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

The Liquid Phase Thermal Isomerization of α-Pinene[1a,1b]

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Among the first studies which involved the liquid phase thermal isomerization of α-pinene was that made in 1853 by Berthelot[3] who heated French turpentine in sealed tubes at 250° for ten hours. Polymerization occurred, accompanied by a change in rotation. He noted that there was no gas formation.

Wallach[4] found that α-pinene formed dipentene and some polymerized material when heated at 250–270°.

Smith[5] heated sealed tubes of α-pinene in a temperature controlled oil-bath and measured the rate of decrease of the optical rotation of the reacting mixture. The temperature range was 184–237°. Smith made practically all of his determinations in the gas phase or in various solvents. However, in one case α-pinene remained in the liquid phase. The rate of isomerization at 184.6° was found to be of the same order of magnitude in both phases. He found it to be of first order and assumed it to be a racemization of the α-pinene, accompanied by the isomerization to limonene of a small percentage of the α-pinene.

Conant and Carlson[6] showed that dipentene was formed in this reaction both in the liquid and vapor phase at about 200°, verifying Wallach's work[4] in the liquid phase. In addition, they noted that an appreciable amount of polymerized material was formed in the tubes in which the reaction went nearly to completion.

Thurber and Johnson[7] made a similar study of α-pinene from two different natural sources. Upon fractionating approximately 20-cc. samples of the reaction mixtures, they found that most of each sample distilled above 159° at atmospheric pressure, which was higher than the boiling point of the reactant. They concluded that the reaction was not a simple racemization.

Due to the lack of agreement between the former investigators and the absence of sufficient information to clarify the course of the reactions in the liquid phase, this study was undertaken.

Recent studies[8,9,10] of the vapor phase isomerization of α-pinene showed the presence of *allo*-ocimene and α- and β-pyronene among the products. As the present investigation proceeded, it became evident that a more complete investigation of the over-all reaction made necessary a study of the effect of heat on *allo*-ocimene in the liquid phase.

Experimental

Purification of Reactants.—A commercial grade of *d*-α-pinene from wood turpentine was carefully fractionated through a five-foot length of spiral screen column of 37 mm. (1.45 inch) inside diameter.[11] This involved the separation of α-pinene from a slightly lower boiling fraction and from camphene which boils about 3° higher than α-pinene. The fact that the rotation and refractive index of the α-pinene obtained varied slightly indicates that traces of impurities were not removed. However, the amounts of these impurities were insufficient to appreciably affect the results.

The *allo*-ocimene[12] was fractionated through a four-foot spiral screen column of inside diameter 10 mm. (0.4 inch).[11]

These compounds had the following range of physical constants: *d*-α-pinene, b. p. (20.0 mm.) 52.3°; n^{25}_{D} 1.4631–1.4632; α^{25}_{D} (2 dm.) +57.52–+58.26°. *allo*-Ocimene, b. p. (10 mm.) 77–78; d^{25}_{4} 0.8050–0.8056, n^{25}_{D} 1.4518–1.5424, M_D found 53.2, calcd. without allowance for exaltation 46.98.

Procedure.—94-cc. (80-g.) portions of freshly distilled α-pinene were placed in 150–180-cc. tubes made from heavy-walled Corning G-1 glass tubing of 27 mm. (1.08 inches) inside diameter. Each filled tube was connected to a vacuum line at 3–4 mm. and evacuated for five minutes. The tubes were then sealed under vacuum. After these sealed tubes had been placed in an oil-bath and heated for the desired length of time, they were opened and the reaction mixtures analyzed by fractional distillation.

Apparatus.—The sealed tubes of α-pinene were heated in a well-insulated bath containing 5 gallons of oil agitated by two motor stirrers. Heat was supplied by two 250-watt blade heaters, one connected to the temperature control circuit and the other directly to the current source. The temperature of the bath over the range of 189.5–265° was maintained constant by means of an Aminco Metastatic Thermoregulator connected to a vacuum tube-relay circuit developed by Hershberg and Huntress.[13] At 285°, the temperature was maintained within ±0.5° by means of a manually operated rheostat to which one heater was connected.

The bath temperature measurements at 189.5 and 204.5° were based on a thermometer calibrated by the U. S. Bureau of Standards (reading directly to 0.1°). Above this, the temperatures were determined by means of a calibrated thermometer graduated in degrees.

Two spiral screen columns of 10 mm. (0.40 inch) inside diameter, four feet in length, were used to analyze the reaction mixtures. Water, cooled to 4–12°, was circulated through the column head condensers. In addition, ice–hydrochloric acid traps were placed in the system between each column and the pump. Very little condensate collected in the traps (usually less than 0.1 g.). All fractionations were made at 20 mm. pressure.

Isomerization of the α-Pinene.—Duplicate tubes of α-pinene were heated at definite temperatures within the

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(3) Berthelot, *Ann. Chim.*, [iii] **39**, 9 (1853).

(4) Wallach, *Ann.*, **227**, 282 (1885).

(5) Smith, THIS JOURNAL, **49**, 43 (1927).

(6) Conant and Carlson, *ibid.*, **51**, 3463 (1929).

(7) Thurber and Johnson, *ibid.*, **52**, 786 (1930).

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

(9) Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935).

(10) Goldblatt and Palkin, THIS JOURNAL, **63**, 3517 (1941).

(11) Stallcup, Fuguitt and Hawkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 503 (1942).

(12) Samples furnished through the courtesy of the Naval Stores Research Laboratory, U. S. D. A., and the Southern Pine and Chemical Company.

(13) Hershberg and Huntress, *Ind. Eng. Chem., Anal. Ed.*, **5**, 344 (1933).

range 189.5 to 285° for lengths of time such that the α-pinene was almost completely reacted. The degree of completion was observed by measuring the optical rotation of each reaction mixture. The reaction mixtures herein reported had slight negative optical rotations.

Identification of Products.—Six components were identified in the mixtures: unreacted α-pinene (seldom in amounts large enough to be detected), α-pyronene, β-pyronene, dipentene, *allo*-ocimene and a polymer. Upon the fractionation of the mixture, the polymer was left in the kettle and was weighed.

Unreacted α-Pinene.—The first two fractions of Tube 14 gave a 3-cc. portion (b. p. (21 mm.) 52.8–53.2°, n^{25}_{D} 1.4630, d^{25}_{4} 0.8525, α^{25}_{D} (2 dm.) +20.46°). A nitrosochloride was made from this by the method of Thurber and Thielke.[14] The white crystalline product melted at 101–103° (cor.). Crystallization from benzene yielded a small amount melting with decomposition at 104–105° (cor.).

α-Pyronene.—A portion (5 cc.) of the combined fractions of the tubes listed in Table II (b. p. 50–57° (20 mm.), n^{25}_{D} 1.4670) was added to maleic anhydride by the method of Goldblatt and Palkin.[10] The crystals melted at 90–91° (cor.). Goldblatt and Palkin reported this addition compound of α-pyronene as melting at 91–92°.

β-Pyronene.—7 cc. of the combined fractions (b. p. 57–70° (20 mm.), n^{25}_{D} 1.4736) was added to maleic anhydride by the same method. The crystals melted at 165–166° (cor.). Goldblatt and Palkin reported the addition compound of β-pyronene as melting at 163–164°.

Dipentene.—Some of the dipentene was combined and fractionated. It contained little impurity. The main portion had the physical properties: b. p. (10 mm.) 59°; d^{25}_{4} 0.8387; n^{25}_{D} 1.4702. The observed optical rotation (2 dm.) of the dipentene obtained from the various tubes varied from −1.0 to −4.6°. It was identified by its tetrabromide, made by precipitation in glacial acetic acid. Upon recrystallization from methyl alcohol the crystals melted 124–125° (cor.). Goldblatt and Palkin[10] reported 124.5–125.5°.

***allo*-Ocimene.**—The *allo*-ocimene was seldom obtained pure in these fractionations. The refractive indices (25°) were in the range 1.5330–1.5410. Only 1–3% of each mixture was found to boil between pure dipentene and the *allo*-ocimene obtained. Fractionation of combined portions of the latter yielded a small amount of dipentene and the *allo*-ocimene. The physical constants of this refractionated *allo*-ocimene were: b. p. (11 mm.) 76–79°; n^{25}_{D} 1.5408–1.5424; d^{25}_{4} 0.8068–0.8083. This portion had a boiling range which could not be attributed to the presence of dipentene as may be seen from the refractive index and density ranges.[15] A similar behavior was noticed during the fractionation of the commercial samples of *allo*-ocimene. However, in this latter case a much higher percentage of higher boiling component was obtained.

The *allo*-ocimene was identified by its maleic anhydride addition product which was prepared by the method of Goldblatt and Palkin.[10] Large white crystals, m. p. 81.0–81.5° (cor.), were obtained. Arbuzov[7] reported a m. p. of 81–82°, and Goldblatt and Palkin, after two recrystallization from hexane, obtained crystals melting at 83–84°.

Polymer.—The polymer obtained had refractive indices (25°) varying from 1.5155 to 1.5182. The lower values occurred at the higher temperatures. A representative sample of the polymer had the following physical constants: n^{25}_{D} 1.5180, d^{25}_{4} 0.8857, M_D (obs.) 93.0. This sample was distilled with the results given in Table I.

Molecular weight determinations by the freezing point depression method were made of fractions 2 and 3, using cyclohexane (n^{25}_{D} 1.4233; f. p. 5.90°; molal f. p. depression 20.0°) as the solvent. Four determinations on fraction 2 gave an average molecular weight of 262 with an average deviation of 0.75% and a maximum deviation of 1.90%. Two determinations on fraction 3 gave values of 284 and 285, respectively. From these results the polymer appears to be a dimer, $C_{20}H_{32}$, or mixture of dimeric isomers, the calculated molecular weight of which is 272.

TABLE I

FRACTIONATION OF THE POLYMER

Fraction no.	Weight, g.	% by weight	B. p., °C.	Mm.	n^{25}_{D}
1	2.4	6.8	120–165	8 mm.	1.5194
2	30.0	84.8	165–175	8 mm.	1.5171–1.5182
3	2.5	7.0	224–226	3–4 mm.	1.5189
Residue	0.5	1.4			

Anal. Calcd. for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.24; H, 11.74.

The polymer consisted mainly of a dimer or dimers which, it is believed, resulted by a Diels–Alder addition of two molecules of the monomer involving a terminal double bond of one molecule and adjacent double bonds of the other molecule of *allo*-ocimene. The dimers contain four double bonds, two of which are conjugated. With no allowance for exaltation the calculated M_D is 90.49. In view of the fact that the double conjugation in *allo*-ocimene produces an exaltation of approximately six units it may be assumed that the exaltation of the single conjugation in the polymer is from two to three units. This would give a calculated M_D from 92.5–93.5 which is a satisfactory check with the observed value of 93.0.

Another method of polymer formation which seems reasonable involves the middle double bond of one molecule and adjacent double bonds of the other molecule. The resulting dimer or dimers would contain four double bonds, with no conjugation. This would result in a calculated M_D of 90.49 which is not in close agreement with the observed value. Hence the mechanism of the first method is preferred.

It is realized that several isomers may be present which differ in the relative orientation of chains (head to head or head to tail), and possibly in geometric configuration. However, this would not alter the calculated value and would likely not cause any great change in the observed values. It is probable that the polymer is a mixture, of such isomers, which contains at least 85% (see Table I) of the dimers formed by the first method mentioned.

Quantitative Estimation of Components.—For the most part the estimations of the percentages listed in Table II were determined from the boiling point curves of the fractional distillations. The refractive indices, optical rotations, densities and boiling points of the fractions obtained from Tube 14, heated 607 hours at 189.5°, are plotted in Fig. 1, as an illustration of the separations effected. The last 26% of the reaction mixture consisted of the dimer which remained as residue in the kettle.

The unreacted α-pinene of Tubes 13 and 14 had the proper boiling point and approximate refractive index and

TABLE II

ANALYSIS OF PRODUCTS

Tube no.	Temp., °C.	Time heated, hours	% α-pinene unreacted	% b. p. 50–57° (20 mm.)	% b. p. 57–70° (20 mm.)	% Dipentene	% *allo*-Ocimen	% Dimer
13	189.5	607	4	1	2	63	4	26
14	189.5	607	5	1	2	63	4	25
29	204.5	267	..	1	2	64	5	28
30	204.5	267	..	2	1	64	5	28
31	225	50	..	1	2	63	6	28
32	225	50	..	2	2	62	6	28
33	245	10.5	..	2	2	61	8	27
34	245	10.5	..	2	3	60	8	27
35	265	2	..	3	4	58	12	23
36	265	2	..	3	4	58	11	24
37	285	0.5	..	5	6	55	15	19
38	285	0.5	..	4	5	57	15	19

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(14) Thurber and Thielke, THIS JOURNAL, 53, 1030 (1931).

(15) Hopfield, Hall and Goldblatt, *ibid.*, 66, 115 (1944).

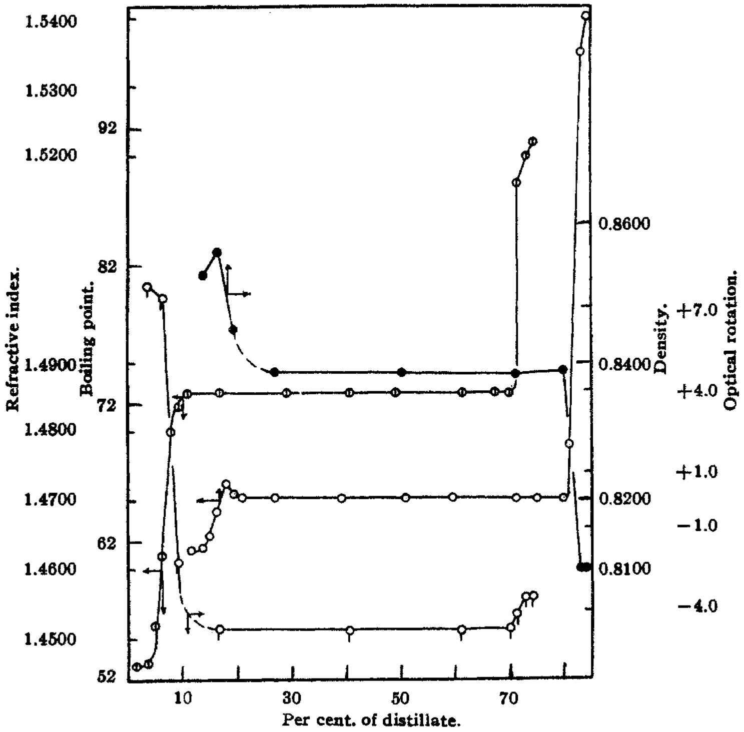

Fig. 1.—Distillation curve of isomerization mixture: ●, density, 25°; ◑, boiling point, 20 mm.; ○, refractive index, 25°; ♀, optical rotation, 2-dcm. tube, 25°.

density. In the analyses of the other reaction mixtures no such fraction was observed. Instead the boiling point increased steadily until that of pure dipentene was attained. This portion was divided into two fractions, that with b. p. (20 mm.) 50–57°, and the second b. p. (20 mm.) 57–70°. See columns 5 and 6, Table II. These two fractions were rich in α-pyronene and β-pyronene, respectively.

Since the *allo*-ocimene was seldom obtained pure, and, since it has been shown to contain some dipentene, it seemed advisable to estimate the dipentene and *allo*-ocimene in the latter part of the fractionations by means of refractive index. Refractive index–composition data for known mixtures of dipentene and *allo*-ocimene were measured. It was found that the maximum deviation from a linear relation is about 1.3% dipentene at 40% dipentene. Such a small deviation when applied to mixtures of not over 10 g. would have no significant effect in the determination of the quantity of dipentene. Therefore all calculations of composition of mixtures of *allo*-ocimene and dipentene were made assuming a linear relation between refractive index and composition.

Effect of Heat on Dipentene and *allo*-Ocimene in the Liquid Phase.—Harries[16] reported that dipentene is unreactive when heated in sealed tubes at temperatures up to 300°. To determine the unreactivity of dipentene under the conditions of these experiments, two sealed tubes, each containing about 14 g. of the purified dipentene, were heated for four hours in an oil-bath at 245–255°. Fractionation of the combined product yielded 26.6 g. of unchanged dipentene and 0.3 g. of a high boiling residue ($n^{25}_{\rm D}$ 1.5007).

A sealed tube containing 17 g. of a mixture of 46% *allo*-ocimene and 54% dipentene was heated for four hours under the same condition. By fractionation of the products the dipentene was recovered unchanged. In addition the product contained about 2% of a lower boiling fraction ($n^{25}_{\rm D}$ 1.4718), 31% of dimer and 13% of unreacted *allo*-ocimene. From this it is apparent that the dipentene remains unchanged and that the *allo*-ocimene forms the dimer.

Sealed tubes of 14–18 g. of *allo*-ocimene were heated for varying lengths of time at 189.5 and 204.5° and then were opened and the *allo*-ocimene was separated from its dimer in the spiral screen analytical columns previously described. A known weight of the mixture was taken for the separation of the components and the dimer remaining in the flask was weighed.

The dimer from pure *allo*-ocimene was more homogeneous than that formed from the products of the α-pinene isomerization. The former boiled at 173–176° (9 mm.) and had a refraction index range (25°) of 1.5208–1.5212. Three molecular weight determinations of this sample by the previously described method gave values of 260, 260 and 262.

The data for the dimerization of *allo*-ocimene are given in Table III. The refractive index (25°) for the total amount of *allo*-ocimene recovered from each tube is given in column 4 of this table. In general this value decreases for those tubes heated for the longer times. This decrease in refractive index may be due to the formation of small amounts of other compounds from the *allo*-ocimene, probably the pyronenes. However, a complete interpretation of this point must await further study.

It was observed that the dimerization does not go to completion. This suggested either that the *allo*-ocimene contained a component that will not polymerize or that the dimer was in equilibrium with its monomer. The recovered *allo*-ocimene (2 g.) from Tubes 66 and 67 was heated twenty-four hours at 189.5°. The product was essentially a dimer, b. p. (10 mm.) 170–178°, $n^{25}_{\rm D}$ 1.5190. The *allo*-ocimene heated in Tube 68 was that recovered from Tubes 58–59. Thus it is seen that the unreacted portion may be dimerized if separated from the dimer already formed.

TABLE III

DIMERIZATION OF *allo*-OCIMENE

Tube no.	Temp., °C.	Time heated, hours	*allo*-Ocimene recovered, $n^{25}_{\rm D}$	Weight mixture, g.	Weight dimer, g.	% Dimer
58–59	189.5	17	1.5412	32.0	25.6	80
68	189.5	17	1.5392	5.5	4.2	76
62	189.5	66.5	1.5355	15.7	13.7	87
63	189.5	66.5	1.5377	15.7	13.7	87
64	189.5	113	1.5413	16.0	14.0	87.5
65	189.5	137	1.5381	15.5	13.4	86.5
66	189.5	221	1.5360	15.6	13.8	88.5
67	189.5	246	1.5340	15.7	14.1	90
80	204.5	58	1.5263	13.6	11.9	87.5
81	204.5	95	1.5260	14.4	12.5	87

Sealed tubes of the recovered dimer were heated to see if *allo*-ocimene could be obtained from it. These data are given in Table IV. The dimer which was undissociated after heating in Tube 90 was recovered and sealed in Tube 91 and heated for the same length of time. The same percentage of *allo*-ocimene was recovered in each case. There can be no doubt that this is a reversible reaction.

Arbuzov[8] heated *allo*-ocimene in a sealed tube for one hour at 250–300° and for one-half hour at 320°. Upon fractionation he obtained 7 g. of material boiling from 55° (14 mm.) to 135° (4 mm.) and 8 g. of a polymer. Arbuzov

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(16) Harries, *Ber.*, 35, 3256 (1902).

TABLE IV

DISSOCIATION OF DIMER

Tube no.	Temp., °C.	Time, heated hours	*allo*-Ocimene recovered $n^{25}\mathrm{D}$	Weight mixture, g.	Weight dimer, g.	% Dimer
90	189.5	148	1.5396	17.3	15.9	92
91	189.5	148	1.5350	13.8	12.7	92
92	189.5	239	1.5423	16.6	14.9	90
93	189.5	390	1.5300	14.5	13.0	89.5
94	189.5	390	1.5415	14.8	13.1	88.5
95	204.5	95	1.5275	17.2	15.2	88.5
96	204.5	135	1.5267	18.2	16.0	88

reported that refractionation of the lower boiling portion yielded 5 g. of a terpene, b. p. 57–58.5° (14 mm.), $n^{25}\mathrm{D}$ 1.4785, d^{22}_4 0.8422. This terpene gave no crystalline tetrabromide nor nitrosite. He did not attempt to prepare the maleic anhydride addition product. From the similarity of the physical properties of this terpene to those reported by Dupont and Dulou[9] for β-pyronene it was suspected that this might be β-pyronene which formed by the cyclization of *allo*-ocimene. To check this point, 60 g. of *allo*-ocimene was heated at 300–310° for two and a half hours in a sealed tube. The products obtained were divided into four main fractions

	%		B. p. Mm.	°C.	$n^{25}\mathrm{D}$
Fraction 1	9		20	43–57	1.4663
Fraction 2	15		20	57–69	1.4791
Fraction 3	12		20	69–90	1.4848
Fraction 4	64	Dimer			1.5166

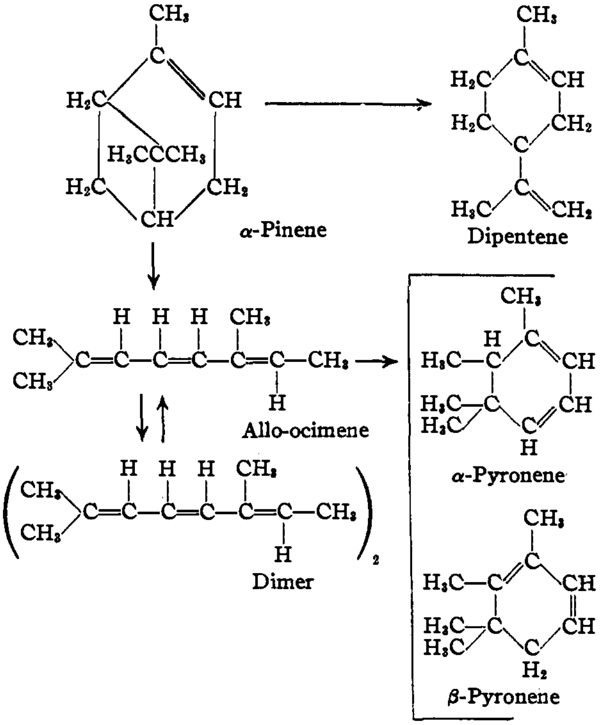
Before the analyses of these fractions were commenced, Goldblatt[17] informed the authors that he had already completed experiments proving that α- and β-pyronene are formed by the cyclization of *allo*-ocimene in the vapor phase. Since Fractions 1 and 2 have physical properties which correspond to those of α- and β-pyronene, respectively, maleic anhydride addition products were made of these two fractions by the method of Goldblatt and Palkin.[18]

4.5 g. of Fraction 1 yielded 3 g. of an adduct, b. p. (12 mm.) 202–204°. This probably contained the addition product of maleic anhydride with α-pyronene which Goldblatt and Palkin reported as boiling at 195° (8 mm.). However, repeated attempts to recrystallize this sample from methanol were unsuccessful.

7.5 g. of Fraction 2 yielded 6 g. of an adduct, b. p. (12 mm.) 195–198°. Crystallization of this from aqueous methanol gave crystals melting at 161–162° (cor.), corresponding to the adduct of β-pyronene.

These findings agree with the report of Goldblatt and Palkin[18] that *allo*-ocimene cyclizes to form the pyronenes. The constituents of Fraction 3 remained unidentified and should be further investigated.

From the above it is concluded that the liquid phase thermal isomerization of α-pinene under the described conditions may be represented by



Summary

The liquid phase thermal isomerization of α-pinene was studied in the temperature range 189.5–285°.

Dipentene, α-pyronene, β-pyronene, *allo*-ocimene and its dimer were identified in the reaction mixtures. It was shown that dipentene and *allo*-ocimene are formed by simultaneous side reactions from the α-pinene and that the *allo*-ocimene in turn yields β-pyronene, quite probably α-pyronene and a dimer.

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(17) Goldblatt, private communication.

(18) Goldblatt and Palkin, THIS JOURNAL, 66, 655 (1944).