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STUDIES IN THE TERPENE SERIES. XV.[1] CYCLOISOMERIZATION OF α- AND β-PINENE, α-TERPINEOL, AND 1,8-TERPIN HYDRATE[2]

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It was shown previously (1, 2) that cycloisomerization of limonene in the presence of silico-phosphoric acid catalyst yields a bicyclic hydrocarbon, 2,6-dimethylbicyclo[3.2.1]-2-octene (I). Further study of the reaction with α-pinene (II) and β-pinene (III), α-terpineol (IV), and 1,8-terpin (V), under similar conditions was indicated, since it seemed to be a valid assumption that this reaction would change part of these terpenes into the intermediate necessary for the formation of the bicyclohydrocarbon mentioned above; polymerization of a small portion was also expected.

It was indeed found that these terpenes yielded a monomer amounting to 50–80 mole-% based on the starting material and consisting chiefly of the unsaturated bicycloterpene, as well as aromatic hydrocarbons and dihydrolimonenes, which were separated by the procedure used in the previous study with limonene. Diolefins were absent from the products of all the reactions inasmuch as the test with sulfuric acid and benzene gave a yellow coloration; in the presence of diolefins the color is brown.

The various types of products formed in the reaction are summarized in Table I.

The aromatic hydrocarbons consisted, according to infrared spectral analysis, of 80–98% *p*-cymene the remainder being a mixture of *o*- and *m*-cymene.[4]

The bicyclic terpene formed from the cycloisomerization of α-pinene proved to have structure I. The structure was confirmed by oxidizing the bicycloterpene to the aldehyde, 6-methyl-2-formylbicyclo[3.2.1]-2-octene (VII), with selenium dioxide, hydrogenating the latter to the alcohol 2-hydroxymethyl-6-methylbicyclo[3.2.1]octane (VIII), and submitting the alcohol to hydrogenolysis. The hydrocarbon produced from this reaction was 2-methylbicyclo[3.2.1]octane (IX), which was identical according to physical constants and infrared spectral analysis with the synthetic hydrocarbon prepared previously (2). To confirm the similarity with the isomer obtained from limonene, the unsaturated bicycloterpene obtained from α-pinene was caused to react with benzene in the presence of hydrogen fluoride. The resulting bicycloalkylate corresponded to compound (X), since its infrared spectrum (Fig. 1) was similar to the bicycloalkylbenzene

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[1] For paper XIV of this series see Pines, Olberg, and Ipatieff *J. Am. Chem. Soc.*, in press.

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obtained from the reaction of benzene with bicycloterpene obtained from limonene. The dinitrophenylhydrazone of the acetylated bicycloalkylbenzene obtained from α-pinene had the same melting and mixture melting point as that produced from limonene (3).

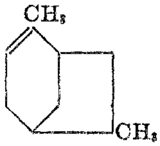
TABLE 1

THE COMPOSITION OF HYDROCARBONS PRODUCED DURING THE CYCLOISOMERIZATION REACTION

STARTING MATERIAL	HYDROCARBONS FORMED, % BY WEIGHT		COMPOSITION OF C_{10} HYDROCARBONS, %		
	C_{10}	Above C_{10}	Aromatics	Monocyclic Olefins	Bicyclic
α-Pinene	47	53	15	24	61
β-Pinene	66	34	15	27	58
α-Terpineol	63	37	17	49	34
1,8-Terpin hydrate[a]	80	20	17	51	32

[a] Ethanol solution of terpin hydrates was used; per 100 g. of glycol, 400 ml. of ethanol was used.

The experimental procedure for identifying the various compounds formed in the cycloisomerization reaction of III, IV, and V was identical. For that reason, details are given only for α-pinene



I

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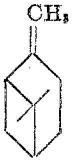

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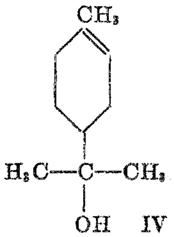

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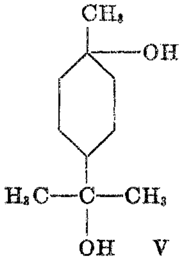

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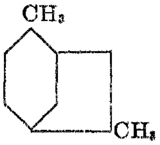

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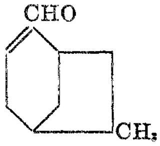

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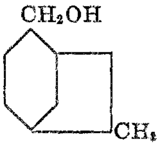

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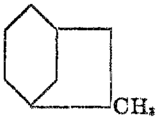

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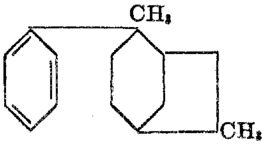

X

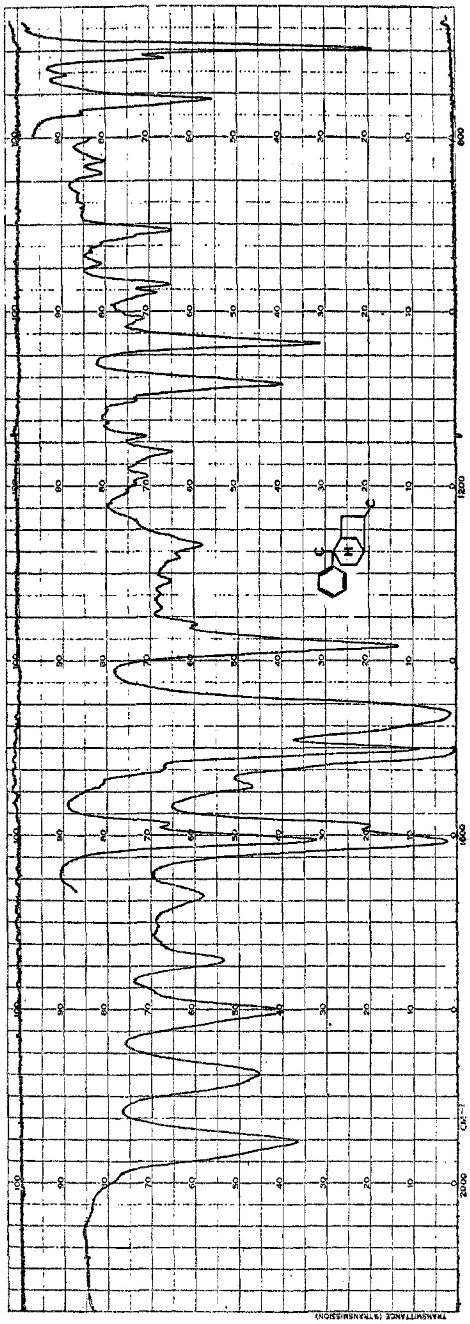

FIGURE 1. THE SPECTRA WERE TAKEN ON A PERKIN-ELMER MODEL 21 SPECTROPHOTOMETER WITH SODIUM CHLORIDE PRISM. The following cells were used: from 2150 cm^{-1} to 1500 cm^{-1} 0.2055 mm. cell thickens, from 1650 cm^{-1} to 800 cm^{-1} 0.0475 mm. cell thickens, and from 800 to 675 cm^{-1} 0.2055 mm. cell thickens and concentration of 33.11 g./liter of carbon disulfide.

EXPERIMENTAL PART

I. ISOMERIZATION OF α-PINENE

α-Pinene (650 g.) was passed over 100 ml. of 4–8 mesh U.O.P. silico-phosphoric (4) acid catalyst at 200° and HLSV[5] = 1. The products obtained from three experiments were, after being washed and dried, combined and distilled. From 1755 g. of product used in the distillation the following main fractions were separated: [1] b.p. 155°, 6.9 g., n_D^{20} 1.4470; [2] b.p. 155–170°, 795 g., n_D^{20} 1.4695; [3] 180–190°, 116 g., n_D^{20} 1.4845, and >190°, 793 g. The hydrocarbons boiling at 155-190° did not contain any diolefins according to the sulfuric acid-benzene color test.

1. *Cut* [2]. The hydrocarbon (100 g.) diluted with an equal volume of pentane was selectively hydrogenated at 50° in a 480-ml. capacity rotating autoclave in the presence of 10 g. of UOP nickel-Kieselguhr catalyst (5) and 120 atmospheres of hydrogen pressure. According to the pressure drop, 0.78 mole of hydrogen was adsorbed per mole of hydrocarbons charged.

a. Separation of aromatics. The hydrogenated product (15 g.), n_D^{20} 1.4570, was diluted with 2 volumes of pentane and passed over silica gel (6). The aromatic hydrocarbons thus separated, amounting to 2.3 g., n_D^{20} 1.4890, consisted according to infrared analysis of 90% *p*-cymene and 10% *o*- and *m*-cymene.

The saturated hydrocarbons, after removal of pentanes, distilled at 158–166°, n_D^{20} 1.4500.

Anal. Calc'd for $C_{10}H_{20}$ (monocyclic): C, 85.63; H, 14.37.
Calc'd for $C_{10}H_{18}$ (bicyclic): C, 86.87; H, 13.13.
Found: C, 86.60; H, 13.41.

b. Dehydrogenation of saturated hydrocarbons. The saturated hydrocarbons, free of aromatics, 46 g., were passed over platinized alumina (7) at 260° at an hourly liquid space velocity of 0.4. There were formed 23% of aromatic hydrocarbons which were separated chromatographically from the unreacted material. The aromatics having an n_D^{20} 1.4898 were composed according to an infrared spectral analysis of 78% *p*- and 21% *m*-cymene.

To insure a complete removal of alkylcyclohexane the saturated hydrocarbons, 31 g., recovered from the dehydrogenation at 260°, were resubmitted to a dehydrogenation at 300–305°. A total of 1115 ml. of hydrogen was liberated. The aromatic hydrocarbons were separated from the unreacted saturated hydrocarbons. The latter distilled at 160–165°, n_D^{20} 1.4500, d_4^{20} 0.8348.

Anal. Calc'd for $C_{10}H_{18}$: C, 86.87; H, 13.13.
Found: C, 86.62; H, 13.23.

The infrared spectra of the hydrocarbons obtained from the dehydrogenation were compared with compound VI obtained from *d*-limonene. The two spectra were similar to the extent of 80%.

c. Oxidation with selenium dioxide. Cut 2 was redistilled on a Podbielniak column of an efficiency of about 50–60 theoretical plates. A fraction boiling at 161–163°, n_D^{20} 1.4624, was separated. It amounted to 25% of the total. Then 72 g. of this product was oxidized with 59 g. of selenium dioxide according to the procedure described previously (2, 8). The aldehydes were distilled on a 70-plate distilling column; 42% of the product distilled at 100–104°/17 mm., n_D^{20} 1.5020.

Anal. Calc'd for $C_{10}H_{14}O$: C, 79.95; H, 9.39.
Found: C, 79.70; H, 9.47.

The *2,4-dinitrophenylhydrazone* melted after three crystallizations from ethanol at 232–233°.

Anal. Calc'd for $C_{16}H_{18}N_4O_4$: N, 17.02. Found: N, 16.92.

There was no depression in melting point when mixed with the dinitrophenylhydrazone of compound VII prepared from the cycloisomer of limonene (2).

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[5] HLSV = hourly liquid space velocity which corresponds to volume of liquid per volume of catalyst per hour.

d. Hydrogenation. The aldehydes (26 g.) were hydrogenated under pressure in the presence of nickel-Kieselguhr to the alcohol VIII, which distilled at 108°/6 mm., n_D^{20} 1.4874.

Anal. Calc'd for $C_{10}H_{18}O$: C, 77.86; H, 11.74.
Found: C, 77.73; H, 11.83.

e. Hydrogenolysis. This was run in a 125-cc. capacity stainless steel rotating bomb, which was charged with 3.8 g. of alcohol VIII, 0.5 g. of nickel-Kieselguhr catalyst, and 60 atm. of hydrogen. The final pressure at room temperature was 53 atmospheres. The hydrocarbon obtained from this reaction distilled at 153–156°, n_D^{20} 1.4574. The sample according to inrared analysis was similar to compound IX prepared synthetically (2), but contained minor intensity bands, indicating the presence of minor amounts of impurities.

f. Cycloalkylation. A 29-g. portion of the fraction boiling at 161–163°, n_D^{20} 1.4624 was contacted with 60 g. of benzene in the presence of 35 g. of hydrogen fluoride at 0°. The main product of the reaction distilled at 140–143°, n_D^{20} 1.5262, 22 g.

Anal. Calc'd for $C_{16}H_{22}$: C, 89.70; H, 10.30.
Found: C, 89.44; H, 10.33.

The infrared spectrum of this compound (Fig. 1) showed it to be similar with the corresponding compound obtained from the bicyclid isomer of limonene.

The *dinitrophenylhydrazone* of the acetylated bicycloalkylbenzene prepared by the method described previously (9) melted at 177–180°; no depression in melting point was observed when mixed with a dinitrophenylhydrazone obtained from the limonene isomer (3).

Anal. Calc'd for $C_{24}H_{27}N_4O_4$: N, 12.8. Found: N, 12.9.

II. β-PINENE

β-Pinene (240 g.), b.p. 162–163°, n_D^{20} 1.4772, was passed over 100 ml. of U.O.P. silico-phosphoric acid catalyst at 200° and HLSV = 1.5. The monomeric fraction boiled at 155–171°. The yield of the various hydrocarbons formed is given in Table I.

III. α-TERPINEOL

The alcohol (267 g.), b.p. 102–104° at 15 mm., was reacted under the conditions specified for β-pinene. The product from the reaction, after steam-distillation, yielded 168 g. of a monomeric fraction composed of a mixture of hydrocarbons (Table I).

IV. 1,8-TERPIN HYDRATE

The glycol (300 g.) dissolved in 1200 ml. of 95% ethanol was passed over 100 ml. of silicophosphoric acid at 220° and HLSV = 1.0. Part of the ethanol was dehydrated to ethylene. The product from the reaction was diluted with three times its volume with water, separated, neutralized with potassium carbonate, dried, and 186 g. of the product was distilled. The composition of the various types of products formed was determined by the method described for α-pinene, and is summarized in Table I.

SUMMARY

α-Pinene, β-pinene, α-terpineol, and 1,8-terpin hydrate when passed over silico-phosphoric acid at 200°, yielded a monomer amounting to 50–80 mole-% based on the starting material and consisting chiefly of a bicyclic terpene, 2,6-dimethylbicyclo[3.2.1]-2-octene, as well as aromatic hydrocarbons (mostly *p*-cymene), and dihydrolimonenes. The products of the reaction were similar to those obtained from limonene.

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