at room temperature forming a yellow resin within a few days when exposed to air.

trans-**Pinocarveol**.—Fractions boiling at 103–105° (20 mm.) formed a *p*-nitrobenzoate which after repeated crystallization from hexane melted at 96.5–97° and showed no optical activity in alcohol. From the mother liquors an optically active ester, m.p. 90–91.5°, $[\alpha]\text{D}$ −45.5° (2% in alcohol) was obtained. Saponification of the inactive ester gave *dl-trans*-pinocarveol; m.p. 14°, $n^{20}\text{D}$ 1.5042, d^{20}_4 0.9887. From the oxidized *l*-α-pinene (run 2) distillate the *p*-nitrobenzoate melted at 90.5–91.5°, $[\alpha]\text{D}$ +39.3° (5% in benzene) and gave on saponification *d-trans*-pinocarveol; $n^{20}\text{D}$ 1.4977, d^{20}_4 0.979, $[\alpha]\text{D}$ +70.8° (3% in ethanol). The terminal double bond gives a relatively strong band at 6.06 μ and a very strong band at 11.18 μ in the infrared absorption spectrum. A small band at 5.80 μ may indicate partial isomerization to pinocamphone.

trans-**Verbenol**.—The fractions which boiled at 108–109° (20 mm.) formed a *p*-nitrobenzoate which after repeated crystallization from hexane melted at 99–100° and was optically inactive. The optically active ester, m.p. 81.5–82°, $[\alpha]\text{D}$ +171° (2% in alcohol) was obtained from the mother liquors. Saponification of the racemic ester gave *dl-trans*-verbenol; m.p. 13–14°, $n^{20}\text{D}$ 1.4914, d^{20}_4 0.9650. Quick freezing of the *dl*-alcohol at −20° gave a crystalline form which melted at 1–2°, recrystallized on further warming and remelted at 13–14°. The alcohol derived from *l*-α-pinene gave a *p*-nitrobenzoate which melted at 79–82°. Repeated crystallization from hexane gave higher and broader melting ranges indicative of enrichment of the *dl*-form. Saponification of the ester gave *l-dl-trans*-verbenol; $n^{20}\text{D}$ 1.4923, d^{20}_4 0.969, $[\alpha]\text{D}$ −87.0° (5% in ethanol). The infrared spectrum was identical to the spectrum of the racemic form. The infrared spectrum shows bands at 6.00 and 12.15 μ assignable to the substituted cyclic double bond and a pair of very strong carbon–oxygen bands at 9.75 and 10.00 μ.

Verbenone.—Fractions boiling at 110–111° (20 mm.) formed a semicarbazone which melted at 207–208° after repeated crystallization from ethyl acetate. The ketone purified by way of the semicarbazone, $n^{20}\text{D}$ 1.4944, d^{20}_4 0.9749, $[\alpha]\text{D}$ +121.9°, showed an absorption maximum ε 6,450 at 253.0 mμ in methanol. The infrared spectrum showed the conjugated carbonyl band at 5.95 μ and conjugated double bond bands at 6.15 and 11.60 μ.

The semicarbazone derived from oxidized *l*-α-pinene melted at 208–209° and gave on hydrolysis *l*-verbenone $n^{20}\text{D}$ 1.4961, d^{20}_4 0.9731, $[\alpha]^{25}\text{D}$ −253.5°.

trans-**Carveol**.—The highest boiling fractions obtained from the oxidation of *l*-α-pinene gave a *p*-nitrobenzoate. m.p. 72–91°, which could not be optically purified by recrystallization from hexane. Saponification of the ester gave *l-dl-trans*-carveol; $n^{20}\text{D}$ 1.4944, d^{20}_4 0.946, $[\alpha]\text{D}$ −88.6° (5% in ethanol). The infrared spectrum was identical to the spectrum of *trans*-carveol.

Acknowledgment.—The authors gratefully acknowledge the helpful comments and suggestions of Dr. L. A. Goldblatt during the early phases of this work and the assistance of Mrs. Mary N. Woodroof in determining the infrared spectra. The authors are especially indebted to Dr. J. P. Bain of the Glidden Company, Jacksonville, Florida, for the authentic specimen of myrtenal and carveol used in this work.

OLUSTEE, FLORIDA

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Study in the Terpene Series. XXVI.[1] Disproportionation of *d*-Limonene in the Presence of Palladium Hydroxide–Barium Sulfate Catalyst

BY H. E. ESCHINAZI[2] AND HERMAN PINES[3]

RECEIVED SEPTEMBER 16, 1955

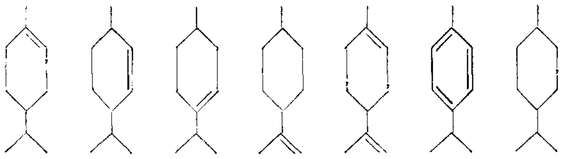
It was previously reported that limonene under reflux in the presence of palladium hydroxide–barium sulfate catalyst underwent hydrogen disproportionation to form *p*-cymene and 8(9)-*p*-menthene. It has now been found that *p*-cymene and a mixture composed of 33% *l*-*p*-menthene, 59% 3-*p*-menthene and only 8% of *trans*-8(9)-*p*-menthene are obtained.

It was reported[4] that the disproportionation of *d*-limonene (V) at its reflux temperature and in the presence of palladium hydroxide–barium sulfate catalyst proceeded by a two-step process involving a hydrogen transfer reaction. In step A *d*-limonene was rapidly converted into an equimolar mixture of *p*-cymene (VI) and *p*-menthene. From the boiling point, refractive index and from the disappearance of optical rotation it was concluded that the cycloölefin produced consisted only of 8(9)-*p*-menthene (IV). In step B the *p*-menthene was disproportionate to *p*-cymene and *p*-menthane (VII).

$$\text{(A)}\quad 2\text{C}_{10}\text{H}_{16} \longrightarrow \text{C}_{10}\text{H}_{14} + \text{C}_{10}\text{H}_{18}$$

$$\text{(B)}\quad 3\text{C}_{10}\text{H}_{18} \longrightarrow \text{C}_{10}\text{H}_{14} + 2\text{C}_{10}\text{H}_{20}$$

In an attempt to prepare compound IV by the above method it has now been found that when the reaction was interrupted at step A, the *p*-menthenes present actually consisted of an isomeric mixture composed of 33% of 1-*p*-menthene (I), 59% of 3-*p*-menthene (III) and only 8% of *trans*-8(9)-*p*-menthene (IV).



I II III IV V VI VII

The 1-*p*-menthene was optically inactive even when isolated from reactions interrupted before the completion of step A. It was observed that contrary to previous reports[4] the reaction involving step B had begun while 10% of *d*-limonene remained unreacted *via* step A. Evidence for this was furnished by the presence of small amounts of *p*-menthane in the reaction product.

The composition of the products obtained from the reaction was determined by a fractional distillation to separate isomers III and IV, b.p. 165–166°, from the mixture of I and VI, b.p. 175–176°.

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[1] For paper XXV of this series see H. E. Eschinazi and H. Pines, *J. Org. Chem.*, **20**, 1667 (1955).

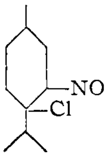
[2] Vladimir Ipatieff Postdoctoral Fellow, 1953–1955.

[3] To whom requests for reprints should be addressed.

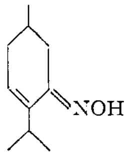
[4] H. E. Eschinazi and E. D. Bergmann, THIS JOURNAL, **72**, 5651 (1950).

The individual fractions from distillation were then chromatographed over silica gel,[5] which permitted the separation of the several isomeric *p*-menthenes as well as compounds VI and VII. The chromatographic procedure was followed by means of infrared spectra.

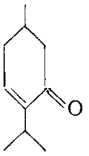
The infrared spectrum of I as separated from the reaction mixture was identical with the spectrum of (+)1-*p*-menthene, ($\alpha^{25}{\rm D}$ +96°), obtained by the hydrogenation of *d*-limonene.[6] Compound III, which was formed in the largest amount, had an infrared spectrum similar to the one reported by Frank and Berry.[7] Its structure was proved chemically by conversion to the nitrosochloride VIII followed by conversion of the latter, *via* an intermediate oxime (IX), to the 3-*p*-menthene-5-one (X)



VIII



IX



X

Compound IV had a spectrum identical to that of *trans*-8(9)-*p*-menthene prepared by Stern[8]; the latter on hydrogenation formed *trans*-*p*-menthane. The 8(9)-*p*-menthene reported by Frank and Berry[7] is most probably the *cis* isomer.

Table I contains the physical constants and the characteristic analytical infrared peaks of pure *p*-menthenes which were isolated from the reaction mixture after distillation and a repeated chromatographic separation. Further chromatographic treatment did not change the infrared spectra of these compounds.

TABLE I

PHYSICAL CONSTANTS AND CHARACTERISTIC INFRARED PEAKS OF PURE *p*-MENTHENES FROM THE REACTION OF *d*-LIMONENE WITH PALLADIUM HYDROXIDE–BARIUM SULFATE CATALYST

Compound	B.p., °C.	$n^{20}{\rm D}$	Characteristic infrared peaks, μ
I	176–176.5	1.4578	8.62, 11.0, 12.56
II[a]	169[b]	1.4504	8.94, 12.0, 13.78
III	166–167	1.4514	8.75, 11.18, 12.38
IV	165.5–166.5	1.4538	6.15, 11.3

[a] Obtained by synthesis as described under Materials. [b] Distilled at 121° under 190 mm. of pressure.

The composition of the products from the step A reaction of *d*-limonene is summarized in Table II.

Since the *p*-menthenes obtained from the reaction of *d*-limonene were composed only of isomers I, III and IV, it was of interest to determine what happens to 2-*p*-menthene (II) in the presence of the palladium catalyst under the same experimental conditions specified for *d*-limonene. For that reason (+)-*trans*-2-*p*-menthene was synthesized. A rapid loss of optical activity was observed.

TABLE II

COMPOSITION OF PRODUCT OBTAINED FROM THE REACTION OF *d*-LIMONENE

Compound	%	Rel. compn. of *p*-menthenes
1-*p*-Menthene (I)	8	33
3-*p*-Menthene (III)	14	59
8(9)-*p*-Menthene (IV)	2	8
p-Menthane (VII)[a]	14[b]	
p-Cymene (VI)	57[c]	
d-Limonene (V)	5[d]	

[a] *p*-Menthane formation was negligible when the reaction was stopped before 90% of the limonene had reacted. [b] Consisted, according to infrared spectra, of the *trans* isomer only. The infrared spectra of *cis*- and *trans*-*p*-menthane were made available to us by Hercules Powder Co., Wilmington, Del. [c] *p*-Cymene was estimated by means of ultraviolet spectroscopy. [d] The *d*-limonene was isolated by chromatography from the high boiling fraction. Its estimation through the 11.3 μ peak in the infrared was in agreement with the estimation based upon the optical rotation of the sample.

The product which resulted from the reaction consisted of a mixture of *p*-menthenes I, III and IV, as well as products resulting from hydrogen disproportionation, namely, VI and VII, exactly as in the case of *d*-limonene.

Experimental

I. **Materials.** *d*-**Limonene** (V).—A crude sample of limonene obtained from orange oil[9] was steam distilled and the distillate after drying was flash distilled under reduced pressure at 110–120° over sodium. The *d*-limonene thus purified had an optical rotation of $\alpha^{25}{\rm D}$ +101°, $n^{20}{\rm D}$ 1.4726.

(+)-*trans*-**2-*p*-Menthene** (II).—This hydrocarbon was prepared from 1-menthyl *p*-toluenesulfonate,[10] according to the procedure of Hückel and co-workers[11]; its optical rotation was $\alpha^{25}{\rm D}$ +106°, $n^{20}{\rm D}$ 1.4504 and b.p. 121° at 190 mm.

Palladium hydroxide–barium sulfate catalyst was prepared according to the method previously described.[4]

II. **Reaction with** *d*-**Limonene.**—Eight hundred ml. of V was heated at reflux temperature with 3 g. of palladium hydroxide–barium sulfate catalyst, according to the method reported previously.[4] The reaction was interrupted near the conclusion of step A, when about 5% of the *d*-limonene still remained. The liquid product, which was recovered in almost quantitative yield, had an optical rotation $\alpha^{25}{\rm D}$ +5° and $n^{20}{\rm D}$ 1.4718. It was distilled on a 50-plate bubble cap column at 37 mm. pressure. Three main fractions were separated: (1) b.p. 83.2–86.0°, $n^{20}{\rm D}$ 1.4476–1.4525, 23%; (2) 86.0–90.8°, $n^{20}{\rm D}$ 1.4620–1.4770, 25%; (3) 90.8–92.5°, $n^{20}{\rm D}$ 1.4830, 50%. Fractions 1 and 2 were again redistilled on Hypercal Podbielniak column and the various cuts were chromatographed,[5] using samples ranging from 7 to 70 ml. The various cuts or in some cases combination of cuts from chromatographic separation were analyzed by means of infrared spectroscopy. In total ten samples were chromatographed and about 35 infrared spectra were taken after chromatography. The amount of *p*-cymene was further confirmed by ultraviolet spectroscopy using 273 mμ as the analytical peak.

8(9)-*p*-Menthene (IV) has a characteristic sharp peak at 6.3 μ and for that reason it was possible to estimate its presence with a high degree of accuracy. The determination of the concentration of compounds I and III was based on the wide and strong infrared peaks given in Table I. It was found that when the presence of I and III in a mixture of hydrocarbons exceeded 70% their respective concentrations could not be accurately determined by calculation. For that reason mixtures of pure *p*-menthenes of known composition were prepared and their spectra compared with that of the samples from the experiment. An accurate deter-

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(6) V. N. Ipatieff, H. R. Appell and H. Pines, THIS JOURNAL, **72**, 4260 (1950).

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(9) Kindly donated by Minute Maid Corp., Plymouth, Florida.

(10) E. R. Alexander and A. G. Pinkus, THIS JOURNAL, **71**, 1786 (1949).

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mination of the concentration of the respective hydrocarbons was achieved when the infrared spectra of the synthetic mixture matched that of the sample obtained from the reaction of *d*-limonene.

The composition of the product obtained from the reaction of *d*-limonene is given in Table II.

Determination of the Structure of III.—(±)-3-*p*-Menthyl nitrosyl chloride (VIII) was prepared from a pure sample of 3-*p*-menthene which was separated by chromatography from the product of reaction of *d*-limonene. The nitrosyl chloride which was obtained by the method described previously[12] melted at 135–136° after crystallization from ethanol. The following melting points have been reported for this compound: 129°,[13a] 128,[13b] 143.5° and 113°.[13c]

Anal. Calcd. for $C_{10}H_{18}ONCl$: C, 59.01; H, 8.85. Found: C, 59.28; H, 8.55.

dl-**3-*p*-Menthene-5-oxime** (IX).—The oxime was prepared by refluxing 0.5 g. of VIII in 1 ml. of pyridine for five minutes. After the addition of 5 ml. of water, extraction with ether and evaporation, the residue was triturated with 50% ethanol, filtered and recrystallized from 50% ethanol. The oxime was obtained in the form of needles which melted at 66–67°.

Anal. Calcd. for $C_{10}H_{17}ON$: C, 71.85; H, 10.18. Found: C, 71.62; H, 10.15.

dl-**3-*p*-Menthen-5-one** (X) was obtained in 90% yield from IX by hydrolysis and steam distillation from a 5% oxalic acid solution. The ketone distilled at 88–90° at 30 mm., $n^{20}\text{D}$ 1.4730.

Semicarbazone melted at 145–146° after crystallization from 40% ethanol and after solidification it remelted at 160–161°. The m.p. has been reported as 142–143°.[13b]

Anal. Calcd. for $C_{11}H_{19}ON_3$: C, 63.16; H, 9.09. Found: C, 63.60; H, 9.27.

The 2,4-dinitrophenylhydrazone after crystallization from ethanol melted at 145–146°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.83; H, 6.02. Found: C, 57.70; H, 5.94.

III. **Reaction with (+)-*trans*-2-*p*-Menthene.**—Twenty-one ml. of II and 0.5 g. of platinum hydroxide–barium sulfate catalyst were heated in a 50-ml. flask provided with a reflux condenser. When the reaction mixture reached its boiling point the heating was stopped. After cooling the colorless liquid was optically inactive and had $n^{20}\text{D}$ 1.4558. It was decanted from the catalyst and distilled on a spinning band column of 50 theoretical plates. The various fractions were analyzed by the procedure described for the reaction with *d*-limonene. The concentration of *p*-cymene present in the various fractions was determined by means of ultraviolet spectroscopy. The amount of *p*-menthenes found was estimated by means of bromine number while *p*-menthane was calculated by difference. The infrared spectrum showed that 3-*p*-menthene was the major component of the *p*-menthene fraction. The experimental results are summarized in Table III.

TABLE III

COMPOSITION OF THE PRODUCTS FROM THE REACTION OF *trans*-2-*p*-MENTHENE

Fraction B.p., °C.	$n^{20}\text{D}$	Vol., %	Menthane, %	Menthenes, %	*p*-Cymene %
173–174	1.4448	70	76	7.5	16.5
174–176.5	1.4635	15	46	7	47
176.5–178	1.4847	15	12.5	16.5	71
Total composition			61.2	8.8[a]	30.0

[a] Major component 3-*p*-menthene.

Acknowledgment.—The authors wish to thank Miss H. Beck for the elementary analyses.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Study in the Terpene Series. XXVII.[1] Isomerization of *p*-Menthenes in the Presence of Sodium–Organosodium Catalyst[2]

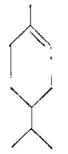
BY HERMAN PINES AND H. E. ESCHINAZI[3]

RECEIVED SEPTEMBER 15, 1955

p-Menthene isomers undergo isomerization when refluxed in the presence of a catalyst prepared by treating an excess of sodium with *o*-chlorotoluene in toluene. The composition of the product obtained from either 1- or 2-*p*-menthene after 20–22 hours of refluxing is 32% 1-*p*-menthene, 63% 3-*p*-menthene and 5% 8(9)-*p*-menthene. It is believed that this corresponds to the equilibrium mixture at about 170°. The mechanism of isomerization is discussed.

In a previous paper of this series it was reported[2] that *p*-menthadienes in the presence of sodium–organosodium catalyst undergo double bond migration and dehydrogenation to *p*-cymene. The purpose of the present investigation was to study the action of the same catalyst upon *p*-menthenes. The migration of a double bond in monoölefins catalyzed by sodium and an organosodium compound had been reported previously.[4] More recently the isomerization of olefins containing a terminal double bond to *trans*-2-olefins in the presence of organosodium compound was described.[5]

It has been found that in the presence of a catalyst composed of sodium-benzylsodium *p*-menthenes undergo reversible isomerization at their reflux temperatures, 165–175°. However unlike *p*-menthadienes they do not undergo dehydrogenation to *p*-cymene. Furthermore it has been determined that when 1-(I), 2-(II) and 3-*p*-menthene (III) react for a sufficient length of time an equilibrium is reached and the product of the reaction consists of 32% of I, 63% of III and 5% of 8(9)-*p*-menthene (IV). None of the other isomeric *p*-menthenes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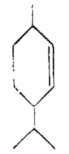
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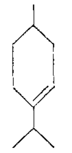
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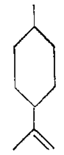
IV

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[1] For paper XXVI of this series see H. E. Eschinazi and H. Pines, THIS JOURNAL, **78**, 1176 (1956).

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