g. of ammonium chloride in a small quantity of water. The mixture was heated at 70° and stirred for 80 minutes, cooled and poured into 1.2 l. of ice-cold 1 *N* hydrochloric acid. The slightly gummy yellow solid was recrystallized from alcohol, yielding 19.7 g. (34%) of pale yellow crystals, m.p. 246–249° (dec.). Several recrystallizations from ethanol yielded pale yellow needles, m.p. 246.5–248.5° (dec.).

(b) **From Acetaldehyde by the Sodium Acetate Method.**—To a solution of 26.6 g. of rhodanine in 120 ml. of glacial acetic acid, 4.4 g. of freshly distilled acetaldehyde and 40 g. of anhydrous sodium acetate were added. The resulting mixture was refluxed from three to five hours and then poured into 600 ml. of cold water, yielding 16.6 g. (57%) of an impure yellow solid, m.p. 236–244°. A sample was recrystallized from glacial acetic acid as pale yellow prisms, m.p. 246–248° (dec.).

(c) From **Ethylidenerhodanine.**[2a,3,4]—A mixture containing 2.2 g. of rhodanine, 1.6 ml. of ammonium hydroxide, 3 ml. of water and 40 ml. of ethanol was stirred and heated at 65–70° while 2.6 g. of 5-ethylidenerhodanine in 80 ml. of ethanol was added. Five minutes later, 1.6 g. of ammonium chloride in 10 ml. of water was added and the resulting mixture heated at 65–75° for two hours longer. The reaction mixture was cooled and poured into 650 ml. of ice-cold 1 *N* hydrochloric acid and after standing, a yellow solid precipitated slowly. The precipitate was collected, washed with water and dried, m.p. 241–246° (dec.); yield 3.3 g. (69%). After three recrystallizations, from alcohol, it was obtained as pale yellow crystals, m.p. 247–248.5° (dec.).

The products obtained by each of the three methods were shown to be identical by mixed melting point determinations.

Hydrolysis and Hydrogenolysis of 1,1-Bis-(2-thio-4-keto-tetrahydro-5-thiazolyl)-ethane.—The rhodanine derivative obtained above (III, R = CH_3; 14.6 g.) was dissolved in a solution of 30 g. of sodium hydroxide in 125 ml. of water and the resulting mixture refluxed for three hours. The cooled solution was acidified with hydrochloric acid and extracted with ether and methylene chloride. The solvents were removed on a steam-bath leaving a viscous orange-colored liquid, probably impure α,α'-disulfhydryl-β-methylglutaric acid, which was not purified further. The crude product was dissolved in 300 ml. of 10% sodium hydroxide solution and heated on a steam-bath for 70 hours during which 50 g. of Raney nickel–aluminum alloy was added in small portions.[7] At the end of this period the nickel residue was allowed to settle and the alkaline solution decanted. The solution was strongly acidified and was extracted with ether. The ethereal extract was treated with Norite, and dried over phosphorus pentoxide. Upon removal of the ether, there was obtained 2.3 g. (37%) of a light-orange oil which solidified on standing overnight. On recrystallization from benzene–ligroin and again from cyclohexane, fine white needles, m.p. 84–84.5° (lit.[10] 85–86°), were obtained. This material gave no depression of melting point when mixed with an authentic sample[10] of β-methylglutaric acid, m.p. 84.5–85°.

Dianilide of β-Methylglutaric Acid.—A sample of the acid obtained by hydrogenolysis was heated with aniline for three hours at 190–200°. The product was recrystallized from ethanol as fine white needles, m.p. 213.5–214°. This was identical with a sample prepared from authentic β-methylglutaric acid.

Anal. Calcd. for $C_{18}H_{20}O_2N_2$: C, 72.95; H, 6.80. Found: C, 73.03; H, 6.75.

The di-*p*-toluidide of β-methylglutaric acid was prepared in a similar manner and crystallized from ethanol as fine white needles, m.p. 221–221.5°. This was identical with a sample prepared from authentic β-methylglutaric acid.

Anal. Calcd. for $C_{20}H_{24}O_2N_2$: C, 74.04; H, 7.46. Found: C, 74.21; H, 7.50.

(10) R. E. Kent and S. M. McElvain, *Org. Syntheses*, **23**, 60 (1943).

DURHAM, N. C. RECEIVED APRIL 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

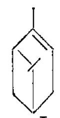
The Preparation of Ocimene from α-Pinene[1]

BY J. ERSKINE HAWKINS AND HARRY G. HUNT

Consideration of the available information led to the conclusion that ocimene is formed as an intermediate product when α-pinene is converted to alloöcimene. A method of obtaining ocimene in this reaction is presented. The refractive index of ocimene at 25° is evaluated and the application of refractive index measurements to the analysis of dipentene–ocimene mixtures is illustrated. The rate of conversion of ocimene to alloöcimene, at 159.5 and 189.5°, and the heat of activation for this conversion are determined.

In the study of the kinetics[2,3] of the thermal isomerization of *d*-α-pinene (I) it became evident that the products, predicted by a simple mechanism[4] for the reactions, would be 1-α-pinene (II), dipentene (III) and ocimene (IV).

The reaction has been considered to produce alloöcimene (V) as a primary product. Arbuzov,[5] Dupont and Dulou,[6] Goldblatt and Palkin,[7] Savich and Goldblatt,[8] and Fuguitt and Hawkins[2,9] found large amounts of alloöcimene but reported no ocimene in their products of isomerization of α-pinene. Since the completion of this work, Goldblatt has stated that he recently has detected small amounts of ocimene.[10] Arbuzov in 1934[11] suggested a mechanism for the production of alloöcimene from α-pinene in which a cyclobutane ring with an unsaturated side chain was the intermediate. Rice and Rice discussing free radicals[12] men-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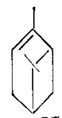
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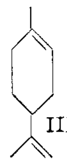
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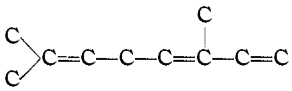
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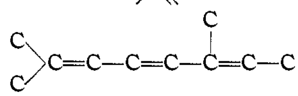
V

(1) The material included in this paper is based upon a partial abstract of a dissertation presented to the Graduate Council of the University of Florida, by Harry G. Hunt, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950, and was presented at the Southeastern Regional Meeting of the ACS which was held at Wilson Dam, Ala., Oct. 18–20, 1951.

(2) R. E. Fuguitt and J. E. Hawkins, THIS JOURNAL, **69**, 319 (1947).

(3) H. G. Hunt and J. E. Hawkins, *ibid.*, **72**, 5618 (1950).

(4) J. E. Hawkins, H. G. Hunt and R. E. Fuguitt, unpublished.

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

(6) G. Dupont and R. Dulou, *Compt. rend.*, **201**, 219 (1935).

(7) L. A. Goldblatt and S. Palkin, THIS JOURNAL, **63**, 3517 (1941).

(8) T. R. Savich and L. A. Goldblatt, *ibid.*, **67**, 2027 (1945).

(9) R. E. Fuguitt and J. E. Hawkins, *ibid.*, **67**, 242 (1945).

(10) Private communication.

(11) B. Arbuzov, *Ber.*, **67B**, 571 (1934).

(12) F. O. Rice and O. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, pp. 163–164.

tioned that α-pinene should pyrolyze to form ocimene and Rice reported the transformation of α-pinene in the vapor phase at reduced pressure to ocimene but mentioned no other products.[13]

Enklaar[14] investigated ocimene, which he obtained from natural oils, and showed that it very rapidly isomerized to alloöcimene at a temperature of about 175°. It therefore seemed probable that at the temperatures and contact times used to pyrolyze α-pinene, any ocimene which might form would be completely changed into alloöcimene. Consideration of this point led to the construction of an apparatus that would permit heating α-pinene to a sufficiently high temperature to bring about the desired reaction but would limit the time of heating so as to eliminate conversion of the ocimene to alloocimene. The description of this successful process constitutes the work described herein.

Experimental

Preparation of Materials.—The α-pinene used in this work was obtained as a 95% commercial product[15] and rectified in a Lecky and Ewell[16] distilling column, of about 60 plates at total reflux, at 20 mm. pressure and about 100 to 1 reflux ratio, to a product boiling with a 0.1° range at 52° and having a n^{25}D of 1.4631.

Apparatus.—A grid was made from number 24 B. & S. gage Nichrome wire by bending it back and forth in one plane so that the parallel wires were about 5 mm. apart. The grid was approximately 2.5 cm. square and contained about 15 mm. of wire. It was suspended about 7 mm. from and parallel to a vertical wall of a water-cooled glass condenser, as shown in Fig. 1.

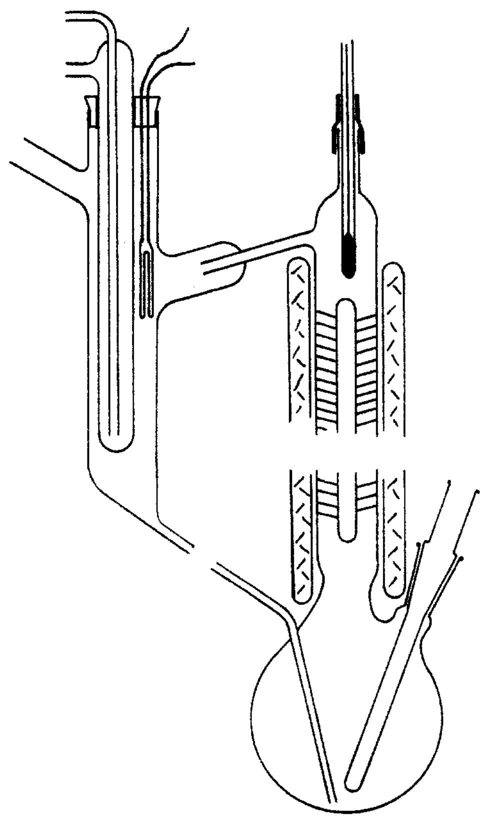

Fig. 1.—Apparatus for the production of ocimene.

(13) U. S. Patent 2,190,369, February 13, 1940.

(14) C. J. Enklaar, *Rec. trav. chim.*, **26**, 157 (1907).

(15) Furnished through the courtesy of the Naval Stores Division of the Glidden Company, Jacksonville, Florida.

(16) Lecky and Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

α-Pinene vapor at 20 mm. pressure (at 52°) was passed through the grid to the condenser at the rate of about one mole per hour. The current used to heat the grid was about 3.2 amperes. Because only a small part of the α-pinene was converted at each pass, a recycling system was employed. The condensate was returned to the pot. Since α-pinene boils at a lower temperature than any of its known isomerization products, a Lecky and Ewell[16] column, 38 mm. in diameter by 61 mm., equivalent to about 24 theoretical plates at total reflux, was interposed between the pot and the grid. The recycling was stopped when the temperature at the head of the distilling column was observed to have risen approximately one degree above the boiling point of pure α-pinene.

In a typical experiment 180 ml. of α-pinene was charged in the pot. The boil-up rate was 4 ml. per min., at a reflux ratio of 1:1. The pot temperature rose from 65 to 75°. After about 24 hours the head temperature read 54° and the process was terminated. The fraction of isomerate boiling from 70–80° at 20 mm. was separated and analyzed as described later. The n^{25}D of the fraction was 1.478–1.482. About 28% ocimene was obtained.

Yields of Ocimene.—Several batches of α-pinene were treated as described. If the grid was too cool the process was unreasonably slow, if too hot the yield of ocimene was poor. The conditions indicated above provided yields of 25 to 37% ocimene, based on the amount of α-pinene which had disappeared.

Analysis of Product

Separation of Fractions.—The product mixture was fractionated at 20 mm. in a Bower and Cooke-type column.[17] The first fraction obtained was principally α-pinene. Its degree of optical rotation was considerably lower than that of the original pinene, due to racemization.[2,8] The second fraction, boiling between 70 and 74° at 20 mm., contained limonene and ocimene. The residue consisted of alloöcimene, boiling at 88°, and its polymers.

In view of the fact that it has been shown that the pyronenes may be formed[7,9] from alloöcimene, it would not have been surprising if they had appeared among the products. However, none of the ultraviolet absorption curves supplied evidence of their presence. They were therefore believed to be absent.

Identification of Ocimene.—A sample of material boiling at 70 to 74° at 20 mm., was analyzed as described below and apparently contained about 50% dipentene. It was reduced with sodium and absolute alcohol. Dipentene is not reduced under these conditions.[18] Upon fractionation of the reduction mixture, it was found that part of the reduced material now boiled at 66–70° at 20 mm. and had an n^{25}D 1.4505. Dihydroöcimene (dihydromyrcene) has been reported to boil at 62–63° at 17 mm. and to have n^{20}D 1.4507.[19] The reduced material was dissolved in cooled ether and bromine added to it dropwise. After removal of the ether and two crystallizations from cooled water–alcohol mixtures, its melting point was 82–85°. Tetrabromodihydromyrcene has been reported to melt at 87–88°.[19] The original boiling range agrees with the value of van Romburgh,[20] 73–74° at 21 mm., and the derivatives indicate the presence of ocimene.

Ultraviolet Absorption Spectra.—The spectrum of a mixture of about 50% ocimene and dipentene was taken with a Beckman DU spectrophotometer using a dilution of 1 to 200,000. There was a strong peak at about 235 mμ, which is somewhat higher than might be expected for a compound of this structure, IV, on the basis of Woodward's rule.[21] This raises the question concerning the universal application of the rule or the correctness of the structure of the compound which is named ocimene. The settlement of this point must await the completion of further study. A sample of the same mixture was heated for an hour at 204.5°, in a sealed evacuated ampoule, and the spectrum again taken. The original peak had disappeared and a complex peak at 278 mμ, showing greater absorption than the first, and characteristic of alloöcimene,[22] appeared.

(17) J. R. Bower, Jr., and L. M. Cooke, *ibid.*, **15**, 290 (1943).

(18) F. W. Semmler, *Ber.*, **34**, 3126 (1901).

(19) F. W. Semmler and W. W. Mayer, *ibid.*, **44**, 2010 (1911).

(20) P. van Romburgh, *Proc. koninkl. Akad. Wetenschap. Amsterdam*, **3**, 454 (1900).

(21) R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

(22) R. D. Walker, Thesis, University of Florida, 1951.

Estimation of Ocimene.—In view of the fact that the boiling points of ocimene and dipentene are only 3° apart, it was not feasible to attempt an analytical distillation. Therefore, analysis by use of the refractometer was adopted.

A sample of an ocimene–dipentene mixture was carefully redistilled to remove all material boiling below 70° and all above 73° at 20 mm. Fifty grams of this material was sealed in an evacuated ampoule and held for an hour at 204.5°. This treatment converted all the ocimene to alloöcimene and its polymers. Fractionation showed 53% dipentene and 47% alloöcimene or its polymers in the heated material.

Previous studies have shown that the relation between the refractive index and composition of binary terpene mixtures are almost linear, for examples: α- and β-pinene,[23] dipentene and α-pinene,[3] dipentene and alloöcimene[2] and limonene and α-pinene.[3] Assuming a linear relationship between the index of refraction of the ocimene–dipentene mixtures, and their composition, and using $n^{25}D$ 1.5701 for pure dipentene and $n^{25}D$ 1.4790 for the unheated mixture, which was analyzed by isomerization and distillation, calculation showed that the $n^{25}D$ of ocimene is about 1.4890. This is higher than the value of $n^{18}D$ 1.4857[14] given in the literature for the natural product.

The original composition of this ocimene–dipentene mixture was also estimated from the index of refraction, $n^{25}D$ 1.5020, of the sample, observed after it was held at 204.5° for an hour. Experiment showed that the refractive index of alloöcimene decreases from 1.5420 to 1.5380 after heating for an hour at 204.5°. The refractive index of dipentene remains 1.4701. Fuguitt and Hawkins[2] showed that the index of refraction for dipentene–alloöcimene mixtures is nearly a linear function of the weight fraction of each. Calculations from these data indicate a composition of 47% alloöcimene in the heated mixture which corresponds to 47% ocimene in the original mixture.

Some samples contained small amounts of alloöcimene. This changed the refractive index of the mixture appreciably. In these cases a simple approximate method of analysis is to measure the refractive index before and after heating for an hour at 204.5°. If a, b and c represent the mole fraction, or weight fraction of alloöcimene, dipentene and ocimene, respectively, then,

$$n_1 = n^{25}\text{D before heating} = 1.5420a + 1.4701b + 1.4890c$$
$$n_2 = n^{25}\text{D after heating} = 1.5380a + 1.4701b + 1.5380c$$

Subtracting

$$n_2 - n_1 = 0.049c - 0.004a.$$

Where a is small, $n_2 - n_1 = 0.049c$ and $c = (n_2 - n_1)/0.049$. When a is large, practically all the alloöcimene can be removed by analytical distillation.

Rate of Isomerization.—The methods of determining ocimene which involve isomerization to alloöcimene depend on the reaction being complete within the time chosen for heating the sample of mixture, in this case one hour at 204.5°. Samples of an available mixture of about 70% ocimene and 30% limonene were sealed under vacuum in inch-long ampoules made from 6-mm. glass tubing. Some were held at 159.5° and others at 189.5° for various periods of time. The ampoules were opened and the index of refraction read. The data are shown in Table I. The first order reaction constant was determined from

$$k = \frac{2.3}{t} \log C_0/C = \frac{2.3}{t} \log \frac{n_\infty - n_0}{n_\infty - n_t} = \frac{2.3}{t} \log \frac{1.5203 - 1.4832}{1.5203 - n_t}$$

where n_∞, n_0 and n_t are the refractive indices of the mixture when all the ocimene is converted to alloöcimene, of the mixture before heating and of the mixture after heating for a time, t, respectively:

TABLE I

Temp., °C.	Time, min.	$n^{25}D$	k, min.$^{-1}$
159.5	9	1.4882	0.016
159.5	20	1.4925	.014
159.5	41	1.4992	.014
159.5	75	1.5083	.015
159.5	160	1.5171	.015
189.5	2	1.4900	.10
189.5	4	1.4958	.10
189.5	8	1.5042	.10
189.5	16	1.5141	.11

The $n^{25}D$ 1.5203 represents the refractive index of a mixture made up of approximately 70% alloöcimene and 30% dipentene.

From the constants contained in the table, the heat of activation for the conversion of ocimene to alloöcimene, calculated by the Arrhenius equation, is about 26,000 calories, and the half-life of ocimene at 204.5° is about 3 minutes. Thus an hour at 204.5° is adequate to completely isomerize ocimene to alloöcimene.

Discussion

The presence of large amounts of ocimene in the vapor phase isomerization products of α-pinene under the conditions described in this paper, and the fact that the half-life of ocimene is only three minutes at 204.5°, indicates that it is probably an unstable intermediate under the usual conditions employed in the formation of alloöcimene from α-pinene. The rapid rate of its disappearance, according to the first order equation, at temperatures high enough to isomerize α-pinene, would result in only small traces existing in the reaction mixtures unless the technique described above is followed. It is therefore not surprising that ocimene has not been reported previously as a product of the thermal isomerization of α-pinene in the liquid phase and so reported only once in the vapor phase process.

GAINESVILLE, FLORIDA RECEIVED JANUARY 31, 1951

(23) R. E. Fuguitt, W. D. Stallcup and J. E. Hawkins, THIS JOURNAL, **64**, 2978 (1942).