after reaction with the 5-ml. olefin sample removed at the time t. The symbol N' refers to the normality of the sodium hydroxide solution and N'' refers to the normality of the sodium thiosulfate solution. The quantity $(b - y)N''/2$ gives the concentration of olefin at time t. Similarly, x is the concentration of alkyl halide hydrolyzed at time t in terms of the sodium hydroxide solution, and xN' gives the concentration of alkyl chloride hydrolyzed at time t. The ratio of these two quantities gives the olefin fraction, $k_E/(k_E + k_S)$, the fraction of the carbonium ions reacting by elimination.

The experimental procedure was tested with a number of olefins. The simpler olefins yielded results with an accuracy of ±1%. The more highly branched olefins were more difficult. In these cases it was necessary to standardize carefully both the time the bromine was in contact with the olefin and the excess of bromine used. Adoption of the procedure outlined permitted the standard solutions of olefins to be determined with an accuracy of better than ±3%. Accordingly, it is believed that the olefin fractions reported are accurate to at least this figure. The results of a typical determination, with abbreviated data, are reported in Table II.

TABLE II

DETERMINATION OF OLEFIN FRACTION IN HYDROLYSIS OF DIMETHYL-*t*-BUTYLCARBINYL CHLORIDE IN "80%" ETHANOL AT 25°: $N' = 0.03530$; $N'' = 0.01997$

t, hr.	x, ml.	k_1, hr.$^{-1}$	$b - y$, ml.	$k_E/(k_E + k_S)$
0	0		0	
3	0.96	0.0394	2.09	0.615
5	1.54	.0394	3.36	.616
7	2.07	.0392	4.61	.629
∞	8.62			

Summary

The quantity of olefin formed in the hydrolysis of twelve tertiary chlorides has been determined. The results indicate the importance of steric effects in unimolecular elimination reactions.

LAFAYETTE, IND. RECEIVED APRIL 30, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF PENNSYLVANIA]

A Study of the Polymerization of α- and β-Pinene with Friedel–Crafts Type Catalysts

BY WILLIAM J. ROBERTS[1] AND ALLAN R. DAY

The catalytic polymerization of the isomeric pinene constituents of turpentine has been the subject of a number of investigations.[2] Until recently, most of the published work has dealt with α-pinene. Burroughs[3] first clearly differentiated between the two pinenes, with respect to polymerization behavior. He reported that β-pinene, under the influence of aluminum chloride, gives a much higher yield of solid polymer. Furthermore, the latter has a higher melting point than the polymer from α-pinene.

In view of the lack of directly comparable polymerization data for the two pinenes, as well as the inconclusive and incomplete information bearing on the nature of the polymerization mechanisms and polymer structures, further investigation seemed advisable.

The catalytic conversion of α- and β-pinenes to polymers, which are non-volatile in superheated steam, was studied with a number of Friedel–Crafts catalysts. The temperature and concentrations were kept constant for this series of experiments. The results of this series of tests, Table I, show that the relative order of efficiencies of the catalysts used is about the same for both isomers. β-Pinene polymerizes very rapidly and with extreme exothermic vigor after less than 1% of aluminum chloride has been added. The polymerization of α-pinene, although highly exothermic, is noticeably less violent.

TABLE I

PINENE POLYMERIZATION TESTS. COMPARATIVE CATALYST EFFICIENCIES UNDER STANDARD CONDITIONS[a]

	α-Pinene		β-Pinene	
Catalyst	% Solid polymer	S. P. °C.[b]	% Solid polymer	S. P., °C.[b]
$AlBr_3$	35.3	85.0	93.2	136
$AlCl_3$	35.2	84.0	94.2	134
$ZrCl_4$	20.0	91.3	96.0	132
$AlCl_3 \cdot (C_2H_5)_2O$	18.0	67.3	76.5	102
BF_3[c]	14.2	67.0	54.0	104
$BF_3 \cdot (C_2H_5)_2O$	11.8	Semi-solid	43.0	68.0
$SnCl_4$	4.7	..	21.3	...
$BiCl_3$	0.1	..	5.6	...
$SbCl_3$	0.2	..	0.7	...
$ZnCl_2$	0.0	..	0.5	...

[a] Concentration of pinene, 50% in toluene; temperature 40–45°; amount of catalyst 5% (based on pinene); average molecular weight of α-pinene polymer 650, average molecular weight of β-pinene polymer 1500. [b] A. S. T. M. Ball and Ring Method D 36–26. [c] Gaseous boron trifluoride passed into the solution until the latter was saturated.

Figures 1, 2 and 3 show the effect of monomer concentration and temperature on solid polymer formation from the two pinenes. The pinenes differ markedly in response to decreasing temperature of polymerization.[3] In general, maximum solid polymer yields were obtained from β-pinene at −30° and from α-pinene at 40°.

The variation in softening point with molecular weight for polymers from α-pinene, β-pinene and

---

[1] Present address: Pennsylvania Industrial Chemical Corporation, 319 Arch Street, Philadelphia 6, Pa.

[2] Frankforter and Poppe, Orig. Com. 8th Intern. Congr. Appl. Chem. (appendix), **25**, 363 (1912); Steinkopf and Freund, *Ber.*, **47**, 411 (1914); Waterman, Leendertse and Koelensmid, *Rec. trav. chim.*, **55**, 7 (1936); Kondakow and Saprikin, *Bull. soc. chim.*, **37**, 1045 (1925); Thomas, U. S. Patent 1,939,932, Dec. 19. 1933; Carmody and Carmody, THIS JOURNAL, **59**, 1312 (1937).

[3] U. S. Patent 2,335,912, Dec. 7, 1943; see also Borglin, U. S. Patent 2,405,558, Aug. 13 ,1946.

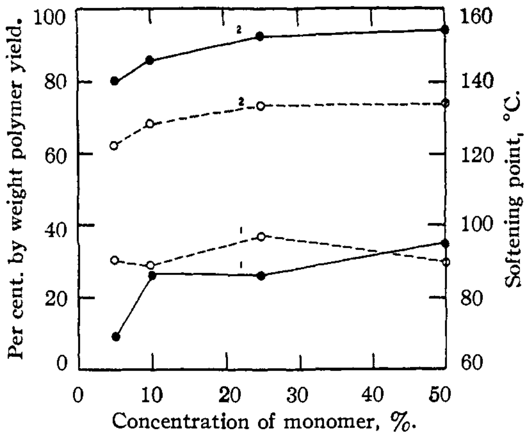


Fig. 1.—Polymerization of isomeric pinenes, at various concentrations in toluene, with aluminum chloride: 1, α-pinene; 2, β-pinene; ●, yield; ○, softening point.

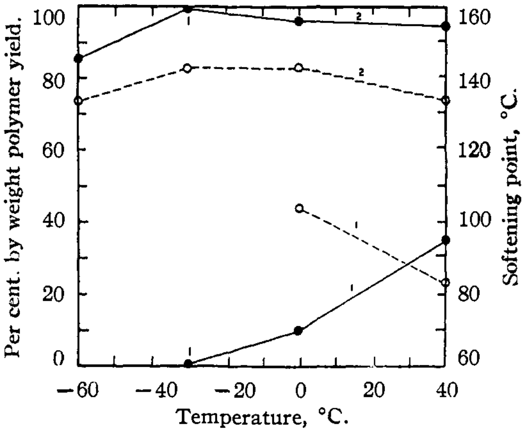


Fig. 2.—Polymerization of isomeric pinenes with aluminum chloride at various temperatures: 1, α-pinene; 2, β-pinene; ●, yield; ○, softening point.

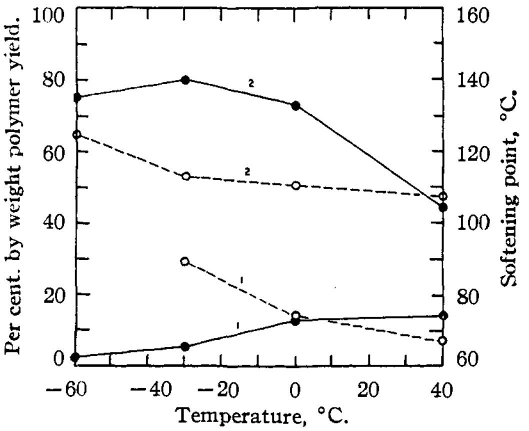


Fig. 3.—Polymerization of isomeric pinenes with boron fluoride at various temperatures: 1, α-pinene; 2, β-pinene; ●, yield; ○, softening point.

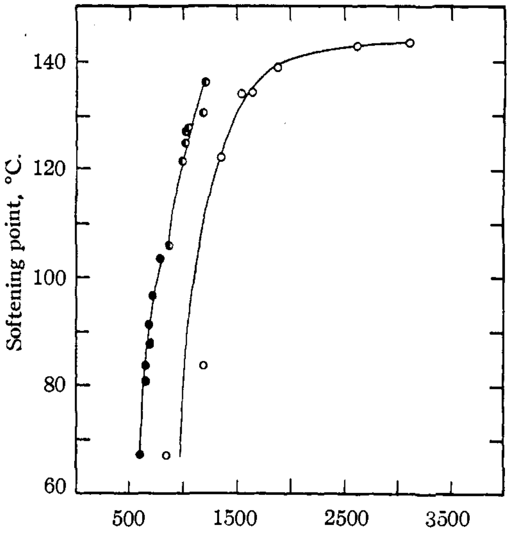


Fig. 4.—Relation of molecular weight and softening point of terpene polymers: ●, α-pinene polymers; ○, β-pinene polymers; ◐, limonene polymers.

d-limonene is shown in Fig. 4. The α-pinene polymers have molecular weights several hundred units lower than those of β-pinene, for a given softening point, suggesting definite structural differences. The polymers made from limonene have a softening point—molecular weight relationship similar to that of the polymer obtained from α-pinene.

Table II lists density, refractive index, and "unit refractivity" data for polymers obtained from α-pinene, β-pinene and limonene. The "unit refractivity" represents the molar refractivity of the recurring $C_{10}H_{16}$ unit, recently defined by Wiley.[4] The physical properties of the

TABLE II

TERPENE POLYMERS: REFRACTIVITY DATA

Source of polymer	S. P., °C.	Approx. mol. wt.	Degree of polymerization	Refractive index	Density	Unit refractivity
β-Pinene	143.2	3100	22.8	1.5272	0.9679	43.31
β-Pinene	142.8	2615	19.2	1.5260	.9707	43.00
β-Pinene	138.8	1874	13.8	1.5249	.9716	42.89
β-Pinene	134.2	1645	12.1	1.5231	.9659	43.02
β-Pinene	134.0	1548	11.4	1.5265	.9664	43.23
β-Pinene	67.5	857	6.3	1.5244	.9640	43.19
Av.			14.3	1.5254	.9678	43.11
α-Pinene	96.5	708	5.2	1.5300	.9818	42.79
α-Pinene	91.3	690	5.1	1.5275	.9837	42.54
α-Pinene	87.8	680	5.0	1.5271	.9817	42.60
α-Pinene	83.8	650	4.8	1.5334	.9859	42.84
α-Pinene	80.8	650	4.8	1.5235	.9791	42.45
α-Pinene	67.3	600	4.4	1.5303	.9838	42.72
Av.			4.9	1.5286	.9827	42.66
Limonene	136.0	1200	8.8	1.5356	.9977	42.48
Limonene	128.2	1035	7.6	1.5325	.9949	42.39
Limonene	127.0	1030	7.6	1.5299	.9950	42.22
Limonene	124.7	1007	7.4	1.5330	.9917	42.56
Av.			7.9	1.5328	.9948	42.41

---

(4) Wiley, *Ind. Eng. Chem.*, **38**, 959 (1946).

α-pinene polymers, despite the lower degree of polymerization, tend to approach those of polylimonene more closely than do those of poly-β-pinene. The similarity of refractivity of α-pinene polymers and limonene polymers is particularly pronounced.

In Table III, the average unit refractivities for these terpene polymers are compared with values calculated for various possible recurring unit structures. The Eisenlohr values for carbon, hydrogen and carbon–carbon double bonds were used and allowance was made for the increment which would result from one additional endocyclic, double bond in a terminal unit of each polymolecule. Since no formaldehyde was detected in the course of the ozonolysis experiments, it is believed that the unsaturated bond in the terminal unit is an endocyclic double bond. For the bicyclic polymer structure two methods have been used to calculate the theoretical refractivity. In one method (see column 5, Table III) no allowance is made for a bicyclic ring structure. In the second method (see column 6, Table III) an additional increment of 0.32 has been allowed for the exaltation caused by the fused cyclobutane ring in pinene.[5]

TABLE III

TERPENE POLYMERS. THEORETICAL AND ACTUAL UNIT REFRACTIVITIES

Source of polymer	Degree of polymerization	Unit refractivity Average observed	Deviation of calculated values Monocyclic	Bicyclic	Pinene
β-Pinene	14.3	43.11	−0.52	+1.21	+0.89
α-Pinene	4.9	42.66	−1.20	+0.53	+0.21
Limonene	7.9	42.41	−1.32	+0.41	

The β-pinene polymers appear to consist largely of recurring monocyclic units. In the case of the α-pinene polymers, the refractivity is close to that calculated for a true polymer (polymer resulting from polymerization without involving isomerization of the monomer). It is not safe to conclude, from refractivity data alone, that α-pinene polymerizes as such. An alternative mechanism would involve the isomerization of at least a part of the α-pinene to limonene, followed by polymerization of the latter to give solid polymers with the observed refractivities. Refractivity data on two samples of the dimer from α-pinene gave values for unit refractivity of 43.14 and 43.07. The average, 43.11, is reasonably close to the calculated unit refractivity for a true dimer of α-pinene, 42.97.

Further information was acquired from a study of the ozone absorption of these terpene polymers (Table IV). The β-pinene polymer shows an ozone absorption corresponding to one double bond per recurring unit and thus indicates a monocyclic unit structure. The α-pinene polymer shows an ozone absorption equivalent to about one double bond per two recurring units. The unsaturation for this particular polymer, $(C_{10}H_{16})_5$, is much higher than can be accounted for by the presence of a terminal double bond in a true α-pinene polymer. The observed data, however, would be in line with the alternative mechanism, suggested above, *i. e.*, partial isomerization of α-pinene to limonene prior to polymerization. The ozone absorption for the dimer from α-pinene also indicates the presence of one double bond per two recurring units. It is probable, therefore, that the α-pinene dimer is made up of two bicyclic units.

TABLE IV

OZONIZATION OF TERPENE POLYMERS

Polymer	S. P., °C.	Wt. % ozone absorbed		Calcd. moles per recurring unit	
Poly-β-pinene	133	38.6	37.1	1.09	1.05
Poly-α-pinene	87.8	14.7	17.5	0.42	0.50
Polylimonene	133	20.6	21.2	0.58	0.60
α-Pinene dimer .		15.2		0.43	

Controlled treatment of α-pinene with aluminum chloride in ether can be effected so as to give a monocyclic terpene fraction which contains limonene. Since the latter is known to give good yields of solid polymer under the influence of aluminum chloride, it is probable that α-pinene is isomerized, in part at least, to limonene which is then converted to a solid polymer.

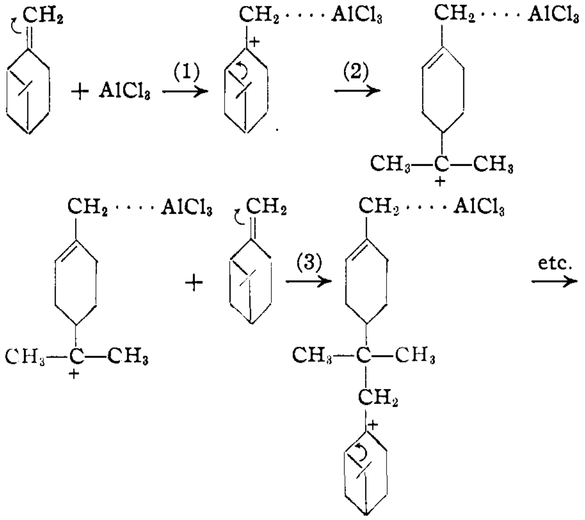
In order to obtain additional information on the influence of structure on polymerization behavior, methylenecyclohexane and 1-methylcyclohexene were prepared and treated with aluminum chloride. Methylenecyclohexane was particularly unreactive, showing that the methylene cyclohexane structure alone is not responsible for the ease of polymerization of β-pinene. The structure corresponding to α-pinene, 1-methylcyclohexene, was reactive and gave mainly low molecular weight liquid polymers but much less solid polymer than α-pinene By comparison with the pinenes, it is evident that the fused cyclobutane ring structure in the latter has a great influence on the ease and extent of polymerization. It is significant that in the simple cyclic olefins the semicyclic double bond is much less reactive than the endocyclic one, whereas in the pinenes the reverse is true, the isomer with the semicyclic double bond being more reactive and giving the greater amount of solid polymer.

It may be concluded from these data that the α- and β-pinenes follow different polymerization paths. The β-isomer gives a monocyclic polymer but does not go through limonene as an intermediate. The following mechanism for the polymerization of β-pinene, based on the mechanism proposed by Hunter and Yohe and also by Houtman[6] for the polymerization of isobutylene, appears plausible.

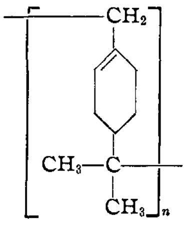
---

[5] Simonsen, "The Terpenes," Vol. I, Cambridge University Press, London, 1931, p. 117.

[6] Hunter and Yohe, THIS JOURNAL, **55**, 1248 (1933); Houtman, *J. Soc. Chem. Ind.* (*London*), **66**, 102 (1947).

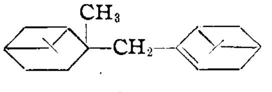


The recurring unit in the final polymer chain would be



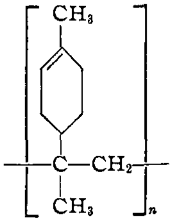
This unit would account for the refractivity and ozone absorption data. As pictured, the chain grows by alternate isomerization and addition steps.

α-Pinene presents a more complex case. Dimer formation occurs to a considerable extent. The refractivity and ozone absorption data, as well as the analogous reactivity of 1-methylcyclohexene, suggests that the dimer is formed without isomerization. It is believed that the dimerization involves hydrogen transfer and the dimer may be formulated (one possibility) as follows

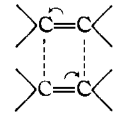


This would account for the presence of one double bond in the dimer.

In view of the demonstrable formation of limonene from α-pinene, with aluminum chloride as catalyst, and the ready polymerization of limonene to solid polymers, it seems probable that the α-pinene in part is isomerized to limonene and the latter then yields the solid polymer. Terpinolene and the terpinenes are negligible sources of solid polymers. This raises the question of the polymerization of limonene itself. The type formula (I) does not explain the fact that considerably more than one double bond per monomer unit disappears during the polymerization. There is a possibility that to some extent polymerization may occur through the addition of an unsaturated grouping in one molecule to a similar group in another molecule.



I



Risi and Gauvin[7] proposed such a saturation in connection with the chain cessation of polystyrene.

Conclusive proof of the structures of the various products obtained in this work will be difficult to obtain except in the case of the dimer. Further work along chemical lines is being planned.

Experimental

Materials.—The α-pinene was redistilled commercial material obtained from sulfate turpentine; b. p. 52.2–53.0° (20 mm.), n^{20}_D 1.4660, d^{20}_4 0.8592, α^{26}_D + 27.88°.

The β-pinene was obtained by careful fractionation of a commercial fraction from sulfate turpentine; b. p. 165.5–167°, n^{20}_D 1.4784, d^{20}_4 0.8706, $\alpha^{26.5}_D$ − 18.93°.

Methylenecyclohexane was prepared from cyclohexylcarbinol through the methyl xanthate procedure,[8] b. p. 102.3–103.3°, n^{20}_D 1.4512, d^{20}_4 0.8083.

1-Methylcyclohexene was prepared from 1-methylcyclohexanol with 50% sulfuric acid, b. p. 108.7–110.3°, n^{20}_D 1.4503, d^{20}_4 0.8121.

Limonene was obtained by fractionating commercial cold-pressed orange oil, b. p. 70.7–71.4° (20 mm.), n^{20}_D 1.4718, d^{20}_4 0.8428, $\alpha^{26.5}_D$ + 123.43°, tetrabromide m. p. 103–104°.

Terpinenes and terpinolene were obtained by the fractionation of an oil obtained by steam distilling 765 g. of α-terpineol, 2100 g. of oxalic acid and 1000 ml. of water.

Terpinene fraction, b. p. 172.8–174.1°, n^{20}_D 1.4778, d^{20}_4 0.8505.

Terpinolene, b. p. 77.2–79.2° (20 mm.), n^{20}_D 1.4858, d^{20}_4 0.8556, tetrabromide (from ethanol) m. p. 114.5–115.5°.

The various halide catalysts were good commercial grades.

General Polymerization Procedure.—To a stirred mixture of equal parts by weight of terpene hydrocarbon and C. P. toluene, the catalyst (5% based on the terpene hydrocarbon) was added gradually. The temperature was maintained at 40–45° during the addition and for an additional two hours by means of a Dry Ice–acetone-bath. The catalyst was removed by stirring with 5% hydrochloric acid, the upper layer was then washed with sodium hydroxide solution and finally with water. The solvent and terpene hydrocarbons were removed by distillation. Higher boiling oils (usually dimers) were removed with superheated steam (250°) and the molten, non-volatile polymer was allowed to cool and harden in suitable vessels.

Polymerization of α-Pinene.—Two hundred grams of α-pinene, with aluminum chloride as catalyst, gave 69.7 g. (34.8%) of solid polymer, softening point 89.9° (A.S.T.M. Ball and Ring Method D 36-26) and 118 g. (59%) of dimer, b. p. 165–185° (11 mm.), n^{20}_D 1.5103, d^{20}_4 0.9450,

---

[7] Risi and Gauvin, *Can. J. Research*, **14B**, 255 (1936).

[8] Tschugaeff, *Ber.*, **32**, 3332 (1899); Whitmore and Simpson, THIS JOURNAL, **55**, 3809 (1933).

mol. wt. 294 (in benzene). A sample of α-pinene dimer from another run had the following physical properties: b. p. 169–180° (10 mm.), n^{20}_{D} 1.5107, d^{20}_{4} 0.9441, mol. wt. 296.

Polymerization of β-Pinene.—Two hundred grams of β-pinene, with aluminum chloride as catalyst, gave 188.4 g. (94.2%) of a solid polymer, s.p. 133.6°. Other samples, obtained in a similar manner, had softening points of 134, 139 and 143°.

Polymerization of Limonene.—One hundred grams of limonene, with aluminum chloride as catalyst, gave 85.7 g. (85.7%) of a solid polymer, s. p. 128.2°. Other samples had softening points 125 to 136°.

Polymerization of Terpinolene and the Terpinenes.—Under similar conditions with aluminum chloride as catalyst, these terpene hydrocarbons give very low yields of non-volatile polymers (0.8–1.5%). Large quantities of oils which are volatile in superheated steam are obtained.

Polymerization of Methylenecyclohexane.—The procedure followed in this case was the same as that described above except that benzene was used as the solvent. Only a small amount of heat was given off on addition of the catalyst and no red color, characteristic of the other polymerizations, appeared. Thirteen per cent. of the starting material was converted to a polymer which was volatile in superheated steam and the remainder was recovered unchanged.

Polymerization of 1-Methylcyclohexene.—A similar polymerization of this compound, in benzene solution, required mild cooling during the addition of the catalyst and for thirty additional minutes and a typical red color developed. The reaction mixture, after neutralization and removal of the aqueous layer, was fractionated at atmospheric pressure to remove unreacted olefin (23.8%). Vacuum distillation of the residue gave a 46.9% of dimer. The residue from the vacuum distillation was then distilled with superheated steam (250°) giving 20.5% of a volatile product and leaving 2.4% of a non-volatile product. Physical properties of dimer, b. p. 142.8–146.5° (20 mm.), n^{20}_{D} 1.4916, d^{20}_{4} 0.9002.

Molecular Weights of Terpene Polymers.—The molecular weight data plotted in Fig. 4 were obtained by cryoscopic methods with benzene as the solvent.

Densities and Refractivities of Solid Terpene Polymers.—For the solid polymers, the densities and refractive indices were determined at 26 ± 1° (Table II). The densities were determined in a calibrated 10-ml. pycnometer with 0.5–1.0 g. of polymer and distilled water. To eliminate errors from air bubbles in the polymers, the latter were melted under vacuum at 200° and poured into bubble-free beads. The refractive indices were measured by holding a clear piece of polymer against the prism of a Zeiss refractometer with a saturated solution of potassium mercuric iodide.

Ozone Absorption by Terpene Polymers.—Solid polymers from α-pinene, β-pinene and limonene were treated with dry ozone from a generator of the type described by Henne[9] following the procedure of Whitmore, Church and McGrew.[10] Solutions of 1.36 g. of polymer in 30 ml. of chloroform were used for the ozone absorption. Preliminary tests showed that when more concentrated solutions were used, β-pinene polymers showed very erratic, non-reproducible ozone absorption and a gelatinous product separated as ozonization proceeded. After ozonization, the solutions were evaporated under vacuum, at room temperature, until constant weight was reached. Since the polymers retain some chloroform, in each case a blank was run in which a similar unozonized polymer solution was evaporated under vacuum to constant weight. The solvent retained in the blank was deducted from the weight increase of the ozonized sample. All tests were run in duplicate (Table IV).

Isomerization of α-Pinene with Aluminum Chloride Etherate.—Preliminary tests showed that if the reaction conditions permit too vigorous a reaction no isomers can be isolated. At 0° little reaction occurs and almost all of the α-pinene can be recovered. At 25° the reaction can be controlled and monocyclic terpenes can be isolated. One thousand grams of α-pinene was treated, at 25°, with 50 g. of aluminum chloride etherate (equal weight of aluminum chloride dissolved in dry ether at 0°). The addition of the catalyst required fourteen minutes and the reaction was continued for forty-five minutes. After neutralization, the upper layer was steam distilled. The oil was dried and carefully fractionated and 155.9 g. (15.6%) of a fraction in the dipentene range was obtained, b. p. 69.6–71.0° (20 mm.), n^{20}_{D} 1.4751, d^{20}_{4} 0.8409, tetrabromide, m. p. 124–125°.

Acknowledgment is made to the Pennsylvania Industrial Chemical Corporation for their interest in this investigation.

Summary

1. The polymerization of α- and β-pinene with metallic halide catalysts has been studied, and certain chemical and physical properties investigated. In addition, the polymerization of related or analogous compounds has been studied.

2. The two pinenes differ in degree of polymerizability and in the nature of the resulting polymers. β-Pinene under ordinary conditions is polymerized almost quantitatively by aluminum chloride to a solid polymer, which has a monocyclic recurring unit. A mechanism involving isomerization within a carbonium ion during polymerization is advanced.

3. α-Pinene gives, under the influence of aluminum chloride under ordinary conditions, a partial yield (*ca.* 35%) of a solid, lower molecular weight polymer, and a greater yield (*ca.* 60%) of a dimer. It is suggested that the solid polymer results largely from limonene first produced by the isomerization of the α-pinene in the reaction medium, while the dimer is probably a true polymer of α-pinene.

PHILADELPHIA, PA. RECEIVED MAY 27, 1948

---

[9] Henne, THIS JOURNAL, **51**, 2676 (1929).

[10] Whitmore, Church and McGrew, *ibid.*, **56**, 176 (1934).