followed was that used by Henne and Hill.[18] Many 15-g. runs were made and the products distilled on a Piros Glover spinning band column. Only one plateau was found, b.p. 124.0–124.6° (104 mm.), $n^{20}D$ 1.4490–1.4500, d^{20}_4 0.9069 ($n^{20}D$ 1.4491); MR_D calcd. 41.57, found 41.48. The yields on various runs ranged from 50–56%. The ketone from ozonolysis gave a positive iodoform test.

Anal. Calcd. $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.28, 76.31; H, 11.20, 11.50.

Its 2,4-dinitrophenylhydrazone, when recrystallized from ethanol–pyridine solution, melted at 128.0–129.5°.

Anal. Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.23; H, 6.29; N, 17.49. Found: C, 56.23; H, 6.23; N, 17.14.

The semicarbazone of the ketone was recrystallized from ethanol–water solution; it melted at 153.5–155.5°.

Anal. Calcd. for $C_{10}H_{19}N_3O$: C, 60.87; H, 9.71; N, 21.30. Found: C, 60.71; H, 9.95; N, 21.04.

E. *cis*-2-*cis*-3-Dimethylcyclopentanecarboxylic Acid (VII).—Hypobromite oxidation of 56.0 g. of ketone VI with 187 g. of bromine, 129 g. of sodium hydroxide in 1.1 l. of water gave after distilling the products on a Piros Glover spinning band column 30.5 g., 52% yield, of acid VII, b.p. 115.0–117.0° (8 mm.), $n^{20}D$ 1.4585, d^{20}_4 1.0088; MR_D calcd. 38.48, found 38.49; neut. equiv. calcd. 142, found 142.

Its amide when recrystallized from benzene melted at 153.0–154.5°.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.25; H, 10.87; N, 10.00.

F. *cis*-2-*cis*-3-Dimethylcyclopentylmethanol (VII).—The common procedure for lithium aluminum hydride reduction was used.[21] From 20.0 g. of acid VII was obtained 16.1 g., 89% yield, of alcohol VIII, b.p. 90–91° (15 min.), $n^{20}D$ 1.4606, d^{20}_4 0.9178, MR_D calcd. 38.47, found 38.29.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 73.02; H, 8.90; N, 5.80.

G. Hydrogenolysis of *cis*-2-*cis*-3-Dimethylcyclopentylmethanol (VIII).—Alcohol VIII, 8.1 g., was hydrogenolyzed in the presence of 1.8 g. of nickel–Kieselguhr catalyst at 160–170° and an initial pressure of 80 atm. The hydrogenolysis product was fractionated on a Piros Glover column, and the fractions were analyzed by infrared spectrophotometry for all the C_7-cycloalkanes except cycloheptane.

The product consisted of 44% 1-*trans*-2-dimethylcyclopentane, 20% 1-*cis*-2-dimethylcyclopentane, 9% 1-*trans*-3-dimethylcyclopentane and 24% methylcyclohexane. Since the original C_{10}-hydrocarbon IV did not contain, according to dehydrogenation, any compounds having a hexamethylene ring, it can be concluded that methylcyclohexane resulted from a skeletal isomerization accompanying hydrogenolysis. Mass spectrometric analysis of the methane formed in the reaction showed that 71% dehydroxymethylation had occurred.

H. *cis*-2-*cis*-3-Dimethylcyclopentylcarbinyl *p*-Toluenesulfonate (IX).—To an ice-cooled solution of 7.5 g. of *p*-toluenesulfonyl chloride in 14 ml. of dry pyridine was added 4.6 g. of alcohol VIII. The solution was cooled with ice for five hours and then allowed to stand at room temperature for 19 hours. The solution was again cooled with ice and to it was added 25 ml. of concentrated hydrochloric acid. The ester which separated failed to crystallize with cooling or scratching.

I. Reduction of *cis*-2-*cis*-3-Dimethylcyclopentylcarbinyl *p*-Toluenesulfonate (IX).—The procedure for reduction of ester IX was similar to that used by Cram.[22] The oily ester IX from above was reduced with 4.0 g. of lithium aluminum hydride in 140 ml. of ether. After distillation and chromatographic separation from the olefin elimination product there was obtained a hydrocarbon X, b.p. 122.5–123.5°, $n^{20}D$ 1.4260. Infrared analysis showed that, although a few foreign minor intensity bands were present, the major component of X was 1-*cis*-2-*cis*-3-trimethylcyclopentane.

Anal. Calcd. for C_8H_{16}: C, 85.71; H, 14.29. Found: C, 85.93; H, 14.30.

Cyclization of the Diolefin Pinane Isomer II.—Pyrolysis of 18.3 g. of 3,7-dimethyl-1,6-octadiene (II), $n^{20}D$ 1.4376, at a temperature of 498–501° and a liquid flow rate of 60 ml./hr. gave 18.0 g. of liquid product $n^{20}D$ 1.4457. Distillation on a Piros Glover column and quantitative hydrogenations of the fractions showed the distilled liquid consisted of 30% diolefin and 70% monoölefin. Infrared spectrograms of the fractionated products showed the low boiling fractions contained isomer III and the high boiling fractions contained isomer IV. No bands other than those of II, III or IV were found.

Preparation of 2,6-Dimethyloctane. A. Preparation of Alloöcimene.—α-Pinene, 414 g., b.p. 155.5–157.0°, $n^{20}D$ 1.4660, was pyrolyzed at a temperature of 373–375°, and a liquid flow rate of 200–225 ml./hr. Vacuum distillation of a Podbielniak Hypercal column gave 44 g., 11% yield, of alloöcimene, b.p. 80.2° (14 mm.), $n^{20}D$ 1.5426.

B. Hydrogenation of Alloöcimene.—Hydrogenation of 9.6 g. of alloöcimene using 1 g. of nickel–Kieselguhr catalyst at 80–90° and an initial pressure of 65 atm. gave 7.7 g. of 2,6-dimethyloctane, b.p. 160.0–160.5°, $n^{20}D$ 1.4114.

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