[Contribution from the Ipatieff High Pressure and Catalytic Laboratory,
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STUDY IN THE TERPENE SERIES. XIII.[1] REACTION OF BENZENE AND p-CYMENE WITH 2,6-DIMETHYLBICYCLO[3.2.1]-2-OCTENE[2]

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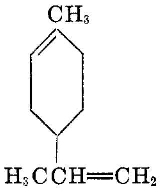
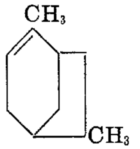
In a previous paper (1) it was shown that the cycloisomerization of limonene (I) in the presence of silico-phosphoric acid yields two plateaus on the boiling point curve at 159–161° and 165–167°. The lower-boiling fraction consisted of 2,6-dimethylbicyclo[3.2.1]-2-octene (II); the fraction boiling at 165–167° was composed of 80% of the bicyclic terpene (II) and 20% of dihydrolimonene. The bicyclic terpenes present in the two fractions on hydrogenation form the same 2,6-dimethylbicyclo[3.2.1]octane (III) as determined by infrared absorption spectra (1).



I



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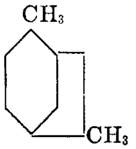

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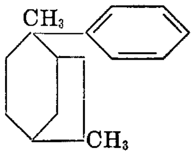

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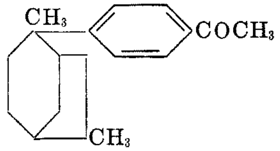

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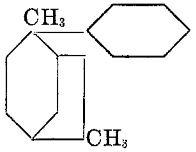

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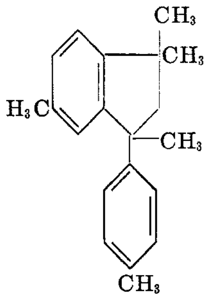

VII

The present study furnishes additional proof that the bicyclic terpenes present in the two fractions are identical. Both fractions on reaction with benzene in the presence of hydrogen fluoride form the same bicycloalkylbenzene to which the structure 2,6-dimethyl-2-phenylbicyclo[3.2.1]octane (IV) was assigned. The aromatic hydrocarbons thus produced on acetylation formed p-acetyl-2-(2,6-dimethylbicyclo[3.2.1]octyl)benzene (V), which formed in both cases a 2,4-dinitrophenylhydrazone which melted at 177–180°. In the case of the higher-boiling fraction it required five crystallizations before a constant melting point

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[1] For paper XII of this series see Ref. 1.

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was obtained; this was most probably due to the presence of 20% of dihydrolimonene in this particular fraction.

Compound IV on hydrogenation formed 2,6-dimethyl-2-cyclohexylbicyclo-[3.2.1]octane (VI).

The reaction of *p*-cymene with II (b.p. 159–161°) in the presence of either sulfuric acid or hydrogen fluoride resulted in a hydrogen transfer reaction similar to the one described previously (2). The main products of the reaction were 1,3,3,6-tetramethyl-1-*p*-tolylindan (VII) and compound III, which was identical with the compound III obtained from the hydrogenation of II.

The higher-boiling fractions (165–167°) underwent a similar hydrogen transfer reaction. The saturated hydrocarbons thus obtained contained besides compound III some *p*-menthane. The latter was dehydrogenated to *p*-cymene and separated chromatographically from the dihydrobicyclic terpene, according to the procedure described previously (1). The saturated hydrocarbon thus obtained was identical according to the physical constants and infrared spectra with the compound III.

Since the results obtained with the two fractions gave almost identical results, the experimental data only for the lower-boiling fraction will be given.

EXPERIMENTAL PART

Reaction of benzene with compound II. The hydrocarbon II, b.p. 159–161° (100 g.), was caused to react with 180 g. of benzene in the presence of 75 g. of hydrogen fluoride at 0° and according to the usual procedure (2). The hydrocarbon layer, after being washed and dried, was fractionally distilled. The main fraction, 58 g., of the condensation product distilled at 116–120° at 4 mm., n_{D}^{20} 1.5260, d_{4}^{20} 0.9558. It corresponds to compound IV.

Anal. Calc'd for $C_{16}H_{22}$: C, 89.55; H, 10.35; MR_D, 68.09.

Found: C, 89.31; H, 10.80; MR_D, 68.71.

Acetylation. Compound IV (6 g.) was acetylated according to the procedure described previously (3). The ketone (V) distilled at 170–173° at 4 mm.

Anal. Calc'd for $C_{18}H_{24}O$: C, 84.37; H, 9.37.

Found: C, 84.07; H, 9.47.

2,4-Dinitrophenylhydrazone of V, after crystallization from a solution of ethanol and chloroform, melted at 177–180°.

Anal. Calc'd for $C_{24}H_{27}N_4O_4$: C, 66.20; H, 6.50; N, 12.8.

Found: C, 65.89; H, 6.40; N, 12.5.

Hydrogenation of 10 g. of IV at 150° under 100 atmospheres of hydrogen pressure and in the presence of nickel-kieselguhr catalyst gave a saturated product which distilled at 280–284°, n_{D}^{20} 1.4937 d_{4}^{20} 0.9209.

Anal. Calc'd for $C_{16}H_{28}$: C, 87.18; H, 12.82. MR_D, 69.46.

Found: C, 87.10; H, 13.10. MR_D, 69.50.

Reaction of p-cymene with II. Compound II (66 g.) was caused to react with 132 g. of *p*-cymene in the presence of 46 g. of hydrogen fluoride at 0°. The hydrocarbon layer, amounting to 188 g., was distilled. A fraction, 137 g., boiling at 155–170° which contained 72% by volume of *p*-cymene was separated. After the removal of *p*-cymene by treatment with 15% fuming sulfuric acid, 34 g. of compound III was obtained, boiling at 163–166°, n_{D}^{20} 1.4542, d_{4}^{20} 0.8524.

Anal. Calc'd for $C_{10}H_{18}$: C, 86.87; H, 13.13. MR_D, 43.98.

Found: C, 86.75; H, 13.20. MR_D, 43.86.

The infrared spectra of this hydrocarbon were similar to the infrared absorption spectra of compound III obtained from the hydrogenation of compound II (1).

The higher-boiling compounds distilled at (a) 155–160° at 4 mm., n_D^{20} 1.5311, 14 g.; (b) 160–172°/4 mm., n_D^{20} 1.5450, 9 g.; (c) 172°/4 mm., 10 g.

Fraction b contained mainly compound VII. It formed a tetranitro derivative which melted at 251° and was identical according to melting and mixture melting point with 1,3,3,6-tetramethyl-5,7-dinitro-1-(4-methyl-3,5-dinitrophenyl)indan (2).

SUMMARY

The cycloisomerization of limonene in the presence of silico-phosphoric acid formed 2,6-dimethylbicyclo[3.2.1]-2-octene, which reacted with benzene to form a condensation compound. In the presence of *p*-cymene and of hydrogen fluoride, a hydrogen transfer reaction occurred resulting in the formation of 2,6-dimethylbicyclo[3.2.1]octane.

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