a mixture of equal amounts of the 1,2,3,5- and 1,2,4,5-isomers.

Prehnitene is converted into a mixture of 83% isodurene and 17% durene.

All of the hydrocarbons yield varying amounts of lower and higher alkylbenzenes in addition to the principal product.

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[CONTRIBUTION FROM NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING]

Vapor Phase Thermal Isomerization of α- and β-Pinene*

BY L. A. GOLDBLATT AND S. PALKIN

Thermal isomerization studies of α- and β-pinene in the past have been confined largely to the liquid state (below 160°) or to the vapor phase at relatively high temperatures (above 450°).[1] Interest in the intermediate range was stimulated by Arbuzov's discovery[2] that pyrolysis of α-pinene yielded, in addition to dipentene, the chain triolefin *allo*-ocimene (2,6-dimethyl-2,4,6-octatriene), the best yield of about 26% being obtained at 340–350°. Later, similar results were reported[3] with respect to β-pinene (20% yield of *allo*-ocimene). This finding, as will be shown presently, is erroneous.

Dupont and Dulou,[4] repeating the work of Arbuzov on α-pinene but using a copper tube filled with copper gauze, obtained in addition to *allo*-ocimene and dipentene two new monocyclic conjugated diolefinic terpenes (up to 50%) which they designated as α-pyronene (1,1,2,3-tetramethyl-3,5-cyclohexadiene) and β-pyronene (1,1,-2,3-tetramethyl-2,4-cyclohexadiene). However, Charlton and Day[5] operating chiefly in the range 380–425°, both with and without a thorium catalyst, did not find *allo*-ocimene or any of its derivatives in the pyrolysate of α-pinene.[6]

Experimental

Special precautionary measures were taken to purify the pinenes used, in view of the apparently contradictory findings of Charlton and Day, the erroneous character of the conclusions of Arbuzov with respect to the products of thermal isomerization of β-pinene,[7] the known difficulties frequently encountered in obtaining the initial terpenes in a pure state, and the consequently confusing conclusions. This included repeated fractionation *in vacuo* in efficient columns. The purified pinenes for this investigation (except for preliminary trials in which the pinenes were of somewhat lower purity) had the following characteristics

α-pinene $[\alpha]_D$ $+32.06°$; n^{20}_D 1.4645; d^{20}_4 0.8600
β-pinene $[\alpha]_D$ $-21.81°$; n^{20}_D 1.4782; d^{20}_4 0.8712

Apparatus.—The reaction apparatus was an all-glass (Pyrex) assembly (Fig. 1), consisting essentially of a charging flask (C), preheater (F), jacketed reaction tube (I) and water condenser (N_1), backed up by a packed condenser (N_2), dry-ice trap (P) and receivers (O). Hot pinene was vaporized with the aid of nitrogen gas as a carrier which was admitted through a fritted glass distributor (D), and the rate of vaporization was varied by changing the rate of flow of nitrogen or the temperature of the liquid pinene or both.

Procedure.—The pinene vapors were passed through the preheater where the temperature of the vapor (measured at Q_1) was raised to 250–300° and were then passed through the reaction tube. For the range 338–375° the temperature in each case was maintained relatively uniform along the entire length of the tube by a jacket of mercury vapor (J) from the mercury boiler (K). With the mercury vapor jacket in operation, the temperature along the entire length of the reaction tube was found to vary less than 5° and usually less than 2°, despite the fact that the reaction is strongly endothermal. The boiling point of the mercury was varied by varying the pressure [gaged by the manometer (L)] from 0.5 to 1.5 atmospheres. Temperature was measured at four points Q_1 to Q_4, by thermocouples leading to a potentiometer through ice junctions. For temperatures above 375° the outer jacket was heated electrically. In such cases, however, the temperature could not be kept uniform along the entire length of the tube, extreme variations sometimes reaching 30° or more. The maximum temperature indicated by any thermocouple was in each case recorded as the temperature of the reaction.

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[1] More than 50 literature citations on thermal reactions of the pinenes and turpentine (β-pinene constitutes about a third of American gum turpentine) are given in *Chem. Rev.*, **14**, 349–352 (1934).

[2] Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[3] Arbuzov, *ibid.* (U. S. S. R.), **6**, 297 (1936).

[4] Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935).

[5] Charlton and Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

[6] *Ibid.*, p. 95. They state: "It was not possible to isolate such a hydrocarbon [*allo*-ocimene], and it was extremely doubtful that the physical constants for the various fractions gave much indication of its presence. When the pinene was passed through the Pyrex tube without the catalyst, other conditions being the same, there was no indication of the presence of an unsaturated open chain compound."

[7] Arbuzov's findings were probably due to working with impure β-pinene, the *allo*-ocimene resulting from α-pinene present as an impurity. This is indicated by the physical constants reported: "b. p. (10.5 mm.) 44.5°; d^{14} 0.8670; n^{14}_D 1.4740; α_D -13.50; α_v/α_j 1.09." The low rotation and high dispersion indicate the presence of a considerable proportion of an impurity which, from the characteristics cited, may well be suspected of being α-pinene.

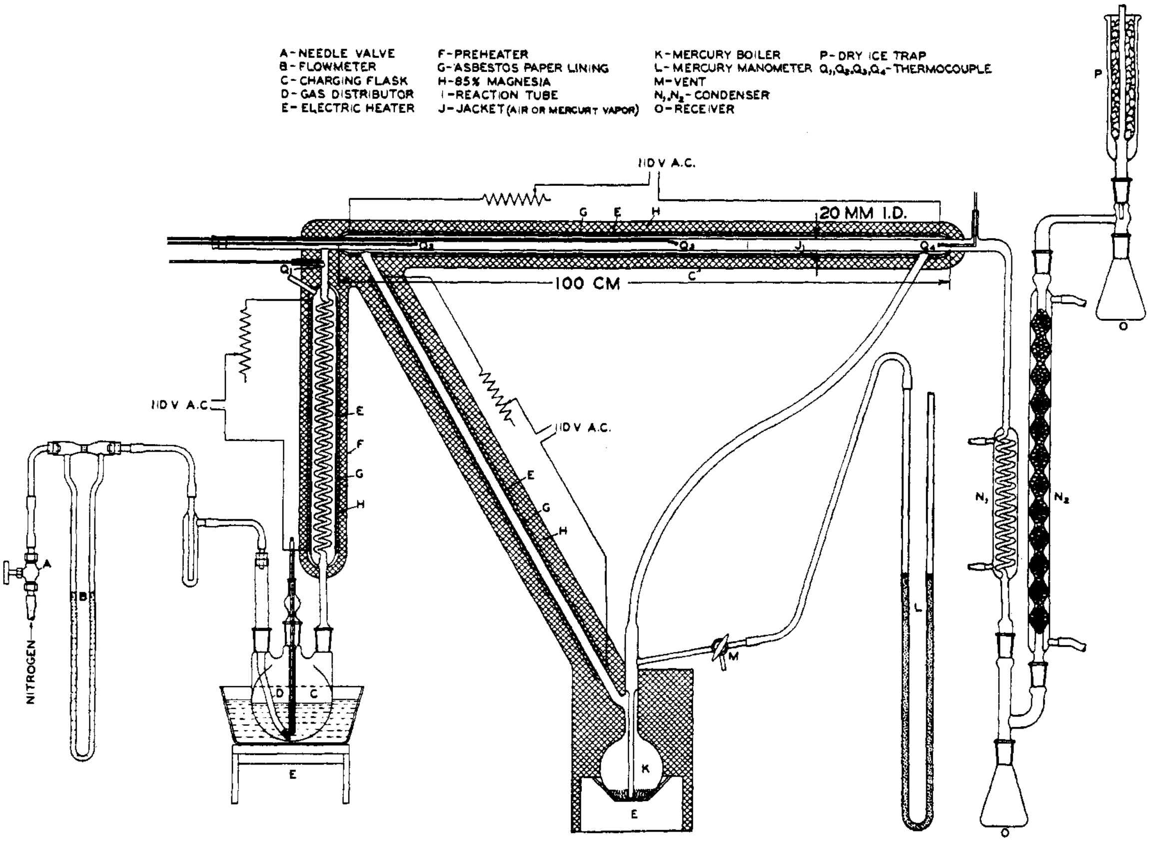

Fig. 1.—Apparatus for thermal isomerization.

Isomerization of α-Pinene.—Since *allo*-ocimene, one of the chief products formed, has a very high refractive index ($n^{20}\text{D}$ 1.544), change in the index was used as a guide in following the extent of isomerization of α-pinene. The effects of changes in temperature and throughput on refractive index for a few selected isotherms are shown in Fig. 2. In general, for any fixed temperature the refractive index increases with increase in throughput to a maximum and then decreases; similarly, for any fixed throughput, the refractive index increases to a maximum and then decreases

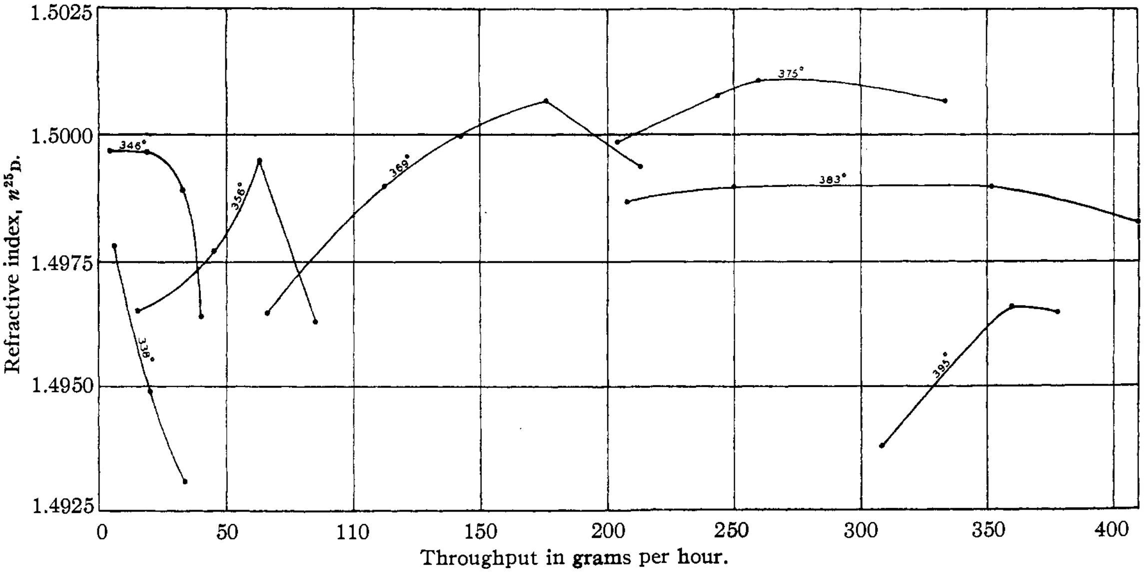

Fig. 2.—Effect of temperature and throughput on refractive index of isomerization product from α-pinene.

as the temperature is increased. The effect of an increase in throughput is more critical at lower temperatures than at higher temperatures. Maximum change in refractive index occurs at a temperature of about 375° and a throughput of 260 g. per hour. This throughput was obtained by passing a stream of 500 ml. per minute of nitrogen through the liquid α-pinene maintained at 146°. Under these conditions the yield of easily condensable product is practically quantitative, 100 g. of α-pinene consistently giving more than 97 g. of product with practically no liquid condensate in the dry-ice trap.

Fractionation and Chemical Examination.—One hundred grams of isomerization product ($[\alpha]D$ +1.42°; $n^{20}D$ 1.5025; d^{20}_4 0.8283) obtained under optimum conditions for *allo*-ocimene formation was separated into 33 fractions at 20 mm. pressure in an efficient all-glass fractionating column (equivalent to about 35 theoretical plates). The refractive index, optical rotation and density[8] of the individual fractions (except for a few densities) were determined. These are plotted together with the distillation temperature in Fig. 3.

Examination of these curves indicates that only about 15% boils in the range where the pyronenes might be expected (48–70° at 20 mm.).[9] The remainder apparently is nearly equally divided between dipentene (b. p. (20 mm.) 71.4°) and *allo*-ocimene (b. p. (20 mm.) 88.4°).

The following tests were used for identifying the individual components of the various fractions.

α-Pyronene.—The first three fractions (9 g., b. p. (20 mm.) 48.4–56.0°) were combined and a portion (5 cc.) of the mixture was heated with 3.5 g. of maleic anhydride on a steam-bath. Complete solution occurred in about one-half hour but heating was continued for another three hours. The product was fractionally distilled, and in addition to unchanged maleic anhydride there was obtained 1.7 cc. of "oil" (b. p. (20 mm.) 50–53°, shown to be largely α-pinene) and 2.65 g. of an adduct (b. p. (8 mm.) 195°). The adduct, after washing with 10 cc. of pentane and two crystallizations from methanol, melted at 91–92°.

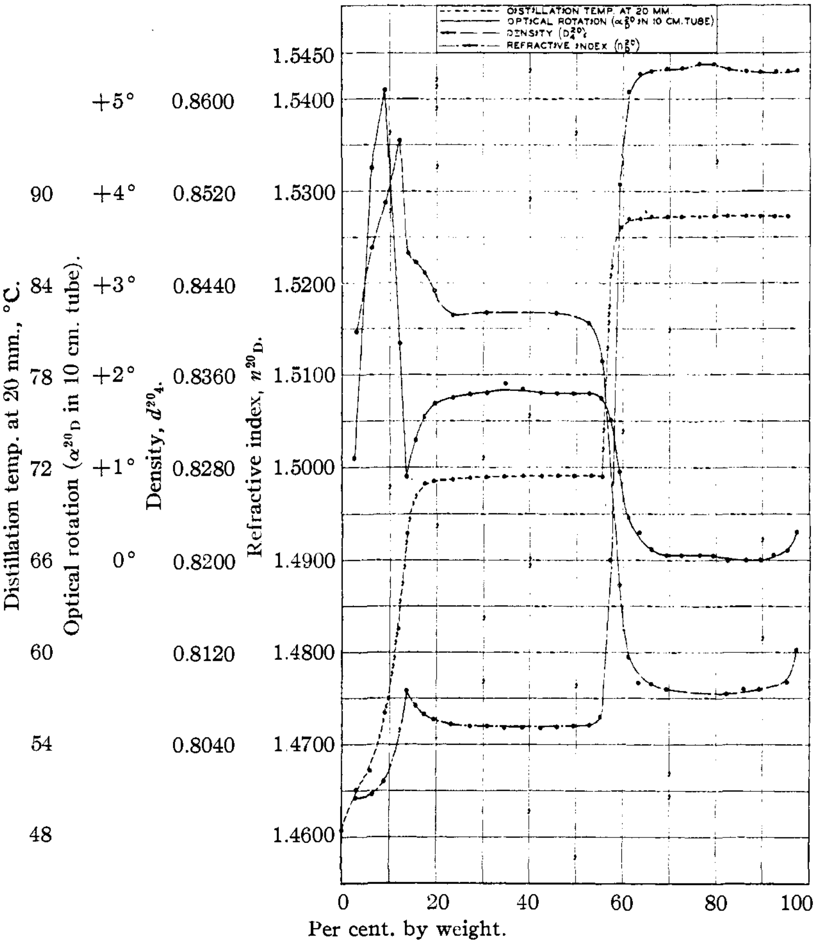

Fig. 3.—Fractional distillation of isomerization product from α-pinene.

α-Pinene (unreacted).—1.5 cc. of the unreacted "oil" mentioned above was again treated with maleic anhydride as before, but there was only a slight yellowing and the melted maleic anhydride and oil remained as two separate layers. The mixture was fractionally distilled and after washing the distillate with water and drying with sodium sulfate there was recovered 1.0+ cc. of oil (b. p. (20 mm.) 52.0°; $n^{20}D$ 1.4675) which formed a nitrosochloride, melting with decomposition at 106–107°, and apparently was essentially unreacted α-pinene.[10]

β-Pyronene.—The next three fractions (6.7 g., b. p. (20 mm.) 56.0–70.1°) which should be rich in β-pyronene, were combined and a portion (5 cc.) was condensed with 3.5 g. of maleic anhydride. This mixture reacted more readily than did the α-pyronene; at 60–70° a vigorous reaction set in and complete solution occurred immediately. However, heating on the steam-bath was continued for

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[8] The densities were determined by Mr. S. A. Hall.

[9] The pyronenes apparently have never been obtained pure. Graphs indicating the physical characteristics of the fractionated α-pinene pyrolysate were published by Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935), and also in *Atti X° Congr. Intern. Chim.*, **3**, 125 (1939). Both graphs indicate practically the same values for density and refractive index, but in the former the values are indicated as for 15° and in the latter for 25°. The constants for the purest α-pyronene are given in the latter reference as b. p. (11 mm.) 43°; $n^{25}D$ 1.4665; d^{25} 0.8347, and for β-pyronene as b. p. (8 mm.) 48–50°; $n^{25}D$ 1.4747; d^{25} 0.8401. Hultzsch, *Ber.*, **72**, 1187 (1939), without giving other physical characteristics, indicates that from the pyrolysate of α-pinene there was obtained an α-pyronene fraction, b. p. (16 mm.) 52–53°, and a β-pyronene fraction, b. p. (16 mm.) 56–57°, which gave adducts in good yield with maleic anhydride.

[10] Dupont and Dulou, *Bul. Inst. Pin*, **20**, 173 (1936); *Compt. rend. acad. sci.*, **22**, 1861 (1936), state that the nitrosochloride of α-pyronene melts at 103°.

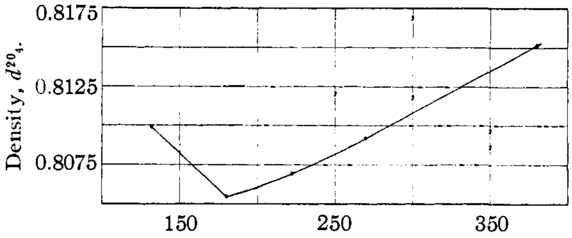

Fig. 4.—Effect of throughput at 403° in density of isomerization product from β-pinene.

another hour. The product was worked up in the same fashion as was that obtained from α-pyronene. In this way there were obtained 1.4 g. of colorless "oil" (b. p. (20 mm.) 57–70°) and 2.8 g. of adduct boiling at 185–190° at 7 to 8 mm. which, after washing with pentane and crystallization from methanol, melted at 163–164°.

Fractions 7–9 (7.7 g., b. p. (20 mm.) 70.1–71.2°), similarly combined and treated with maleic anhydride, reacted only very slightly. The major portion was recovered apparently unchanged (b. p. (20 mm.) 65–70°; n^{20}_D 1.4730) and only a few drops of adduct boiling at 185–195° at 8 mm. were obtained.

Dipentene.—3.5 cc. of a fraction boiling at 71.4° (20 mm.) was treated with 2 cc. of bromine according to the method of Godlewski.[11] After evaporation of the ether, the crystalline mass was recrystallized from methanol, yielding 2.3 g. of product which melted at 124.5–125.5° and showed no depression in melting point when mixed with an authentic sample of dipentene tetrabromide.

***allo*-Ocimene.**—Three fractions boiling at 88.4° (20 mm.) were combined, and 5.9 g. of the mixture was treated with 4.4 g. of maleic anhydride. An exothermal reaction occurred as soon as the maleic anhydride melted, but heating on the steam-bath was continued for another hour. The product was then distilled, yielding 8.8 g. of adduct boiling at 188° at 8 mm. This was washed with pentane. After two recrystallizations from hexane it melted at 83–84°.

From these data, rough calculations indicate that the product obtained by the isomerization of α-pinene at 375° contains about 3% unchanged α-pinene, about 12% of α- and β-pyronene, about 42% dipentene and 40% *allo*-ocimene.

Isomerization of β-Pinene

Preliminary experiments with β-pinene of about 95% purity ([α]D −20.69; n^{20}_D 1.4790; d^{20}_4 0.8689; α_v/α_i = 1.057) indicated that, unlike α-pinene, change in refractive index was too small to be useful, therefore, change in density was used as a guide in following the extent of isomerization. In general, for any fixed throughput the change in density increases to a maximum and then decreases with an increase in temperature, and for any fixed temperature, increases with increase in throughput to a maximum and then decreases. Figure 4 indicates the manner in which density changes with an increase in throughput at 403° (the optimum temperature).

The optimum conditions for producing the maximum change in density (optimum production of myrcene) were found to be a temperature of about 403° and a nitrogen flow of about 400 ml. per minute, with the liquid β-pinene at a temperature of 160–161°. Under these conditions, about 175 g. of isomerization product is produced per hour. Purified β-pinene ([α]D −21.81°; n^{20}_D 1.4782; d^{20}_4 0.8712), isomerized under these conditions, was converted practically quantitatively to an isomerization product having the following physical characteristics: ([α]D −14.93; n^{20}_D 1.4730; d^{20}_4 0.8053).

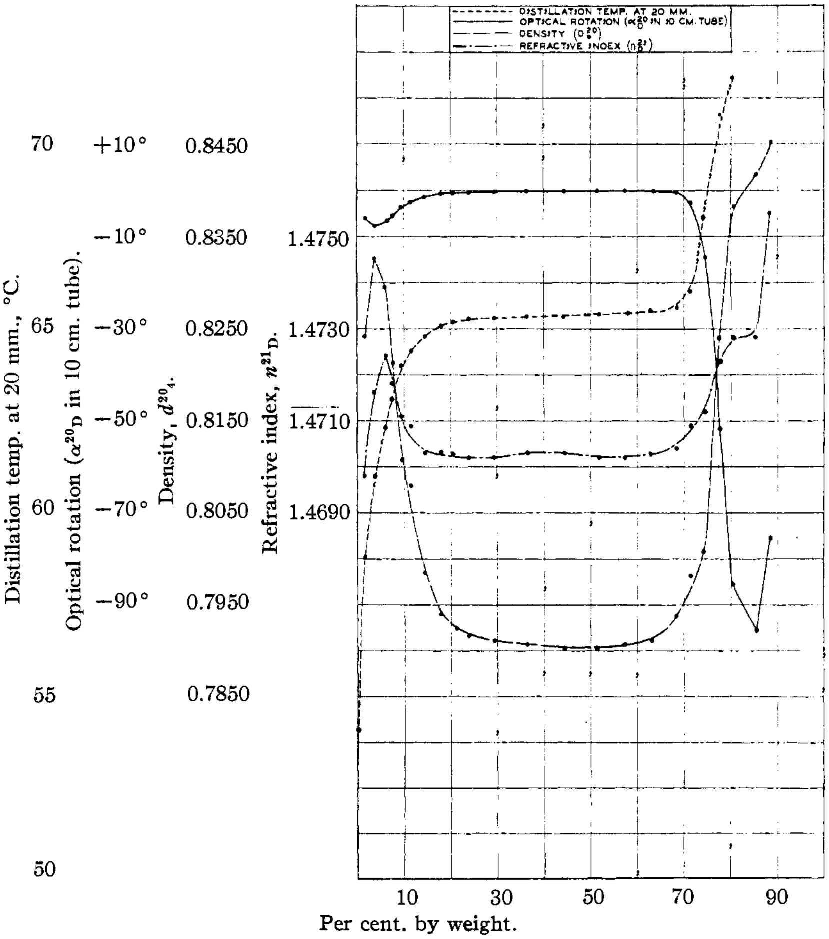

Fig. 5.—Fractional distillation of isomerization product from β-pinene.

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(11) Godlewski, *Chem.-Ztg.*, **22**, 827 (1898).

Fractionation and Chemical Examination.—Six hundred grams of this isomerization product was separated into 24 fractions at 20 mm. pressure in an efficient all-glass fractionating column packed with glass helices and the density, refractive index and optical rotation of the individual fractions were determined. These values are plotted together with the distillation temperature in Fig. 5. The first 6 fractions (65.8 g., b. p. (20 mm.) 54.3–64.35°) together with the condensate in the dry-ice trap (2.8 g.) were combined and refractionated in an all-glass semimicro column at 20 mm. The last three distillate fractions (64.3 g.) were also combined and refractionated. The physical characteristics of the fractions thus obtained by refractionation are plotted, together with the distillation temperature, in Fig. 6.

The following tests were used to identify the individual components of the various fractions.

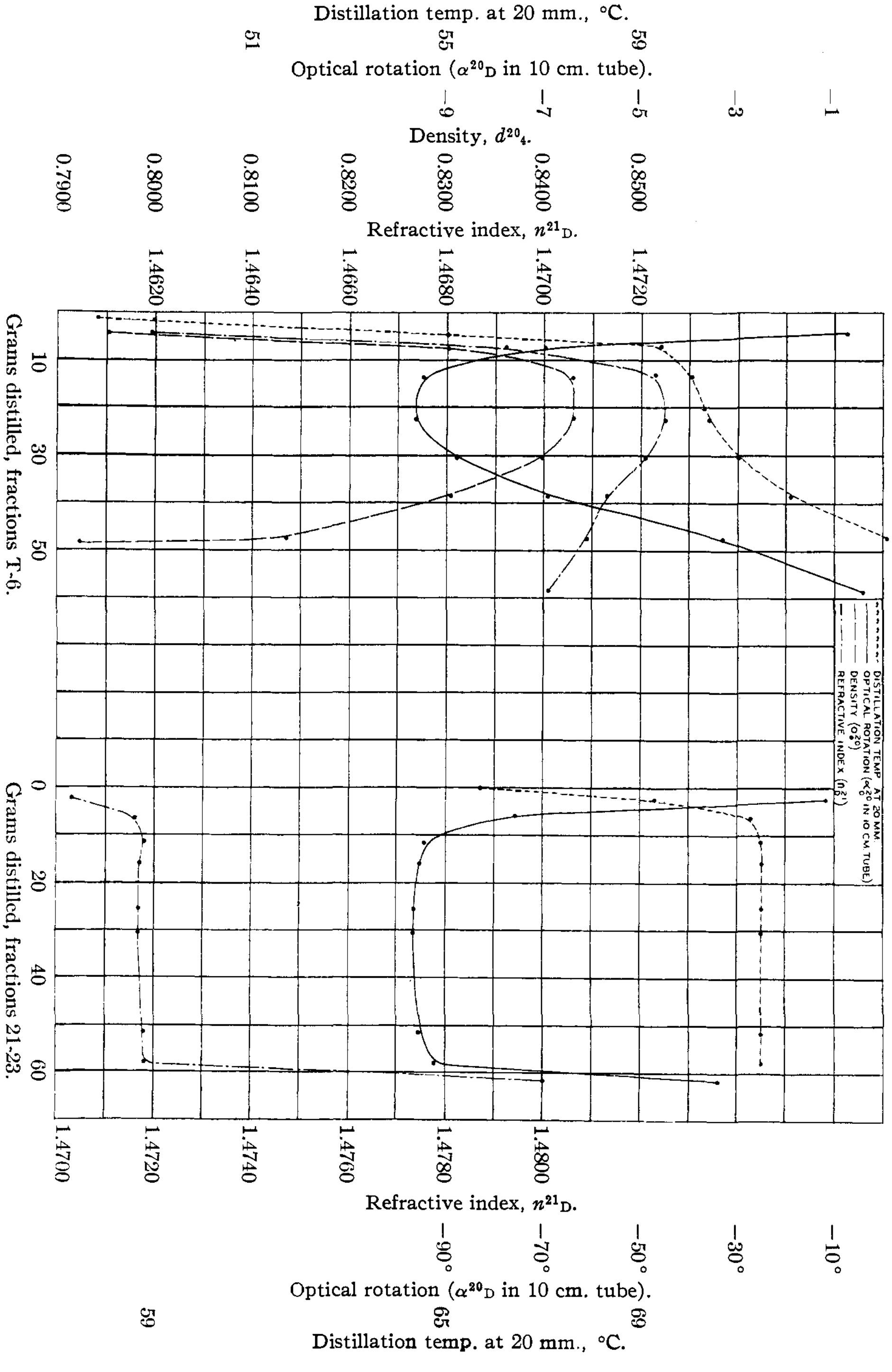

Fig. 6.—Refractionation of fractions T-6 and 21-23.

β-Pinene (unreacted).—Preliminary experiments on prepared mixtures of β-pinene and myrcene showed that a large excess of alkaline permanganate is necessary to detect β-pinene (by oxidation to nopinic acid) in the presence of myrcene. Five cc. of refractionated pyrolysate (b. p. (20 mm.) 60.05–60.4°, Fig. 6) was added to 500 cc. of a cooled solution containing 30 g. of potassium permanganate and 5.5 g. of potassium hydroxide. The solution was kept below 15° and stirred mechanically until it was decolorized (eight and one-half hours). This suspension was then filtered, evaporated to 100 cc. *in vacuo* and treated with 10 cc. of saturated sodium sulfate. The precipitated sodium nopinate, allowed to collect in an ice-box overnight and then filtered and dried, weighed 1.05 g. The free acid liberated with sulfuric acid, extracted with ether, and crystallized from benzene, melted at 128–129°.

Myrcene.—This was identified both by formation of the adduct with maleic anhydride and by reduction to the dihydro compound and conversion of the latter to the tetrabromide.

1. Maleic anhydride adduct—13.6 g. (0.1 mole) of a fraction distilling from 65.35–65.4° at 20 mm. (Fig. 5) was condensed with 10.0 g. maleic anhydride by gentle warming on the steam-bath. (*Caution:* The reaction mixture should be shaken and cooled before the maleic anhydride is completely melted as the reaction is explosively exothermal). When the vigorous reaction subsided the product was vacuum distilled. The adduct distilled at 190–195° at 8 mm.; the light-colored product, after crystallization from pentane, melted at 33–34°. The yield was practically quantitative. The dicarboxylic acid prepared by warming with 1% sodium hydroxide and acidification with 1 *N* sulfuric acid melted at 122.5–123.5° after a single crystallization from acetonitrile.

2. **Dihydromyrcene and Tetrabromide.**—27 g. (0.2 mole) of a fraction distilling at 65.4° at 20 mm. (Fig. 5) was dissolved in 250 cc. of absolute alcohol and treated with 30 g. of sodium. Warming was necessary to complete the reaction. The reaction product was poured into a liter of ice-water and the reduction product, separated and dried with sodium sulfate, was treated with 5.0 g. of maleic anhydride on the steam-bath for one hour to remove any unreacted myrcene and was then distilled at 20 mm. The distillate was washed with water to remove maleic anhydride, dried with sodium sulfate and again distilled at 20 mm. There was thus obtained 22.5 g. of a product with b. p. (20 mm.) 67–67.5°, d^{20}_4 0.7755, and n^{21}_D 1.4489. A portion (3.5 cc.) of this product which had been dissolved in a mixture of 5 cc. absolute ethyl ether and 5 cc. amyl alcohol was added dropwise to a solution of 2 cc. of bromine in 10 cc. of absolute ether maintained below 5°. The ether was evaporated in vacuum, and the crystalline product which was filtered off and crystallized once from acetonitrile melted at 88–89°.[12] Repeated crystallization from methanol and acetonitrile yielded a product with a constant melting point of 95.4–96°.

Anal. Calcd. for $C_{10}H_{18}Br_4$: Br, 69.81. Found: Br, 69.88, 70.18 (Parr bomb).

***l*-Limonene.**—3.2 cc. of refractionated pyrolysate (b. p. (20 mm.) 71.5°, Fig. 6) was brominated by the same procedure used for the preparation of the tetrabromide of dihydromyrcene. After a single crystallization from acetonitrile the white crystalline product melted at 103–104°.

Camphorene.—The residue obtained from the first fractionation of the pyrolysate was fractionated at 8 mm. Considerable polymerization occurred, but 20.5 g. of product boiling mainly at 178–179° (at 8 mm.) with n^{20}_D 1.4998 and d^{20}_4 0.8813 was obtained. Three grams of this dissolved in ether and treated with gaseous hydrochloric acid according to the method of Semmler and Jonas[13] gave 4.6 g. of a crystalline product which, after crystallization from absolute alcohol, melted at 128–131°.

A nitrosochloride test for the presence of α-pinene in this pyrolysate (first fraction, b. p. (20 mm.) 47.8–55.0°, Fig. 6) was negative.

Another 200 g. of the β-pinene thermal isomerization product was treated with maleic anhydride (in ten 20-g. portions) to remove conjugated olefins. The product was steam distilled and the physical characteristics of the distillate thus obtained were in agreement with those to be expected in an isomerization product from which the myrcene had been removed.

From these data, rough calculations indicate that the isomerization product of β-pinene contains about 3% unchanged β-pinene, about 13% *l*-limonene and about 67% myrcene. In addition, about half the residue (9.5%) consists of the dimer of myrcene, α-camphorene.

The assistance of S. A. Hall of the Naval Stores Research Division in carrying out the fractional distillations is gratefully acknowledged.

Summary

1. The vapor phase thermal isomerization of α-pinene and of β-pinene in the range favoring the formation of *allo*-ocimene from α-pinene and myrcene from β-pinene was investigated.

2. Optimum conditions for the formation of *allo*-ocimene from α-pinene giving a yield (40%) substantially higher than any hitherto reported were developed.

3. Under optimum conditions for *allo*-ocimene formation an approximately equal quantity of dipentene is formed together with minor quantities of α-pyronene and β-pyronene.

4. Vapor phase thermal isomerization of β-pinene has been shown to produce myrcene as the principal product (70% yield).

5. *l*-Limonene of singularly high rotation ([α]D − 114.9°) is formed at the same time as myrcene with a yield of about 13%.

6. Contrary to previous reports, no evidence was found for the formation of *allo*-ocimene as one of the products from the thermal isomerization of β-pinene in the vapor phase.

WASHINGTON, D. C. RECEIVED MAY 12, 1941

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[12] Enklaar, *Rec. trav. chim. pays-bas*, **26**, 164 (1907), gives 88° after repeated crystallization from methyl alcohol.

[13] Semmler and Jonas, *Ber.*, **46**, 1566 (1913).