Summary

1. The intermolecular esterification of ω-hydroxydecanoic acid has been studied and found to proceed easily with the formation of mixtures of chain polymers. These mixtures were separated by crystallization into fractions of average molecular weights ranging from 1000 to 9000.

2. These poly-esters were titrated quantitatively with standard alcoholic potash solutions and average molecular weights thus determined. By boiling with excess alcoholic potassium hydroxide, they were converted back to the original acid.

3. A twenty-two-membered dimeric lactone of ω-hydroxydecanoic acid was prepared by dry distillation of the product obtained by the action of acetic anhydride on its potassium salt.

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THE APPARENT RACEMIZATION OF PINENE

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RECEIVED JUNE 21, 1929 PUBLISHED NOVEMBER 8, 1929

The thermal decomposition of *d*-pinene was noted by Wallach[1] many years ago in connection with his study of the action of heat on a variety of essential oils. He showed that at 250–270° the final products were dipentene and polymerized material. Very recently Smith[2] has made a quantitative study of the loss of optical activity of pinene at somewhat lower temperatures (185–237°) and concludes that the reaction consists for the most part of a simple racemization. This view he supported by distillation of a sample which had been heated until it had lost about a third of its original optical activity. This evidence did not seem to us conclusive, however, and we decided to determine, if possible, whether the loss of optical activity of pinene was the result of racemization or rearrangement. From a physico-chemical point of view the question is probably of relatively little significance and most of Smith's conclusions are not affected by our final results, which establish that the process he was measuring was in reality a rearrangement and not a racemization. From the standpoint of the organic chemist, however, the point at issue is obviously of importance.

A few experiments convinced us that a definite answer to the problem could not be obtained by fractional distillation. Although there is a 20° difference in the boiling points of pinene (155°) and dipentene (176°), a mixture of equal amounts of the compounds was very incompletely separated by several fractionations through an efficient Widmer column.

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[1] Wallach, *Ann.*, **227**, 282 (1885).

[2] Smith, THIS JOURNAL, **49**, 43 (1927).

The incompleteness of the separation was evidenced both by the unsatisfactory boiling points of the high and low fractions and also by the optical activity of what should have been pure inactive dipentene and the low rotation of what should have been pure pinene. We therefore turned to another method of determining the amount of pinene and dipentene in a mixture.

The catalytic hydrogenation of mixtures of pinene and dipentene proved to be a very satisfactory method of determining the proportion of the two constituents. Pinene absorbs one mole of hydrogen, dipentene two; the two compounds are isomeric; therefore the composition of a mixture may be calculated from the amount of hydrogen absorbed by a given weight of material. The method was tested by using both pure compounds and known mixtures; the accuracy of the method is about ±4% of the total hydrogen absorbed. Since difficulty was experienced in obtaining pure dipentene, *d*-limonene was substituted for it in making the known mixtures (*dl*-limonene = dipentene). The hydrogenation was carried out in a special constant volume apparatus using Adams' catalyst and glacial acetic acid as a solvent. The details are given in the experimental part of this paper.

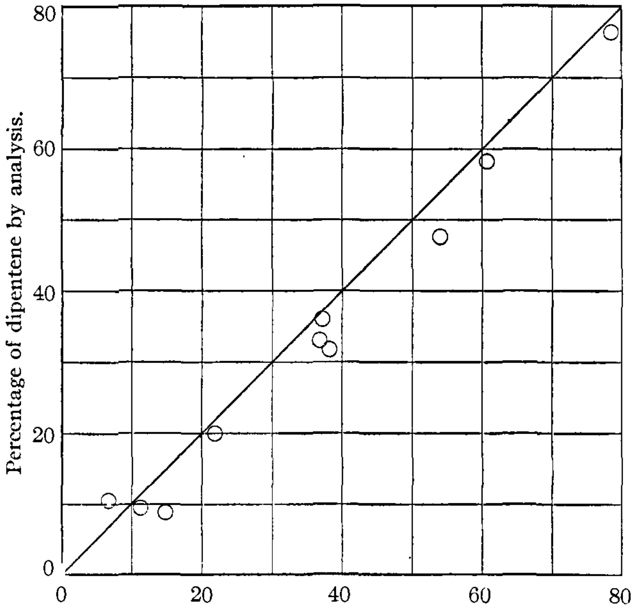

Fig. 1.

Using this method of analysis the amount of dipentene was determined in samples of pinene which had been heated in the gaseous phase at 200 ± 5°

until the optical activity had been diminished. The results are shown graphically in Fig. 1. It is clear that there is a complete parallelism between the amount of dipentene found by the hydrogenation method and the loss of optical activity. There seems no escape from the conclusion that the apparent racemization of pinene is in reality a rearrangement of pinene to dipentene.

Similar results were obtained on heating *d*-pinene in the liquid phase at 200°. Samples heated until all of the optical activity had been lost (in some cases the rotation became slightly levo) absorbed between 90 and 95% of the amount of hydrogen calculated for pure dipentene. Wallach's original observations were verified by distilling some material which had been heated for 100 hours at 200°. About 30% of polymerized high-boiling material was found and the distillate (b. p. 167–183°) on treatment with bromine yielded crystalline dipentene tetrabromide, though in low yield, which is to be expected in view of the difficulty of obtaining satisfactory amounts of crystalline bromide from pure dipentene.[3]

The Rearrangement of *d*-Pinane.—The saturated dicyclic compound, *d*-pinane, is much more difficult to rearrange than the corresponding unsaturated compound (*d*-pinene). For example, heated in the liquid phase for 176 hours at 200°, it lost only 14% of its actvity, whereas the rearrangement of *d*-pinene at the same temperature was practically complete in fifty hours. It was necessary to heat *d*-pinane to 285° in order to obtain a rate of rearrangement that was comparable to that of *d*-pinene at 200°. As in the case of the unsaturated compound, hydrogenation showed that the loss of optical activity is to be attributed to rearrangement and not to racemization. This is clear from Table I, in which the percentage of isomerization was calculated from the amount of hydrogen absorbed, assuming that the product was a monocyclic unsaturated compound, $C_{10}H_{18}$.

As in the case of *d*-pinene, the rearrangement is accompanied by some polymerization. A sample which had been heated to 285° for fifty hours yielded on distillation a 10% residue of very high-boiling material. The

TABLE I

ISOMERIZATION OF *d*-PINANE IN THE LIQUID PHASE

Time of heating, hours	Temp., °C.	Percentage isomerization	
		Calcd. from loss of optical activity	Calcd. from hydrogenation
50	200	10.3	7
76	200	12.2	11
176	200	14.1	12
176	200		
and 50	250	35.1	24
52.5	250		
and 50	285	82.4	64

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[3] Wallach, *Ber.*, **40**, 603 (1907).

major portion of the distillate boiled at 165–167°, and on catalytic hydrogenation absorbed 65% of the amount of hydrogen calculated for a monocyclic unsaturated compound, $C_{10}H_{18}$. No attempt was made to separate this mixture; undoubtedly a number of isomeric monocyclic compounds are produced and the possibility of some open chain dienes is not excluded.

Experimental

The *d*-pinene used was purified by fractional distillation over sodium. Two samples were employed in this work which had the following constants: (1) b. p. 156–156.3°, $[\alpha]^{23}_{D}$ (pure liquid) +43.94°, n^{20}_{D} 1.4658, d_{20} 0.8600; (2) b. p. 155.3–155.6°, n^{20}_{D} 1.4560, d_{20} 0.8591, $[\alpha]^{23}_{5461}$ (in acetic acid solution) +65.2°. The *d*-pinane used was prepared by the catalytic hydrogenation of *d*-pinene using Adams' catalyst and pressure of 35 lbs. Two samples had the following constants: (1) b. p. 167–168.5°, $[\alpha]^{23}_{5461}$ (pure liquid) +26.84°, n^{20}_{D} 1.4619, d_{20} 0.8579; (2) b. p. 166–166.7°, $[\alpha]^{23}_{5461}$ (pure liquid) +23.71°, n^{20}_{D} 1.4621, d_{20} 0.8571.

Method of Analysis by Catalytic Hydrogenation.—The catalytic hydrogenation was carried out in a constant volume apparatus so arranged that there was no rubber connection between the reaction vessel and the supply of hydrogen. The reaction vessel, which was a tube about 9 cm. long and had a capacity of about 10 cc., was attached by a ground-glass joint on its upper side and an inverted elbow to a reservoir bulb of about 50-cc. capacity. The bottom of this bulb was constricted and attached by rubber tubing to a leveling bulb. The total volume of the apparatus to a graduation on the constricted bottom of the reservoir was 76.34 cc. About 0.1 g. of material was employed, 2 to 4 mg. of Adams' catalyst and exactly 3 cc. of glacial acetic acid. The apparatus was filled with hydrogen by evacuating and filling three times. The course of the hydrogenation was followed by measuring the pressure difference between the leveling bulb and the constant volume mark. During the hydrogenation a positive pressure of about 3–4 cm. of mercury was maintained. The agitation of the reaction vessel was accomplished by rocking the whole apparatus back and forth about an axis at right angles to the plane of the reaction tube. The pressure was read every half hour until it was constant. The volume of hydrogen absorbed by the catalyst was found to be negligible for one lot of catalyst; for another a correction of 2 cc. per 35 mg. had to be made.

The following data on the hydrogenation of pure pinene are typical: barometer reading, 757.5; temp., 21.2°; 95.3 mg. of sample; 2.7 mg. of catalyst; pressure difference in mm. of Hg, after 1 hr., 190 mm., after 2 hrs., 189 mm.; cc. of hydrogen found, 17.5; cc. of hydrogen calculated, 16.95.

In Table II are collected some of the results which demonstrated the applicability of the method for analyzing mixtures of dipentene and *d*-pinene. Since the best samples of dipentene we could obtain absorbed only 80% of the calculated quantity of hydrogen, we substituted *d*-limonene for dipentene.

TABLE II

ESTIMATION OF *d*-PINENE AND *d*-LIMONENE BY CATALYTIC HYDROGENATION

Composition of material taken	Pinene, %	100	0	41	60
	Limonene, %	0	100	59	40
Composition found by catalytic hydrogenation	Pinene, %	103	...	48	53
	Dipentene, %	...	102	52	47

Isomerization of *d*-Pinene in the Vapor Phase.—The pinene was weighed in a thin-walled bulb which was sealed off and introduced into a bulb of pyrex glass of 300-cc. capacity which was evacuated and sealed. The smaller bulb was then broken and the whole heated in an electric oven at 200 ± 5°. The large bulb. after cooling, was opened and glacial acetic acid added from a weight buret. The rotation of this solution was taken in a decimeter tube using the green mercury line 5461, and the specific rotation calculated and compared with that of the original pinene in glacial acetic acid solution. The analyses of a weighed portion of the solution were then carried out by the catalytic hydrogenation method described above.

In Table III a few typical results are given in full; all of the experiments are summarized in Table IV; the points in Fig. 1 are from Table IV.

Table III

Typical Data Obtained in the Isomerization of Pinene

Temp., 200 ± 5°; time of heating, 1080 min.; $[\alpha]_{5461}$ + 65.2° in acetic acid initially

Expt.	Pinene, mml.	Acetic acid, g.	$[\alpha]_{5461}$	Loss in rotation, %	Sample for analysis, g.	$C_{10}H_{16}$ in sample, mml.	H_2 absorbed, mml.	Dipentene found, %
1	2.978	8.856	+51.0	21.8	3.082	0.9897	1.178	19.1
					3.121	1.005	1.210	21.0
2	3.295	8.743	+40.9	37.7	3.067	1.097	1.515	38.1
					3.111	1.115	1.494	34.0

In calculating $[\alpha]_{5461}$ the density of all of the solutions (which had nearly the same percentage composition) was taken as 1.03.

Since the percentage of dipentene is calculated from the formula

$$\%\ \text{dipentene} = \frac{\text{moles } H_2 - \text{moles } C_{10}H_{16}}{\text{moles of } C_{10}H_{16}} \times 100$$

it is evident that the error in determining the amount of hydrogen absorbed is magnified in the calculation of the percentage of dipentene. An error of a few per cent. in the total hydrogen absorbed may make an error of as much as 20% in the percentage of dipentene. if this is small. This effect is evident in Table IV. For this reason duplicate analyses were always carried out.

Table IV

Summary of Results on the Isomerization of *d*-Pinene in the Gaseous Phase at 200 ± 5°

Heating, min.	Loss of rotation, %	Percentage of dipentene by analysis (hyd. method)			Heating, min.	Loss of rotation, %	Percentage of dipentene by analysis (hyd. method)		
		1	2	Av.			1	2	Av.
720	6.6	11.0	10.0	10.5	2070	36.9	33.9	32.0	33.0
1110	14.9	10.6	7.0	8.8	1080	37.7	38.1	34.0	36.0
1440	11.2	6.74	12.2	9.5	1680	53.7	44.7	50.5	47.6
1080	21.8	19.1	21.0	20.0	2070	60.4	61.7	54.7	58.2
2220	38.2	31.6	31.7	31.7	3030	78.5	77.9	74.7	76.3

Since no attempt was made to hold the temperature constant, the rate of isomerization varied from experiment to experiment. The range of the monomolecular constants was 23.6 × 10^{-5} to 4.2 × 10^{-5} with a mean of ten experiments of about 20 × 10^{-5}. Smith gives the value for 198° as 8.6 × 10^{-5} and for 218° as 54 × 10^{-5}. It is thus evident that our process was proceeding at a rate comparable to his and we were studying the same reaction.

Isomerization of *d*-Pinene in Liquid Phase.—Samples of *d*-pinene were sealed in Carius tubes and heated in a gas furnace to 200 ± 10°. A sample heated for fifty hours showed $[\alpha]_D$ +2.4°, as compared with $[\alpha]_D$ +43.9° initially, percentage loss in rotation, 95; 87.8 mg. of the material with 2.4 mg. of catalyst absorbed 29.3 cc. of hydrogen at 763 mm. and 23°; the calculated amount for pinene is 15.6, the percentage of dipentene was therefore 90. Other samples heated for 100 or 150 hours showed a slight levorotation ($[\alpha]_D$ −0.44 to −0.78°); they absorbed 90 to 95% of the amount of hydrogen corresponding to pure dipentene. 8.8 g. of *d*-pinene which had been heated to 200° for 100 hours yielded 6.7 g. of a distillate, b. p. 167–183.5°; the residue of 1.9 g. was very high boiling. A sample of the distillate absorbed 91% of the amount of hydrogen calculated for dipentene; 2 g. of the same distillate was treated with bromine in ether and alcohol at 0°. On spontaneous evaporation 2.7 g. of crude crystals was left which on recrystallizing from ethyl acetate yielded 1.3 g. of dipentene tetrabromide (m. p. 125°), which was identified by a mixed melting point. . Pinene which had been heated for 200 hours at 200° yielded only about 50% of a volatile material (b. p. 172–177°); the residue on distilling *in vacuo* boiled at 180–235° at 2 mm. The fraction which boiled at 172–177° absorbed 92% of the amount of hydrogen calculated for dipentene and yielded the crystalline tetrabromide on brominating.

Isomerization of *d*-Pinane.—The pinane was heated in a Carius tube in the same manner as pinene. The material was tested for any unsaturated material before heating, by catalytic hydrogenation in acetic acid in the manner described. No appreciable amount of hydrogen was absorbed. The impurity was therefore less than 1.8%. The results of the isomerization experiments have already been summarized in Table I. The rotation was measured in the pure liquid; the analysis by catalytic hydrogenation was exactly as described for pinene–dipentene mixtures. The amount of unsaturated monocyclic compound, $C_{10}H_{18}$, was taken as equal to the amount of hydrogen absorbed.

A sample of *d*-pinane (6 g.) which had been heated for fifty hours at 285° yielded 4.8 g. of a distillate, b. p. 165–167°; 0.4 g. of b. p. 170–300°; viscous residue about 0.5 g.; 85.2 mg. of the distillate, b. p. 165–167°, absorbed 9.9 cc. of hydrogen at 767 mm. and 26°; calcd. for $C_{10}H_{18}$ (unsat.), 15.0; 95.6 mg. of the higher fraction absorbed 9.7 cc. of hydrogen at 772 mm. and 26°; calcd. for $C_{10}H_{18}$ (unsat.), 16.7.

Summary

1. The loss of optical activity of *d*-pinene on heating in the liquid or gaseous phase has been shown to be due to the isomerization to dipentene and not to simple racemization. The presence of dipentene in amounts sufficient to account for the loss of activity has been shown by catalytic hydrogenation.

2. *d*-Pinane on heating to above 200° in the liquid phase is isomerized with loss of optical activity and the formation of unsaturated hydrocarbons. The process is much slower than in the case of *d*-pinene.

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