TABLE I (*Concluded*)

Compound	Solvent	Absorption maxima Wave length	Absorption maxima Intensity
9-Phenyl-1,2,3,4,7,8-tribenzfluorene[c] (XIII)	*n*-Heptane	2460	4.80
		2560	4.81
		(2610)	4.80
		2800	4.68
		2930	4.61
		(3000)	4.20
		(3310)	4.02
		(3410)	4.10
		3490	4.20
		(3550)	4.12
		3660	4.09
Hydrocarbon of Bergmann and Israelashwili (m. p. 133°)[c] (XV)	*n*-Heptane	2240	4.91
		2480	4.75
		2530	4.80
		2700	4.35
		2770	4.33
		2840	4.27
		2970	4.24
		3140	3.14
		3250	3.03
		3320	3.03
		3400	2.95
		3480	2.98
		(3550)	2.70
		(3630)	2.58
Monochloro derivative of 9-phenyl-1,2,3,4,7,-8-tribenzfluorene[c] (XVI, X = Cl)	*n*-Heptane	(2420)	4.73
		2470	4.80
		2580	4.82
		2640	4.82
		(2860)	4.55
		2900	4.57
		3015	4.59
		(3280)	3.56
		(3420)	3.74
		3580	3.87
		3660	3.86
		(3820)	3.66
Monobromo derivative of 9-phenyl-1,2,3,4,7,-8-tribenzfluorene[c] (XVI, X = Br)	*n*-Heptane	2480	4.82
		2600	4.80
		(2650)	4.77
		2930	4.58
		3060	4.60
		(3450)	3.56
		3610	3.65
		3860	3.48

[a] Compound supplied by Dr. R. C. Clapp. [b] Compound supplied by Dr. E. Berliner. [c] Compound supplied by Dr. F. Bergmann. [d] See Maynoerd and Roe, *Proc. Roy. Soc.* (London), **A158**, 634 (1937). [e] Wave lengths in parentheses refer to points of inflexion.

Acknowledgment.—The author wishes to thank Dr. F. Bergmann, Dr. E. Berliner, and Dr. R. C. Clapp for supplying most of the compounds used in this investigation; thanks are also due to Mrs. G. D. Thorn for technical assistance. Financial support from the Penrose Fund of The American Philosophical Society is gratefully acknowledged.

Summary

The ultraviolet absorption spectra of three aryl carbinols are compared with the computed summation spectra which would be predicted for compounds of this type on the assumption that each aryl group contributes to the spectrum as an independent chromophore. The effects on the spectra of the cyclic dehydration of these carbinols to polybenzfluorenes are noted, and on the basis of these observations structures are assigned to two hydrocarbons which have been isolated by Bergmann and Israelashwili from the products of the reaction between phenanthrene-9-aldehyde and α-naphthylmagnesium bromide.

KINGSTON, CANADA RECEIVED JUNE 13, 1945

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Continuous Thermal Isomerization of α-Pinene in the Liquid Phase

BY T. R. SAVICH AND L. A. GOLDBLATT

The thermal isomerization reaction of α-pinene at atmospheric pressure in the vapor phase at temperatures from 300–400° has been extensively studied by Arbuzov,[1] Charlton and Day,[2] Dupont and Dulou,[3] and Goldblatt and Palkin.[4] The results of the vapor phase reaction at 375° indicate that roughly equal proportions of dipentene and *allo*-ocimene each in approximately 40% yield[4] could be obtained with substantially complete conversion of α-pinene. The remainder of the product included about 12% α- and β-pyronenes. It has been further shown by Goldblatt and Palkin[5] that α- and β-pyronenes result from *allo*-ocimene cyclization.

Previous study of the reaction in the liquid phase by Wallach,[6] Smith,[7] Thurber and Johnson,[8] Conant and Carlson,[9] and Fuguitt and Hawkins[10] has been limited to batch reactions in

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

(2) Charlton and Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

(3) Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935); *Atti X° Congr. Intern. Chim.*, **3**, 127 (1939).

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

(5) Goldblatt and Palkin, *ibid.*, **66**, 655 (1944).

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

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

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

(9) Conant and Carlson, *ibid.*, **51**, 3464 (1929).

(10) Fuguitt and Hawkins, *ibid.*, **67**, 242 (1945).

sealed glass reaction vessels at relatively low temperatures in the range from 185–285°.

The present work covers the temperature range of 188° to approximately 500° and in addition to conventional batch methods, uses the convenient technique, requisite for the study of the controlled liquid phase reaction at higher temperatures, of pumping α-pinene, maintained in the liquid phase either by an applied pressure or by vapor pressure, through a reactor heated to the reaction temperature. The correlation between the reaction in the liquid phase and that in the vapor phase noted in the work of Smith[7] and Conant and Carlson[9] at lower temperatures has been extended to higher temperatures. The study of the effect of reaction temperature on yields of the various reaction products has confirmed the findings of Fuguitt and Hawkins[10] for the range 185–285° and has been extended to much higher temperatures. Besides the obvious advantages of liquid phase operation, the charring and resin formation that are sometimes observed in the vapor phase reactor in the vaporization and condensation zones are eliminated.

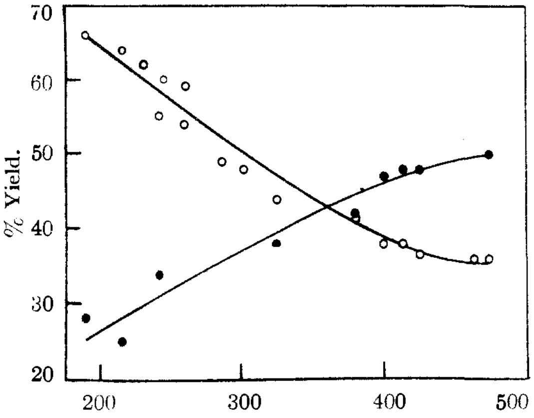

Fig. 1.—O, % yield of dipentene; ●, % yield of *allo*-ocimene.

To attain the maximum yield of *allo*-ocimene at reaction temperatures below approximately 300° it was necessary to use a reaction time too short for the complete conversion of α-pinene. The maximum yield of *allo*-ocimene increased with increasing temperature of reaction; for example, it was 25% at 190° with a contact time of about a hundred hours and with 25% conversion of α-pinene, whereas it was approximately 50% at 500° with a contact time of less than one-half of a second and with 100% conversion of α-pinene. The yield of dipentene decreased with increasing temperature, being approximately 65% at 190° and 35% at 500° (Fig. 1). When reaction time at a given temperature was prolonged, the *allo*-ocimene produced reacted further to form monomeric cyclization products at higher temperatures, *e. g.* 450°, whereas, at lower temperatures, *e. g.*, 190–300°, a polymer became the main product of the *allo*-ocimene side reactions.

The dipentene formed at temperatures up to approximately 325° was slightly levorotatory, as found by Fuguitt and Hawkins[10] at temperatures up to 285°. However, the dipentene formed at temperatures above 350° was slightly dextrorotatory.

No evidence was found which indicated racemization of limonene. A sample of limonene having $\alpha^{25}D$ −95.17 (10-cm. tube) was heated for 120 hours at 203°. After separation from the small amount (less than 2%) of polymer formed, the limonene showed $\alpha^{25}D$ −95.13, and its other physical properties were also unchanged.

Some evidence was found which indicated racemization of the α-pinene, perhaps to the extent of 25%.[11] In runs showing low conversion, none of the α-pinene recovered showed as high a rotation as that of the α-pinene charged, despite fractionation at high reflux ratios (50:1) in an efficient Podbielniak heli-grid column. It is significant that the other properties of the recovered α-pinene (b. p., density, refractive index) were identical with those of the α-pinene charged. This recovered α-pinene was heated for one hour on a water-bath with maleic anhydride to remove any compounds with a conjugated diene structure such as pyronenes, but no change was observed in the rotation of the recovered α-pinene as a result of this purification.

Experimental

The α-pinene was carefully purified by vacuum fractional distillation at 20 mm. in efficient columns of approximately 40 theoretical plates and had the following properties, which fresh distillation did not alter: d^{20}_4 0.8593, $n^{20}D$ 1.4656, $\alpha^{25}D$ +8.35° (in a 10-cm. tube), b. p. (20.0 mm.) 52.0°. In certain experiments an α-pinene with a higher rotation ($\alpha^{25}D$ +29.60° in a 10-cm. tube) was used, but the other physical properties were identical.

Apparatus.—In the batch runs at 188.5 and 203° an insulated oil-bath was used, and temperature was controlled by a mercury type thermoregulator and adequate stirring. Temperature was measured by a National Bureau of Standards calibrated thermometer, but assurance of constancy at all times was obtained by recording the e. m. f. of a thermocouple, immersed in the bath, with a Brown recording potentiometer.

The technique of pumping α-pinene, maintained in the liquid phase by an applied pressure of nitrogen gas, through a reactor heated to reaction temperature by a tube furnace or a lead-bath was used over the temperature range of 200 to 500°. The apparatus (Fig. 2) included a charge cylinder, A, of 4.5-liters capacity and a Zenith gear pump, B (0.29 cc. per revolution, type B), with suitable motors and gears to change the pumping rate. This pump afforded a controlled feed rate that was constant to within

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[11] Smith (ref. 7) made a quantitative study of the loss of optical activity of α-pinene at temperatures of 185–237° and concluded that the loss of optical activity consisted, for the most part, of a simple racemization. Conant and Carlson (ref. 9) re-investigated this reaction and concluded that the loss of optical activity was due to isomerization to dipentene and not to simple racemization. Fuguitt and Hawkins (ref. 10) reported recovery, from heat-treated α-pinene, of impure α-pinene fractions of markedly reduced optical activity. Although they did not conclude that α-pinene was racemized, their data support this conclusion.

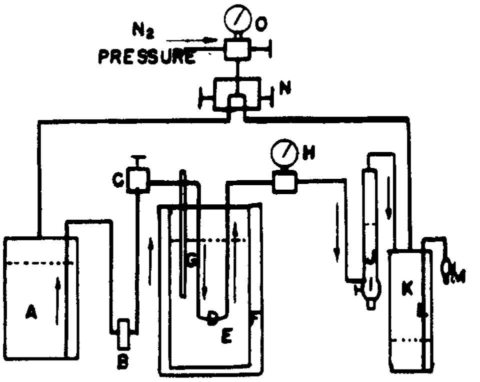

Fig. 2.—Apparatus: A, charge cylinder; B, zenith pump; C, needle valve; D, reactor; E, lead bath; F, electric autoclave heater; G, thermocouple well; H, pressure gage; I, Hoke needle valve; J, sample reservoir; K, storage tank for product; L, eduction tube; M, Hoke needle valve; N, 3-way needle valve; O, needle valve and pressure gage.

the limits of the accuracy of the measurement used, approximately 2%. For pumping rates up to 16 r. p. m., small motors (approximately 1/100 h. p.) were suitable. However, for 30 r. p. m. and faster, it was found necessary to use a more powerful $^1/_4$ h. p. motor. No preheater was required. For reactor volumes of 0.1 to 1 cc. a U-shaped reactor, D, was constructed from $^1/_4''$ super-pressure steel tubing (American Instrument Company). This tubing provided a reaction volume of 0.04 cc. per 1″ length. In the runs made at the highest temperatures this volume was decreased to 0.02 cc. per inch by the introduction of no. 18 B. and S. gage nichrome wire. The reactor was heated by immersion in a lead-bath, E, which in turn was heated by a 2 KVA electric autoclave heater, F. The lead-bath container was constructed from a 14″ length of 5″ iron pipe. The effective reactor volume was varied by lowering or raising the lead-bath. From the reactor the effluent passed into the bottom of a sample reservoir, J, of approximately 30-cc. capacity. A needle valve, I, fitted to the bottom of this reservoir, served to drain off the effluent. The sample reservoir overflowed into a larger, 2-liter, reservoir, K, which served as a ballast and emergency storage tank for effluent. This was provided with an eduction tube, L, so that product could be drained off through a needle valve, M. The top of the tank, K, was connected by means of a 3-way needle valve, N, with the pressure source, a nitrogen tank, and the charge cylinder. The pressure of the entire system was thus equalized. Temperature was measured by a thermocouple, contained in a steel guard tube, G, immersed in the lead-bath.

For runs at temperatures below 325°, a tube of 160-cc. capacity, made of extra heavy 1″ steel pipe approximately 14″ long was used in place of the U-shaped reactor. It was mounted vertically, and the feed entered the bottom end. Heat was supplied by a 1-foot combustion-tube furnace. Temperature stability of ±2°, was obtained by a constant voltage transformer, the output of which was connected to a variable voltage transformer (Variac). Temperature was measured by a thermocouple brazed to the middle of the reactor tube, and a continuous record of temperature was kept with a recording potentiometer.

Pressure.—All pressures were read with calibrated Bourdon spring gages. Preliminary batch runs at temperatures between 200 and 400° gave an indication of the pressures required to prevent the vaporization of the charge and effluent, and thus to ensure a liquid phase. These data indicated that a pressure of approximately 400 p. s. i. at 500° would keep α-pinene in the liquid phase. In actual operation somewhat higher pressures were applied by connecting a nitrogen tank, filled to a pressure somewhat higher than desired, to the system. The tank served as an additional large ballast as well as a pressure source. Although pressure was not kept constant, it did not vary more than 25 p. s. i. in the runs from 325–500°, and in all cases the applied pressure exceeded that necessary to maintain a liquid phase.

Operation and Results.—In the runs from 325–500° α-pinene was introduced into the charge cylinder. The temperature of the bath and reactor was raised to somewhat below that considered necessary for optimum conversion of α-pinene. The pump was started. Valves O, N and C were opened. The variable transformer was regulated so that the temperature kept rising during the run. Product was withdrawn as it accumulated in the sample reservoir, and its refractive index and density were measured. From a curve of refractive index–composition data, such as that referred to by Fuguitt and Hawkins,[10] the yield of *allo*-ocimene could generally be estimated with an accuracy of ±1%, which was at least as accurate as could be expected if the analysis were made by fractional distillation. In all runs n rose to a maximum and then declined as temperature continued to rise (Fig. 3). Thus, for a given throughput, an optimum temperature for conversion to maximum n was established. These data for seven runs are presented in Table I.

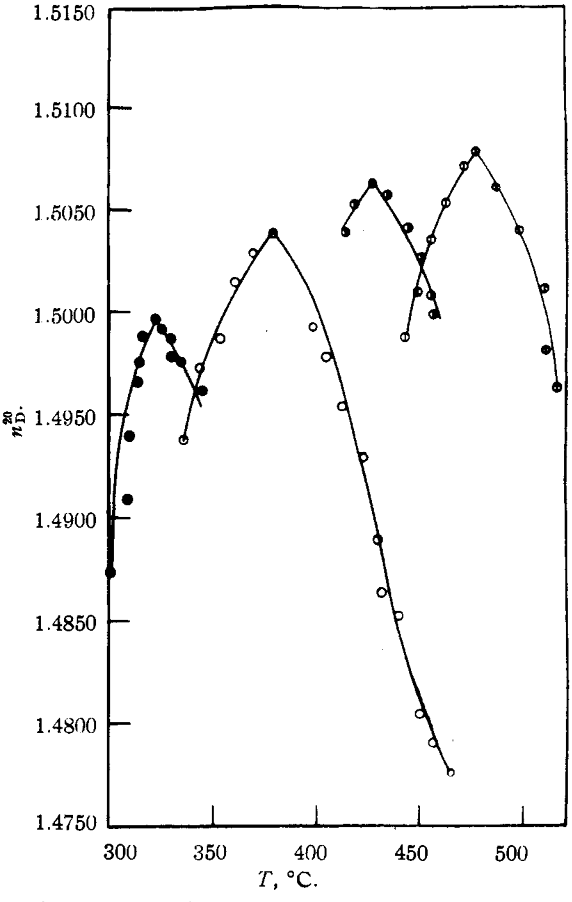

Fig. 3.—Refractive index *vs.* reaction temperature at various constant throughputs of α-pinene: ●, 0.6 vol./min., 1-cc. reactor; O, 3.3 vol./min., 0.2-cc. reactor: ◑, 16.5 vol./min., 0.2-cc. reactor; ⦶, 105 vol./min., 0.1-cc. reactor.

In each run those samples having a refractive index which approximated the maximum n obtained in that run were combined and analyzed by fractional distillation. The pyrolysates which were distilled, therefore, represent product formed at a given throughput over a relatively narrow range of temperature.

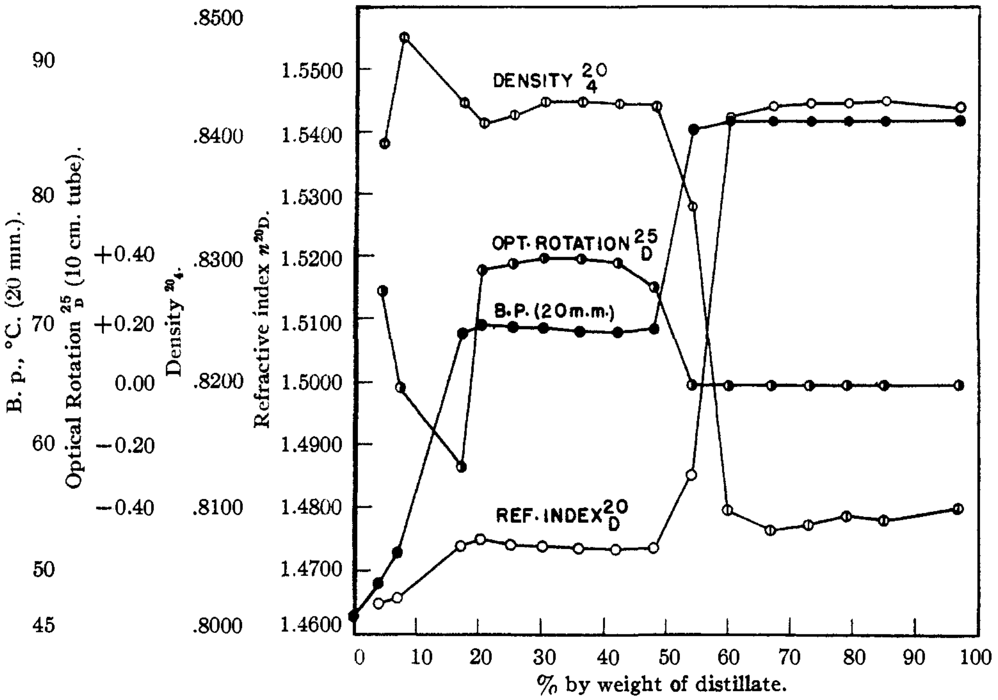

Fig. 4.—Fractional analytical distillation of a 400-g. batch of α-pinene pyrolysate produced at 452–490°, at a throughput of 105 vol./min.; reactor volume is 0.1 cc.

TABLE I

TEMPERATURES REQUIRED FOR PRODUCT OF MAXIMUM REFRACTIVE INDEX AT VARIOUS RATES OF THROUGHPUT

Throughput vol./min.	Reactor. vol., cc.	T. °C., for max. n^{20}	Max.[a] n^{20}	% Yield of *allo*-ocimene based on n	Pressure, p. s. i. gage
0.6	1.0	325	1.4998	38	450
3.2	0.2	380	1.5039	44	430
3.1	1.0	380	1.5027	42	450
8	0.2	400	1.5058	47	450
11	1.0	413	1.5063	48	480
16	0.2	427	1.5063	48	475
105	0.1	473	1.5078	50	525

[a] Represents substantially complete conversion of α-pinene.

TABLE II

COMPOSITION OF PRODUCTS SHOWING CONSTANT REFRACTIVE INDEX AND DENSITY AT SPECIFIC TEMPERATURES AND TWO RATES OF THROUGHPUT

Throughput, vol./min.	$T \pm 2$°C.	% Conversion	% Polymer[a]	% Dipentene[a]	% *allo*-Ocimene[a]	Pressure, p. s. i. gage
0.0005	215	28	0	64	25	180
.0005	230	66	12	62	20	160
.0005	244	82	19	60	14	135
.0005	258	95	25	54	10	120
.0005	280	100	36	45	4	210
.0041	242	45	5.5	55	34	163
.0041	260	75	11	59	26	225
.0041	269	89	16	54	19	225
.0041	286	99	19	48	16	220
.0041	302	100	23	48	13	255

[a] On basis of α-pinene converted.

Two extended runs were made in which the 160-cc. reactor was used with throughputs of 0.0005 vol./min. and 0.0041 vol./min. In each run temperature was stabilized within ±2°. When the effluent reached a constant n and d at a specific temperature, samples were taken for fractional analytical distillation. The temperature was then raised, and the procedure repeated. At a throughput of 0.0041 vol./min., the temperature range studied was 242–302°. At a throughput of 0.0005 vol./min., the temperature range studied was 215–280°. Five samples were taken at each throughput and analyzed. Results are presented in Table II.

Two temperatures of reaction were studied in the batch runs. The results are tabulated in Table III.

TABLE III

COMPOSITION OF PRODUCTS OBTAINED IN BATCH RUNS AT TWO SPECIFIC TEMPERATURES

Bath temp., °C.	Time of reaction, hr.	% Conversion	% Polymer[a]	% Dipentene[a]	% *allo*-Ocimene[a]
188.5	98	25	0	66	28
188.5	194	53	12	65	14
188.5	410	84	22	66	3
203	45	61	16	59	14
203	74	77	18	58	13

[a] On basis of α-pinene converted.

It was experimentally determined that at 325° and a throughput rate of 0.6 vol./min., 100% conversion of α-pinene occurred with no polymer formation. From this and from the data in Tables II and III it appears that for each reaction temperature below 300° there is a throughput and corresponding incomplete conversion of α-pinene such that no polymer is formed and a maximum yield of *allo*-ocimene is obtained. With increasing reaction temperature this maximum yield of *allo*-ocimene increases, as does the corresponding per cent. conversion.

Analysis and Chemical Examination.—Analysis was accomplished by the vacuum fractional distillation technique, using Podbielniak heli-grid-packed columns 4 feet long. Batches of 225–700 g. were distilled in a 25-mm. i. d. column. Batches of 75–165 g. were distilled in a 13-mm. i. d. column. All distillations were conducted at a pressure of 20 mm. The b. p. (20 mm.), n^{20}D, d^{20}_4 and α^{25}D of practically all of the fractions were measured and plotted against the per cent. by weight of total charge. A typical graph, which depicts the separations effected, is presented in Fig. 4. The calculations of composition were made from the physical properties of the fractions. No evidence of any substance boiling between dipentene and *allo*-ocimene was found.

The temperature–plateau materials of each distillation were combined, and crystalline derivatives were prepared from portions of each composite.

Dipentene was identified as the tetrabromide. For example, 3 g. of terpene from a composite of fractions boiling at 69.2–69.5°, fractions 6 to 9 (Fig. 4), reacted with bromine in the cold in ether and amyl alcohol solution, according to Godlewski's method.[12] On evaporation of the ether the yield of crude crystals was approximately 4.5 g. After two crystallizations from methanol the m. p. was 124–125°. *allo*-Ocimene was identified by formation of the maleic anhydride adduct, according to the methods of Hultzsch[13] and Goldblatt and Palkin.[4] For example, 4 g. of terpene from a composite of fractions boiling at 86°, fractions 13–15 (Fig. 4), reacted with 3.5 g. of maleic anhydride. The reactant was distilled and yielded 4.5 g. of adduct, which, after crystallization from methanol and recrystallization from hexane, melted at 82–83°.

The presence of the pyronenes was established by the formation of the maleic anhydride adducts. The adduct of β-pyronene was readily obtained in crystalline form from fraction 3 (Fig. 4) which had b. p. (20 mm.) 52–68.5°, n^{20}D 1.4740, and d^{20}_4 0.8424; after crystallization from hexane followed by recrystallization from methanol, it melted at 163–164°. The adduct of α-pyronene was obtained in crystalline form from fraction 1 (Fig. 4) which had b. p. (20 mm.) 46.5–49°, n^{20}D 1.4647, d^{20}_4 0.8391; after two crystallizations from methanol, it melted at 90.5–91°.

Acknowledgment.—For the loan of the Zenith gear pump and the helpful advice on its use, we are indebted to A. L. Merrifield of the Southern Regional Research Laboratory. For assistance in various phases of the work, we are indebted to Frances O. Batson, Dorothy M. Oldroyd and William J. Runckel, all of the Naval Stores Research Division.

Summary

1. The isomerization of α-pinene in a continuous liquid phase process has been investigated over the temperature range 200–500°.

2. The data indicate that the reactions take place throughout this temperature range in the same manner found by Fuguitt and Hawkins in batch experiments over the temperature range 189.5–285°. The yield of dipentene decreases and the yield of *allo*-ocimene increases with increasing temperature. The cyclization of *allo*-ocimene to α- and β-pyronene occurs throughout the range investigated. If the contact time is limited to that required for substantially complete conversion of α-pinene, the polymerization reaction becomes relatively unimportant at reaction temperatures somewhat above 300°.

3. At incomplete conversions of α-pinene, the α-pinene is partially racemized.

4. At a given temperature the same products are obtained in roughly the same yields for both vapor phase and liquid phase reaction.

NEW ORLEANS 19, LOUISIANA RECEIVED APRIL 14, 1945

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(12) Godlewski, *Chem. Ztg.*, **22**, 827 (1898).

(13) Hultzsch, *Ber.*, **72**, 1187 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

Synthesis of a Homologous Series of Optically Active Normal Aliphatic α-Monoglycerides (L-Series)

BY ERICH BAER AND HERMANN O. L. FISCHER

Asymmetric substitution in the glycerol molecule leads to compounds capable of occurring in enantiomorphic forms. Many glycerol derivatives of biological origin have been shown to possess an asymmetric structure, but in spite of this fact up to the present time, only four of these, namely, α-glycerophosphoric acid,[1,2] batyl alcohol,[3,4a] chimyl alcohol[3] and selachyl alcohol[5] have exhibited measurable optical activity. It took considerable time and effort to establish the optical activity of these four compounds beyond doubt, since their rotations are not only small but also change in magnitude and sign with changes in concentration.

The natural fats and oils, especially those of seed fats and marine animal fats, which, according to newer investigations,[4b] contain a large percentage of mixed glycerides with three different acids in each molecule, should also possess optical activity. For reasons only now understood, and which will be explained in this paper, the optical activity of most fats and oils is negligible. Some fats and oils exhibit small rotations but these have been traced back either to the presence of optically active acids or traces of optically active substances of a different chemical type. Suzuki and Inoue[6] found that rapidly prepared samples of

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(3) E. Baer and H. O. L. Fischer, *ibid.*, **140**, 397 (1941).

(4) (a) Earlier literature, *cf.* T. P. Hilditch "The Chemical Constitution of Natural Fats," Chapman and Hall, Ltd., London, 1940, p. 362; (b) p. 14.

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(6) B. Suzuki and Y. Inoue, *Proc. Imp. Acad. (Tokyo)*, **6**, 71 (1930); *C. A.*, **24** 4265 (1930).