[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY,
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# STUDIES IN THE TERPENE SERIES. XII.[1] CYCLIC ISOMERIZATION OF LIMONENE. PROOF OF THE STRUCTURE OF A NEW BICYCLOTERPENE

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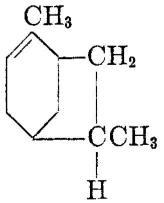
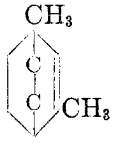
In a previous paper (1) it was shown that limonene undergoes cycloisomerization when passed over silico-phosphoric acid at 200°. Structure I, 2,6-dimethylbicyclo [3.2.1]-2-octene was assigned to the bicyclic hydrocarbon produced.



I



II

According to the preliminary results obtained, however, structure II could not be excluded.

This study has now been extended to prove the structure of the cyclic isomer produced. For that reason, large quantities of optically active limonene were passed over silico-phospsoric acid and the monomeric product obtained from the reaction, amounting to 37% based on the original limonene charged, was redistilled on a precision fractionation column. It yielded two main fractions boiling at 159–161° and 165–167° respectively, both of which consist of bicyclic hydrocarbons having the empirical formula $C_{10}H_{16}$; these two fractions represent 30% of the monomers.

In order to decide between structures I and II, the nature of the two rings was determined by degradative oxidation. The determination was based on the observation (2) that sodium salts of organic acids containing a cyclopentane ring, on hydrogenolysis, are decomposed into methane, while those containing a cyclohexane ring form aromatic hydrocarbons and methane. The unsaturated isomer was oxidized with potassium permanganate to a keto acid; the latter was reduced by the modified Wolff-Kishner method to a saturated acid, which was then subjected to hydrogenolysis. The products expected from the proposed structure I are Ia and Ib and from that of II are IIa and IIb

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[1] Presented before the XII International Congress of Pure and Applied Chemistry, September 10–13, 1951, New York, N. Y. For paper XI of this series see Ipatieff, Czajkowski, and Pines, *J. Am. Chem. Soc.*, **73**, 4098 (1951).

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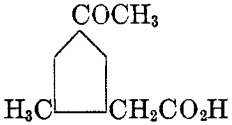
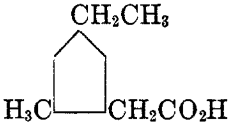
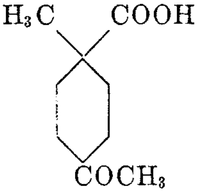
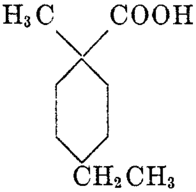

Ia

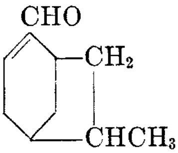

Ib

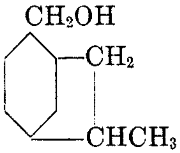

IIa

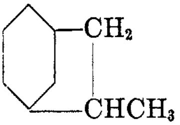

IIb

The hydrogenolysis of the aqueous solution of the sodium salt of the cyclic acid in the presence of a nickel oxide catalyst yielded methane and no aromatic hydrocarbons which favors Structure I.

In order to prove the structure of the isomer more conclusively, it was decided to degrade it to a simpler hydrocarbon. This was accomplished by oxidizing the lower-boiling (b.p. 159–161°) bicyclic isomer (I) with selenium dioxide to the corresponding aldehyde (Ic), and hydrogenating the latter to the saturated alcohol (Id). The alcohol was then hydrogenolyzed in the presence of nickel-kieselguhr catalyst to form 2-methylbicyclo[3.2.1]octane (Ie), methane, and water.

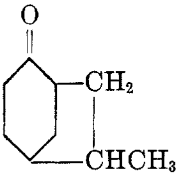

Ic

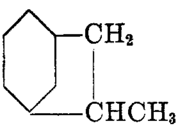

Id


Ie

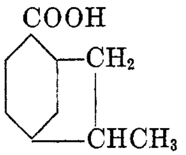
The hydrogenolysis of an alcohol to a hydrocarbon containing one carbon atom less than the original alcohol can be carried out without skeletal isomerization of the ring, even in such a case as that of conversion of myrtanol to nopinane (3).

Another method of degradation of the saturated bicyclic alcohol (Id) consisted in oxidizing the alcohol with chromic acid to 2-oxo-6-methylbicyclo-[3.2.1]octane (If) followed by a Wolff-Kishner reduction of the ketone to the bicyclic hydrocarbon (Ig)

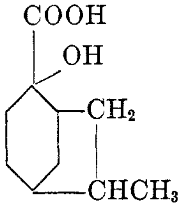

If


Ig

The oxidation of the alcohol (Id) proceeded stepwise; among the products of reaction 2-carboxy-6-methylbicyclo [3.2.1] octane (Ih) was isolated, which formed an anilide melting at 137–138°. The latter oxidized most probably to 2-hydroxy-2-carboxy-6-methylbicyclo[3.2.1]octane (Ii) which on further oxidation yielded the ketone (If). The 2,4-dinitrophenylhydrazone of the ketone melted at 140–141°.

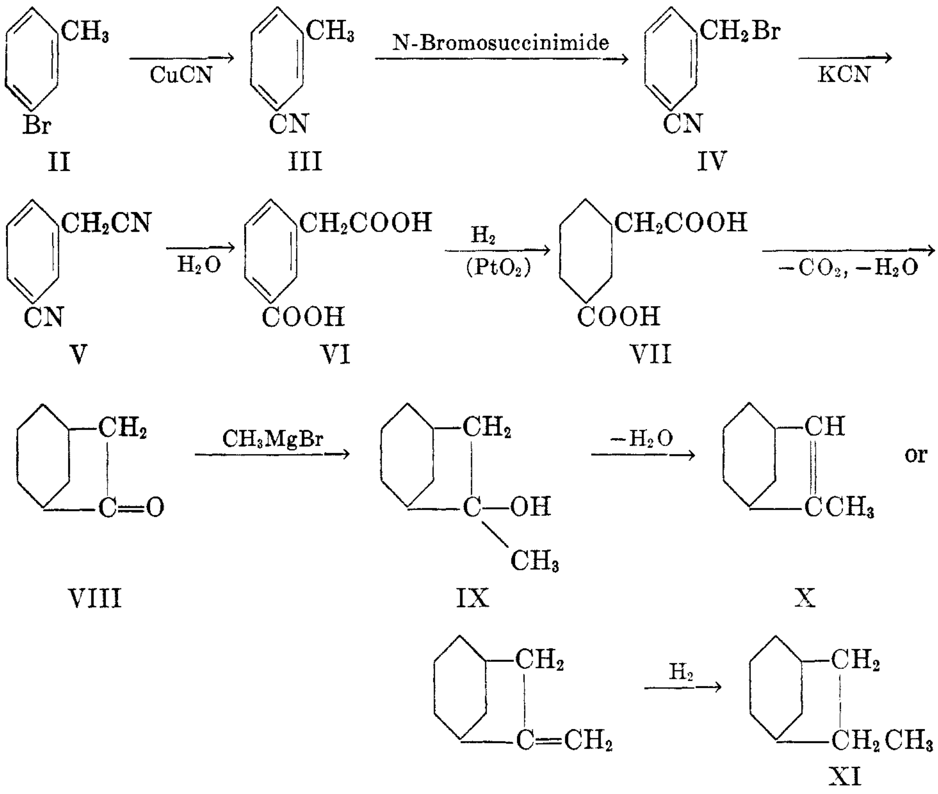


Ih



Ii

The physical constants and infrared spectra of hydrocarbons (Ie) and (Ig) were compared with a synthetically prepared 2-methylbicyclo[3.2.1]octane (XI). The synthesis of this hydrocarbon was accomplished as follows:



The physical constants and infrared absorption spectra of XI (Fig. 1) was substantially identical with that of (Ie). The infrared spectroscopic analysis of hydrocarbon (Ig) showed that it contained compound XI as a major constituent, admixed with some other hydrocarbons.

The higher-boiling monomeric isomer of limonene (b.p. 165–167°) contained the lower-boiling hydrocarbons (b.p. 159–161°) admixed with other hydrocarbons. It was found that the latter consisted of monocyclic dihydroterpenes corresponding to menthenes. The bicyclic olefinic hydrocarbons could not be separated from the monocyclic olefinic hydrocarbons by means of distillation. It was possible, however, to separate the hydrogenated bicyclic compounds from the monocyclic hydrocarbons. The latter on dehydrogenation over platinized

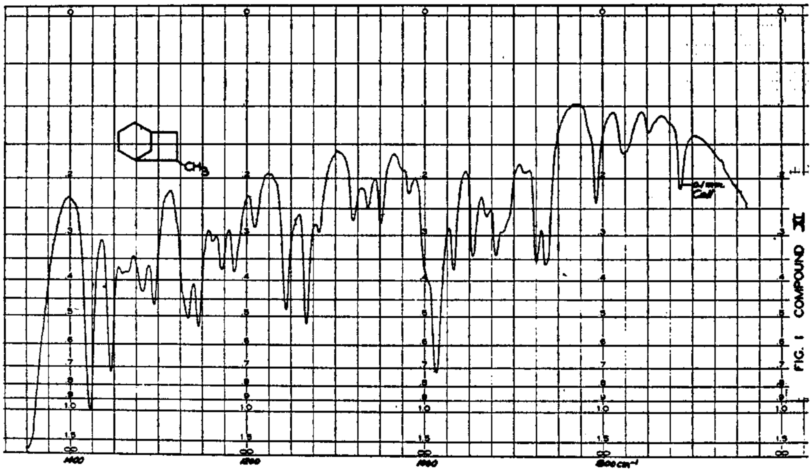


Fig. 1. Compound XI, Synthetic 2-Methylbicyclo[3.2.1]octane.

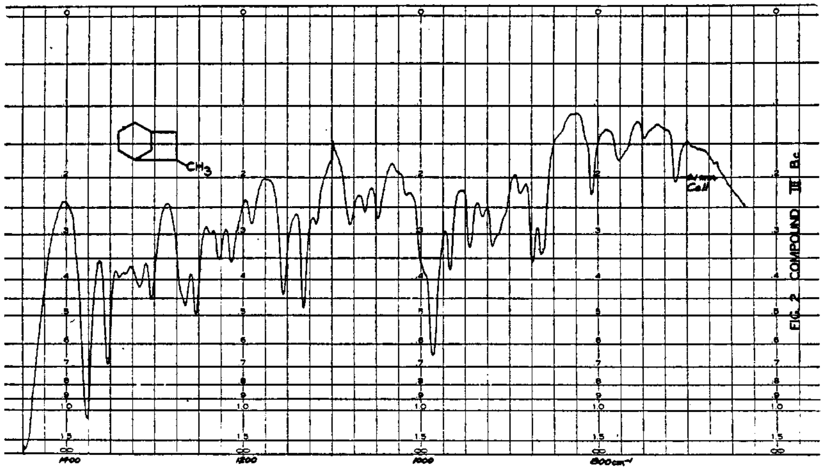


Fig. 2. Compound III Bc, 2-Methylbicyclo[3.2.1]octane from the dehydroxymethylation of 2-Hydroxy-6-methylbicyclo[3.2.1]octane obtained from the hydrocarbon boiling at 165–167°.

alumina at 280° formed *p*-cymene, while the saturated bicyclic hydrocarbons were stable towards the dehydrogenation.[4] The bicyclic saturated hydrocarbons separated from the *p*-cymene, and having the empirical formula $C_{10}H_{18}$ (XIIa), were compared with the lower-boiling fraction (b.p. 159–161°) after it was hydrogenated (XII). It was found that the infrared spectra of the two samples were practically identical (Figs. 4 and 5).

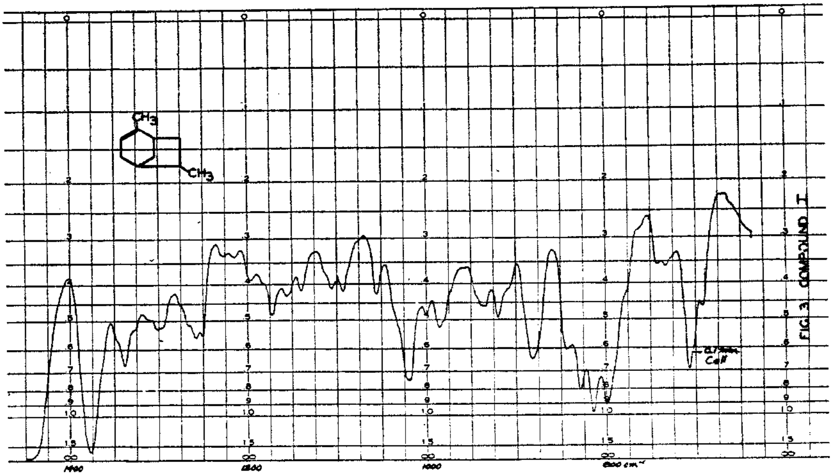


FIG. 3. COMPOUND I, 2,6-Dimethyl-2-bicyclo[3.2.1]octene from the cycloisomerization of limonene.

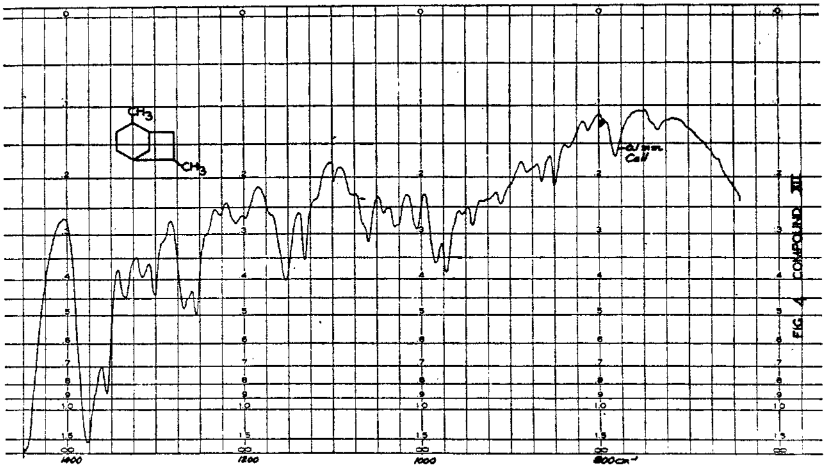


FIG. 4. COMPOUND XII, 2,6-Dimethylbicyclo[3.2.1]octane from the hydrogenation of the bicycloterpene fraction boiling at 159–161°.

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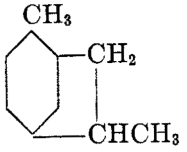
[4] The dihydroterpene obtained from the lower-boiling fractions (b.p. 159–161°) did not undergo dehydrogenation when passed over platinized alumina catalyst, indicating the absence of alkylcyclohexanes.

The higher-boiling fractions (b.p. 165–167°) were oxidized with selenium dioxide and the aldehydes produced were hydrogenated to the alcohols which



XII

were then hydrogenolyzed to $C_9$ hydrocarbons, according to the procedure described for the lower-boiling fraction. Owing to the fact that the original

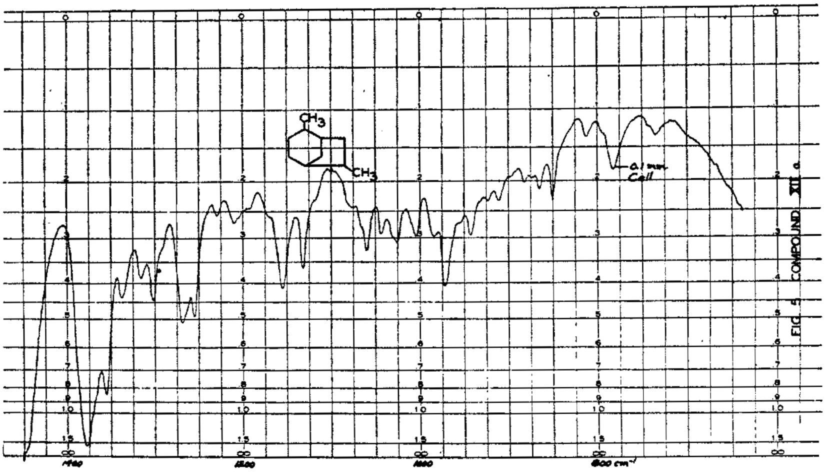
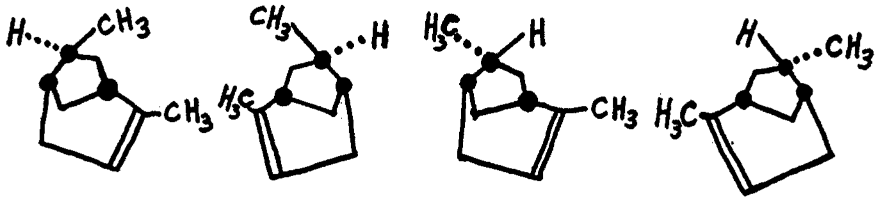


FIG. 5. COMPOUND XIIa, 2,6-Dimethylbicyclo[3.2.1]octane from the hydrogenation of bicycloterpene fraction boiling at 165–167°, followed by the removal of alkylcyclohexanes.

product contained 20% of monocyclic hydrocarbons, the final product also consisted of a mixture of mono- and bi-cyclic hydrocarbons containing nine carbon atoms. These hydrocarbons were dehydrogenated over platinized alumina. The aromatic hydrocarbons thus produced were separated chromotographically from the saturated hydrocarbons with silica gel. The bicyclic hydrocarbon IIIBc, having the empirical formula $C_9H_{16}$ and free of the monocyclic hydrocarbons, was similar, according to physical constants and infrared absorption spectra (Fig. 2), to hydrocarbon Ie produced from the lower-boiling fractions and to hydrocarbon XI (Fig. 1), prepared synthetically. Besides all the major bands, it contained a few minor bands not present in either Ie or XI, which indicates that it contained a small amount of some impurities.

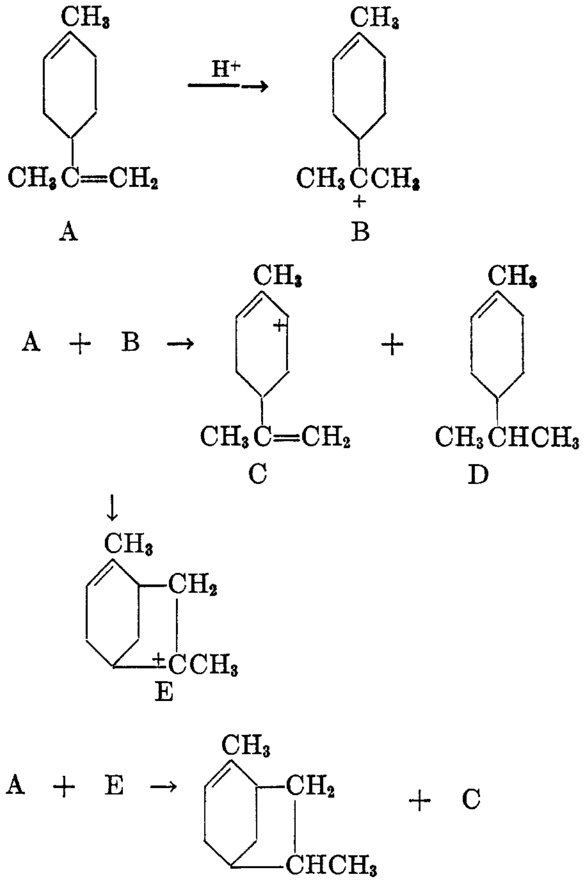
The formation of two cyclic isomers (low- and high-boiling) is best explained by stereoisomerism. A spatial formula shows that the hydrocarbon I corresponds to 4 stereoisomeric structures, divided in 2 groups of enantiomorphs ($I_1$, $I_2$); the fact that the products are optically inactive shows that each enantiomorph in each group is present in equal amounts:



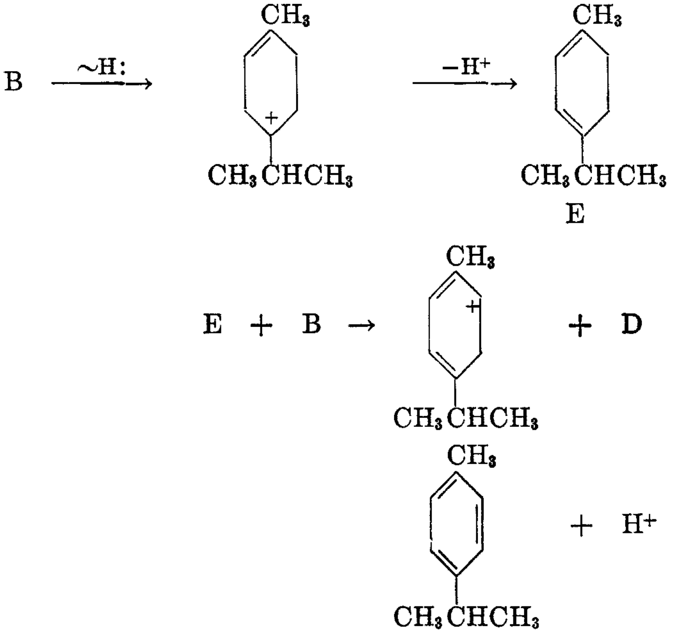
$I_1$ $I_2$

● = asymmetric carbon atom

The formation of the various hydrocarbons found in the monomeric fractions proceeds most probably through an ionic mechanism involving hydride shift and transfer as shown by the following series of equations:



This accounts for the cyclic isomer of limonene and dihydrolimonene. *Para*-cymene can be explained by the usual hydride shift and hydride transfer reactions. This can be presented by the following example which is one of the many routes for obtaining *p*-cymene.



## EXPERIMENTAL PART

### I. CYCLOISOMERIZATION OF LIMONENE

The *limonene* used for cycloisomerization was of a technical grade, obtained from Eastman Kodak; b.p. 174–176°; $n_D^{20}$ 1.4752, $[\alpha]_D$ 106°.

Ten liters of limonene were passed over 200 g. of silico-phosphoric acid (4) catalyst at 200–210° with a rate of 200 ml. per hour. The product obtained from the reaction, which was deeply colored, was steam-distilled in the presence of a small amount of sodium hydroxide. The distillate, which was optically inactive, had a terpenic odor quite different from that of limonene; the monomeric fraction having $n_D^{20}$ 1.4760, represented 50% of the starting material; the remainder consisted of polymers. The monomeric fraction did not contain any diolefins as determined with a benzene-sulfuric acid color test (1).

The distillate, after being dried, was repassed over fresh catalyst, and the product obtained was again steam-distilled; 75% of the monomeric product was obtained of which 90% distilled between 162 and 178°. The yield of monomeric product based on limonene charged was 37%.

The monomeric fraction was distilled on a column of an efficiency of 70–80 theoretical plates. The fractions which distilled up to 167° and which represented about 50% of the total product did not contain aromatic hydrocarbons. The higher-boiling fractions contained *p*-cymene, as determined by ultraviolet absorption spectra.

The monomeric fraction contained menthenes, bicyclic terpenes, and *p*-cymene; the composition of this fraction was similar to the one given in the previous paper (1).

The monomeric fractions boiling at 159–161° and 165–167° were investigated.

### II. INVESTIGATION OF THE STRUCTURE OF BICYCLIC TERPENE

This substance had b.p. 159–161°, $n_D^{20}$ 1.4621, $d_4^{20}$ 0.8566, $MR_D$ calc'd 43.5, found 43.5. Infrared absorption spectrum is given in Fig. 3.

*A. Dihydrobicyclic terpenes. (XII).* The hydrocarbon (13 g., b.p. 159–161°), dissolved in 9 ml. of *n*-pentane, was hydrogenated at 40° in the presence of 1.5 g. of nickel-kieselguhr (5) catalyst and 84 atmospheres of hydrogen. The hydrogenated product did not undergo dehydrogenation when passed over platinized alumina (6) at 270°, indicating that it was free of monocyclic hexahydroaromatic hydrocarbons. The hydrogenated product was distilled on a micro column having an efficiency of 50 theoretical plates. About 80% of the product distilled at 159–162°, $n_D^{20}$ 1.4512.

*Anal.* Calc'd for $C_{10}H_{18}$: C, 86.87; H, 13.13.

Found: C, 86.65; H, 13.30.

The infrared absorption spectra of a fraction b.p. 160° is given in Fig. 4.

*B. Potassium permanganate oxidation and the hydrogenolysis of the acid. a. Oxidation.* The procedure followed was essentially that used by Baeyer (7) as modified by Perkin and Simonsen (8) in the oxidation of pinene. In each oxidation experiment 107 g. (0.785 mole) of hydrocarbons b.p. 159–161°, and 250 g. (1.570 moles) of potassium permanganate were used. The hydrocarbons were emulsified with 600 ml. of water and cooled on an ice-bath to 2°. A hot solution (90°) of the permanganate in 1500 ml. of water was added during a period of 7 hours. During the time of addition, the temperature of the reaction was kept below 12°. After the permanganate was added, the temperature was allowed to rise to room temperature under continuous stirring. The resulting manganese dioxide slurry was filtered and washed with hot water. The filtrate was extracted with ether. The combined ether extracts gave the *neutral product* of the oxidation which was most probably a glycol.

The water solution was evaporated to about 500 ml. and neutralized by 157 g. of 37% hydrochloric acid. An oily layer separated with evolution of carbon dioxide; the solution was extracted several times with ether. The water solution was then saturated with 150 g. of ammonium chloride and extracted again with ether. The combined ether extracts gave the *acidic products* of the oxidation.

In total, 562 g. of the bicyclic terpene was oxidized.

*b. Neutral product.* The oil product (186 g.) was separated; it distilled at atmospheric pressure as follows: (*a*) b.p. 160–175°, 103 g., $n_D^{20}$ 1.4610 (colorless liquid); (*b*) 213–224°, 56 g., $n_D^{20}$ 1.4780. The residue weighed 20 g. and was of a dark color. The neutral products were not investigated.

*c. Acidic product.* The acidic material was in the form of a dark brown oil which weighed 220 g. The following fractions were separated on distillation: (*a*) 50–141°/4 mm. 54 g., $n_D^{20}$ 1.4710; N. E. (Neutral equivalent) 211; (*b*) 138–151°/3 mm., 33 g., 1.4745, N. E. 161; (*c*) 155–166°/4.5 mm., 24 g., 1.4785, N. E. 147; (*d*) 167–173°/4.5 mm., 31 g., 1.4785, N. E. 136. The remainder of the acids consisted of a high-boiling residue. All fractions showed a positive iodoform test. Fraction *c* was analyzed.

*Anal.* Calc'd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.76; N. E. 184.

Calc'd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00; N. E. 100.

Found: C, 63.61; H, 8.53.

This fraction seems to contain 35% of dibasic acids.

1. *Esterification.* The acids (fraction *c*, 11 g.) were dissolved in 25 ml. of absolute ethanol and hydrogen chloride was bubbled through for one hour. The temperature was raised to 50°, the addition of hydrogen chloride discontinued, and the solution refluxed for one hour. After cooling, the contents of the flask were poured into water, extracted with ether, washed with 10% sodium carbonate, and dried. The ketoester distilled at 138–142° at 11 mm., $n_D^{20}$ 1.4525.

*Anal.* Calc'd for $C_{12}H_{20}O_3$: C, 67.92; H, 9.45.

Found: C, 68.46; H, 9.25.

2. *Wolff-Kishner reduction of the ketoester.* The ketoester described above (8 g.) was reduced according to the method of Huang-Minlon (9). After neutralization, 6. g. of crude acid was obtained; it yielded on molecular distillation under 0.005 mm., 4.1 g. of a colorless oil, $n_D^{20}$ 1.4560.

*Anal.* Calc'd for $C_{10}H_{18}O_2$: C, 70.41; H, 10.41; N. E. 170.

Found: C, 69.85; H, 10.60; N. E. 175.

3. *Wolff-Kishner reduction of the ketoacid.* (Same procedure used as for the ketoester.) From 57 g. of ketoacid (fractions *b* and *c*), 45 g. of crude acid were obtained of which 21 g. distilled at 102–106°/2.5 mm., $n_D^{20}$ 1.4550.

*Anal.* Calc'd for $C_{10}H_{18}O_2$: C, 70.41; H, 10.41. N. E. 170.

Found: C, 70.78; H, 10.81. N. E. 165.

The *acyl chloride* was prepared by treatment with thionyl chloride; Yield 72%, b.p. 111–119° at 30 mm., $n_D^{20}$ 1.4605.

*Acid anilide,* from the acyl chloride; does not crystallize.

*Anal.* Calc'd for $C_{16}H_{23}NO$: N, 5.65. Found: N, 6.05.

4. *Hydrogenolysis of the sodium salt of the acid.* The acid (10 g.) was neutralized with 1 *N* sodium hydroxide. The solution was concentrated to 35 ml. and placed with 3 g. of powdered nickel oxide in a 450-ml. capacity stainless steel rotating autoclave. The autoclave was pressured with 100 atm. of hydrogen and heated for 3 hours at 335–345°. The maximum pressure was 180 atm.; the final pressure was 30 atm. at 20°. The gaseous product from the reaction, which was analyzed with a mass spectrograph,[5] consisted of carbon dioxide 10.7%, methane 75.4%, hydrogen 9.6%, and nitrogen 2.1.

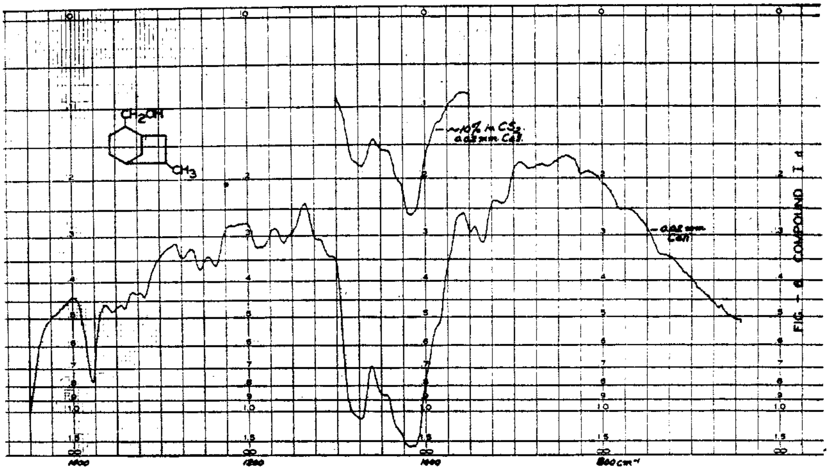


FIG. 6. COMPOUND Id, 2-Hydroxy-6-methylbicyclo[3.2.1]octane obtained from bicyclic terpenes b.p. 159–161°.

The water solution contained 3 g. of solid residue, composed of sodium carbonate.

*C. Oxidation with selenium dioxide and hydrogenolysis of the alcohol. a. 2-Formyl-6-methylbicyclo[3.2.1]-2-octene* (Ic). The procedure used was similar to that of Stallcup and Hawkins (10). A mixture consisting of 136 g. (1 mole) of the bicyclic olefin, 111 g. (1 mole) of selenium dioxide, and 400 ml. of absolute alcohol was refluxed for five hours; the alcohol was then distilled off until the temperature of the reaction mixture reached 100°. The organic material remaining in the flask was steam-distilled. The distillate, 103 g., was dried over sodium sulfate and distilled at reduced pressure. The aldehyde, 2-formyl-6-methyl-2-bicyclo[3.2.1]octene (Ic) distilled at 70–77° at 4 mm., $n_D^{20}$ 1.4912. Yield 83 g., or 56%.

*Anal.* Calc'd for $C_{10}H_{14}O$: C, 79.95; H, 9.39.

Found: C, 80.10; H, 9.59.

The *dinitrophenylhydrazone,* which was crystallized from a solution of ethanol and chloroform, melted at 225–227°.

*Anal.* Calc'd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96.

Found: C, 58.39; H, 5.68; N, 17.02.

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[5] The analysis was made by the Physics Laboratory of the Universal Oil Products Company.

The *semicarbazone*, crystallized from 95% ethanol, melted at 199°.

*Anal.* Calc'd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27.

Found: C, 64.07; H, 8.13; N, 20.16.

*b. 2-Hydroxymethyl-6-methylbicyclo[3.2.1]octane* (Id). The aldehyde (Ic) (70 g.) dissolved in 81 ml. of cyclohexane was hydrogenated in the presence of 8 g. of nickel-kieselguhr catalyst. The hydrogenation was made at 60–65° in an autoclave (see B.4 above) at 110 atmospheres of initial hydrogen pressure. The alcohol (Id) distilled at 95–98° at 6 mm., $n_D^{20}$ 1.4870, $d_4^{20}$ 0.9791. Yield 90%. The infrared spectrum is given in Fig. 6.

*Anal.* Calc'd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. $M_R$, 45.2.

Found: C, 77.60; H, 11.90; $M_R$, 45.5.

The *dinitrobenzoate* was crystallized from methanol, m.p. 76–77°.

*Anal.* Calc'd for $C_{17}H_{20}N_2O_6$: C, 58.61; H, 5.79; N, 8.04.

Found: C, 59.06; H, 5.31; N, 8.06.

*c. Hydrogenolysis of alcohol* Id. The alcohol (Id) (30 g., 0.2 mole), 4 g. of nickel-kieselguhr catalyst, and hydrogen at an initial pressure of 63 atmospheres were heated for 6 hours at 155° in the autoclave. The final pressure at room temperature was 49 atmospheres. The gaseous products from the reaction, amounting to 24.2 liters, were analyzed with a mass spectrograph. The gases consisted of 82.2% hydrogen, 15.8% methane, and the remainder carbon monoxide and carbon dioxide. Twenty four grams of the liquid product was distilled on a Piros-Glover microcolumn to give 16 g. at 149–150° at 755 mm., $n_D^{20}$ 1.4592, $d_4^{20}$ 0.8612, m.p. 6°.

The hydrocarbon (Ie) corresponded to 2-methylbicyclo[3.2.1]octane (XI).

*Anal.* Calc'd for $C_9H_{16}$: C, 87.10; H, 12.90, $M_R$ 39.4.

Found: C, 87.35; H, 12.85, $M_R$ 39.4.

The spectrum of (Ie) is very similar to that of XI, however the former contained a few minor intensity bands not found in XI. Spectrum of sample XI has one minor intensity band not present in hydrocarbon (Ie). Sample (Ie) seems to be not as pure as XI. The order of impurity is very small.

## III. INVESTIGATION OF THE STRUCTURE OF BICYCLIC TERPENE OF B.P. 165–167°, $n_D^{20}$ 1.4641.

*A. Dihydrobicyclic terpene* (XIIa). The hydrocarbon (12 g., b.p. 165–167°) was hydrogenated as described above. The hydrogenated product, $n_D^{20}$ 1.4534, was passed twice over platinized alumina at 260° in order to remove the alkylcyclohexanes present. About 20% of the product was dehydrogenated to aromatic hydrocarbons. The latter were separated from the saturated hydrocarbons chromotographically using silica gel (11). The aromatic hydrocarbons ($n_D^{20}$ 1.4917) contained, according to infrared spectral analysis, *p*-cymene as a major constituent.

The saturated hydrocarbons, free of alkylcyclohexanes distilled at 162–164°, $n_D^{20}$ 1.4529.

*Anal.* Calc'd for $C_{10}H_{18}$: C, 86.87; H, 13.13.

Found: C, 86.56; H, 13.40.

The infrared spectra of the dihydrobicyclic hydrocarbon (Fig. 5) was compared with the dihydrobicyclic hydrocarbon obtained from the isomer boiling at 159–161° (Fig. 4). Both spectra were similar, almost identical, but each of them contained impurities not common to both samples.

*B. Oxidation with selenium dioxide and hydrogenolysis of the alcohol. a. Oxidation with selenium dioxide.* The procedure used was the same as described above and 136 g. of the hydrocarbon was used for oxidation. The main product obtained from the reaction distilled at 212–223°, $n_D^{20}$ 1.4902. Yield 67 g. or 43%.

*b. Hydrogenation.* The aldehydes obtained above, 63 g., were hydrogenated at 60–75° according to the description given above in the section (IICb). About 79% of the alcohols distilled between 88–95° at 3 mm. The alcohols were redistilled on a precision column and a fraction distilling between 97 and 100° at 5 mm. was separated, $n_D^{20}$ 1.4860; it represented 50% of the total alcohols formed. The infrared absorption spectrum of this alcohol (Compound IIIBb) (Fig. 7) was similar but not identical to Id (Fig. 6). Besides dihydrobicyclic terpenic alcohols, the product contained also monocyclic alcohols.

*c. Hydrogenolysis.* Twenty grams of the alcohols (b.p. 97–100°/5 mm.) obtained above was hydrogenolyzed to the $C_9$ hydrocarbons according to the procedure described under IIBc. The gases collected from the reaction and amounting to 21.2 liters consisted of 85.5% hydrogen and 9.5% methane. The product obtained from the hydrogenolysis amounting to 16 g. was distilled over sodium; b.p. 149–154°, $n_D^{20}$ 1.4592.

The hydrocarbons obtained from hydrogenolysis were passed over platinized alumina at 260–270° according to the procedure described previously (6). The small amount of aromatics formed from the monocyclic hydrocarbons was removed by chromotographic separation as described under III A.

The bicyclic hydrocarbon, $C_9H_{16}$, (IIIBc) (Fig. 2) distilled at 152°, $n_D^{20}$ 1.4583. Its infrared spectrum was almost identical to that of XI and Ie.

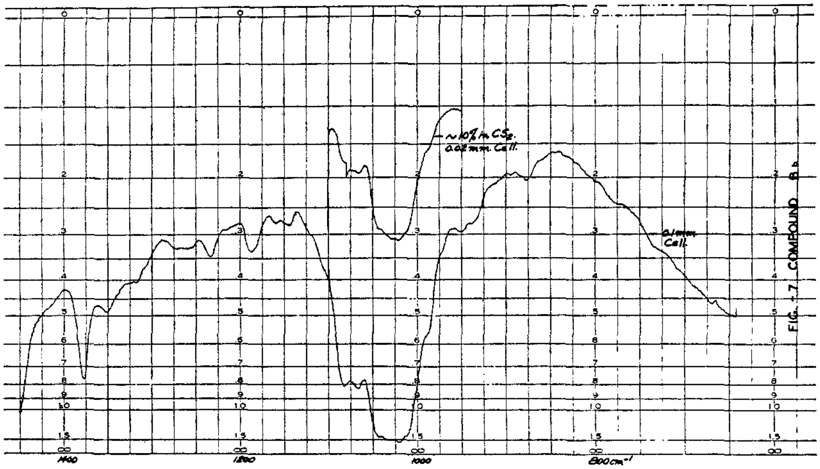

FIG. 7. COMPOUND IIIBb, Mixture of mono- and bi-cyclic alcohols obtained from the hydrocarbons fraction b.p. 165–167°.

### IV. SYNTHESIS OF 2-METHYLBICYCLO[3.2.1]OCTANE

1. *m-Toluonitrile* (III). One mole (179 g.) of *m*-bromotoluene was heated in a stainless steel rotating autoclave for 3 hours at 220–240° with 0.7 mole of cuprous cyanide and 2 moles of pyridine. The maximum pressure developed was 25 atmospheres. The yield of *m*-toluonitrile amounted to 65% (76 g.); b.p. 207.5° at 752 mm., $n_D^{20}$ 1.5252. The ultraviolet absorption spectra shows a maximum at 275 mμ, $E_m$ = 2000.

2. *m-Cyanobenzyl bromide* (IV). The use of N-bromosuccinimide as a bromination agent was reviewed by Djerassi (12). To 117 g. (1 mole) of *m*-toluonitrile in 200 ml. of carbon tetrachloride was added slowly 179 g. (1 mole) of N-bromosuccinimide containing 1 g. of benzoyl peroxide. This was refluxed for 45 minutes. The succinimide was decanted, filtered, and the filtrate washed with carbon tetrachloride. The solvent was distilled off until the liquid reached the temperature of 110°. The *m*-cyanobenzyl bromide, which crystallized out on cooling, was filtered and recrystallized from ethanol. It melted at 98.5°, b.p. 130° at 4 mm. The average yield of 7 experiments was 90% (166 g.). The ultraviolet spectra showed a maximum absorption at 275 mμ. The product was a strong lacrymator; on contact with the skin, red spots were formed slowly, which caused an itching lasting many days.

*Anal.* Calc'd for $C_8H_6BrN$: C, 48.98; H, 3.05.
Found: C, 48.28; H, 3.00.

3. *m-Cyanobenzyl cyanide* (V). The method of Reinglass (13) was used. A solution consisting of *m*-cyanobenzyl bromide, (196 g., 1 mole), sodium cyanide (49 g., 1 mole), ethanol (1000 ml.), and water (300 ml.) was refluxed for 30 minutes. About 800 ml. of liquid was then distilled off. On cooling an oily layer separated which before it had a chance to crystallize, was poured into a separatory-funnel containing ether. The ether extract was dried, evaporated to dryness, and the *m*-cyanobenzyl cyanide recrystallized from ethanol. The average yield of *m*-cyanobenzyl cyanide from six experiments was 80% (113 g.); it melted at 87°. The maximum absorptions spectra were at 272.5 and 280 mμ.

4. *Homoisophthalic acid* (VI). A solution consisting of 142 g. (1 mole) of *m*-cyanobenzyl cyanide, 500 ml. (9 moles) of sulfuric acid (*d*, 1.84), and 500 ml. of water was refluxed for 5 minutes. The organic acid produced was filtered, washed with small amounts of water, and crystallized from boiling water. The average yield of 5 experiments was 90% (160 g.). The homoisophthalic acid melted at 184–185° (bloc melting point apparatus). The ultraviolet spectra in dioxane show two maxima at 277.5 and 285 mμ.

5. *3-Carboxycyclohexylacetic acid* (VII). This was prepared by the method described by Smith (14). Homoisophthalic acid (VI) (10 g.) in 60 ml. glacial acetic acid was hydrogenated in the presence of 0.25 g. of Adams platinum oxide catalyst for 5 hours. The acetic acid solution was filtered from the catalyst, the filtrate evaporated until it almost became very viscous, and the 3-carboxycyclohexylacetic acid was crystallized from hot water. The average yield of the acid from 9 experiments was 65%. The acid melted at 150–152°.

*Anal.* Calc'd for $C_9H_{14}O_4$: C, 58.02; H, 7.50; Neut. equiv., 600.
Found: C, 58.53; H, 7.70; N. E., 600.

6. *Bicyclo[3.2.1]-1-octanone* (VIII). The cyclization was carried out according to the method of Kommpa (15). One part by weight of 3-carboxycyclohexylacetic acid and one part of lime were mixed in a porcelain evaporating dish with enough of water to form a fluid paste. The mixture was evaporated to dryness, and the solid calcium salt of the acid was transferred to a distilling flask and heated at 350–450° on a metal-bath in the presence of a stream of nitrogen. There was recovered from this operation, 0.3 equivalent weight of solid and 0.4 weight of oil. The solid was purified by sublimation, while the oily layer was distilled on a molecular still. A white crystalline material was recovered, identical with the one obtained from the solid. The average yield of 9 experiments was 40%. The bicyclo-[3.2.1]-1-octanone melted at 150–153°; the *semicarbazone* melted at 190–192°. The maximum adsorption was at 240 mμ and 260 mμ.

7. *2-Methyl-2-bicyclo[3.2.1]octanol* (IX). To an ether solution containing 0.1 mole of methylmagnesium bromide was added 9.2 g. (0.066 mole) of 2-bicyclo[3.2.1]octanone (VIII). The carbinol (IX) distilled at 197–205° and melted at 80–82°. Yield 60%.

*Anal.* Calc'd for $C_9H_{16}O$: C, 77.14; H, 11.43.
Found: C, 77.30; H, 11.92.

8. *2-Methyl-2-bicyclo[3.2.1]octene or 2-methylenebicyclo[3.2.1]octane* (X). The alcohol IX (5 g.) was dehydrated by heating slowly up to 155° with 10 g. of oxalic acid. The yield of the olefin was 68%, $n_D^{20}$ 1.4781.

9. *2-Methylbicyclo[3.2.1]octane* (XI). The olefinic hydrocarbon (X) (2.5 g.), dissolved in 1.5 ml. of acetic acid, was hydrogenated in the presence of 0.06 g. of Adams platinum oxide at room temperature in a micro hydrogenation apparatus. The 2-methylbicyclo[3.2.1]-octane distilled at 153–155°, $n_D^{20}$ 1.4655. Yield 73%. The infrared absorption spectrum is given in Fig. 1.

*Anal.* Calc'd for $C_9H_{16}$: C, 87.10; H, 12.90.
Found: C, 87.05; H, 13.00.

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## SUMMARY

The structure of the new bicycloterpene produced from the isomerization of limonene over silico-phosphoric acid catalyst was shown to be 2,6-dimethyl-2-bicyclo[3.2.1]octene.

The structure of the bicyclic terpene was determined by means of oxidation with selenium dioxide to the corresponding aldehyde which on hydrogenation formed 2-hydroxymethyl-6-methylbicyclo[3.2.1]octane. The latter on hydrogenolysis formed 2-methylbicyclo[3.2.1]octane.

2-Methylbicyclo[3.2.1]octane was synthesized from *m*-toluonitrile by well established procedures.

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## REFERENCES

(1) Ipatieff, Pines, Dvorkovitz, Olberg, and Savoy, *J. Org. Chem.* **12**, 34 (1947).
(2) Ipatieff, Germain, and Pines, *Bull. soc. chim.* (*France*) [5] **18**, 259 (1951).
(3) Ipatieff, Czajkowski, and Pines, *J. Am. Chem. Soc.*, **73**, 4098 (1951).
(4) Ipatieff, U. S. Patents 1,993,513; 2,081,065; 2,018,066; 2,020,649; 2,057,433; 2,060,871.
(5) Ipatieff and Corson, *Ind. Eng. Chem.*, **20**, 1039 (1938).
(6) Pines, Olberg, and Ipatieff, *J. Am. Chem. Soc.*, **70**, 533 (1948).
(7) Baeyer, *Ber.*, **29**, 23, 326, 1907, 2788 (1896).
(8) Perkin and Simonsen, *J. Chem. Soc.*, **95**, 1174 (1909).
(9) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).
(10) Stallcup and Hawkins, *J. Am. Chem. Soc.*, **63**, 3340 (1941).
(11) Mair and Forziati, *J. Research Nat. Bur. Standards*, **32**, 151, 165 (1944).
(12) Djerassi, *Chem. Revs.*, **43**, 271 (1948).
(13) Reinglass, *Ber.*, **24**, 2417 (1891).
(14) Smith, *J. Am. Chem. Soc.*, **71**, 81 (1949).
(15) Kommpa, *Ber.*, **36**, 3611 (1903); *Ann.*, **521**, 242 (1936).