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The temperature was then allowed to rise until all but a few tiny crystals remained. It was then kept constant for some minutes until no change in the amount of the solid phase appeared to take place. Then the temperature was again allowed to rise slowly, and the point at which all the crystals disappeared was taken as the freezing point. All temperatures were measured by a standardized mercury thermometer above 0° C. and by a standard pentane thermometer below. The results are listed in the following table:

			Temp. at Which	h
Weight of			One Liquid	Incipient
Decalin	SC)2	Disappeared	Freezing Points
Grams	Grams	Mole %	° C.	° C.
	0	0		-35.5
1.9455	0.0860	8.77	-14.90	-37.5
1.8942	0.2315	20.93	3.95	-37.3
2.0529	0.5146	35.06	25.20	-38.3
1,4815	0.6011	46.70	32.60	-38.4
1.3925	0.6611	51.67	35.50	-37.9
0.5419	0.3799	60.63	40.40	-39.6
0.4192	0.4564	70.23	41.35	39.9
0.1668	0.2692	77.72	41.80	-40.4
0.3648	1.0910	86.58	41.65	-40.9
0.2226	1.0139	90.78	39.95	-41.1
0.2078	1.8629	95.15	26.80	-41.3
0.0588	0.6994	96.37	22.40	-41.9
		100		-75.4

By plotting mole per cent sulfur dioxide against temperature, the curve in the figure is obtained. The critical solution temperature is thus shown to be 41.8° C. Region I contains one liquid phase; region II, two liquid phases; and region III, solid Decalin and one liquid. The peculiarity



about the diagram is the shape of line BC' along which the freezing points fall. It does not coincide with line BC because we are here dealing with a ternary system and the freezing points under the experimental conditions are not true equilibrium states. If the solubility of the two forms of the hydrocarbon were the same, there would not be this difference.

The C. S. T. for the dicyclic ringed compound with sulfur dioxide is thus 28.3° C. higher than that of cyclohexane and 4.5° higher than that of *n*-decane.

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Isomerization and Hydration of Pinene

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THE study of the isomerization, hydration, and polymerization products of pinene as produced by the action of various agents (mostly acids) offers an interesting but complicated subject. Many products are formed, and, in spite of the large amount of published work, it appears to be almost impossible, except in a few cases, to control such reactions so as to obtain any one product in good yields.

The isomerization of pinene has been reported by various workers to yield in varying amounts the following hydrocarbons:



Dupont (11) showed the value of Raman spectra in the analysis of such hydrocarbon mixtures. After treating pinene with 50 per cent sulfuric acid at a temperature not over 50° C. for 24 hours and working up the resulting mixture, he was able to show the presence of the following compounds: p-cymene, camphene, limonene, α -terpinene, γ -terpinene, terpinolene, and 1,4-cineole. This probably

represents the most complete qualitative treatment to date. In general, however, the literature is vague both as to the constituents and the amounts present.

The same may be said of the isomerization and hydration of pinene but to a lesser extent. Although many papers and patents refer to the direct formation of α -terpineol, terpine hydrate, borneol, and isoborneol or their derivatives, relatively few refer to actual yields. Small amounts of fenchyl alcohol have also been reported:





Because of the qualitative nature of so much of the earlier work and the conflicting statements in others, it was thought desirable to repeat some of the previous work under somewhat different conditions and at the same time investigate some new methods.

Sulfuric and phosphoric acids were used as isomerization agents.

In general, phosphoric acid was much less effective but similar in its action to sulfuric acid. Only the experiments with sulfuric acid are reported in this paper. In the acid isomerization, terpinolene was the only hydrocarbon which could be isolated in a relatively pure state by fractionation, and it was obtained in fair yields. Dipentene was always present in the 174-178° C. fraction but was never obtained pure. The presence of limonene could not be established in any of the runs by chemical means. It is extremely doubtful if the hydrocarbons present (165-180° C.) can be successfully fractionated. Conant and Carlson (9)experienced similar difficulties in the fractionation of mixtures of pinene and dipentene. p-Cymene was found in the 174-178° C. fraction in all cases examined, although in small amounts. At times tests for α -terpinene (nitrosite, melting point 155° C.) were obtained in the range 174-183° C., but the results were not consistent and duplicate runs seldom gave the same data. Camphene, cincole, and γ -terpinene were not found.

An attempt was also made to isomerize pinene by passing its vapor over 20-mesh pumice impregnated with thorium The isomerization and hydration of α -pinene as produced by sulfuric acid and phosphoric acid were studied. Only terpinolene, terpineol, and terpine hydrate could be readily isolated in pure form. The vapor-phase isomerization of α -pinene over heated thorium oxide was studied. The main product was dipentene with appreciable amounts of camphene.

oxide. This method yielded quite different results; the major product was dipentene with appreciable amounts of camphene.

Both sulfuric and phosphoric acids were employed for the hydration experiments. Again phosphoric acid, under the same conditions, proved much less effective. In these runs terpine hydrate and terpineol could be readily isolated. Hydration was never complete, and the reaction mixtures contained some mixed hydrocarbons, of which only terpinolene could be separated in a pure state. Small amounts of borneol were isolated in the runs where ethyl alcohol was not used.

Of the numerous experiments carried out, only the more important results are tabulated here. All of the results included were verified by duplicate runs. If the conditions are rigidly followed, fairly good check results can be obtained.

The pinene used was obtained from rectified American turpentine oil. It was allowed to stand over potassium hydroxide, steam-distilled, and dried. It was then fractionated over sodium. The 155–156.5° C. fraction had the following constants: d_{20}^{20} , 0.8665; n_{20}^{20} , 1.4777; $[\alpha]_{21}^{21} + 16^{\circ}$.

Acid Isomerization, Liquid Phase

The pinene was added slowly, with vigorous stirring, to the cold sulfuric acid-ethyl alcohol solution, the rate being so adjusted that the temperature remained fairly constant. At the end of the reaction the two layers were separated; the upper layer was neutralized at once with sodium bicarbonate and then washed with water. The lower layer was added to water, when more oil separated. The latter was treated as just described and added to the first oil separated. The total oil was then steam-distilled to separate the polymer which was not volatile in steam. The steam-volatile oil, after drying over anhydrous sodium sulfate, was fractionated in vacuum (10 mm.) and finally fractionated at normal pressure over sodium. The final product was collected in the following fractions:

° C.	Fraction
156–161	Mostly pinene
161–170	Some pinene and dipentene (very small)
170–174	Impure dipentene (small)
174–178	Mostly dipentene and p-cymene
178 - 184	Dipentene and terpinolene
184 - 188	Terpinolene

The terpineol (vacuum fractions, 94-98° C. at 10 mm. pressure) was not fractionated at atmospheric pressure.

		TABL	ьI.	Liqi	ло-Рн	ASE]	SOMER	ZATION				
Run No.	Reagents	Temp.	Tir Ada	ne of dition <i>Min</i>	Total Hr	Time Min	Steam- Volatile Oil	Polymer	Terpinolene Grame	Terpineol Grams	Terpin Hydrate Grams	Recovered Pinene Grams
	TRACH ARCHOULANTED	· U.	<u>п</u> т.	12174.	<u>п</u> т.	<i>Mm</i> .	100 8	10	24.2	A	0	0
1 2 3 4	$\begin{array}{c} 136 \\ 272 \\ C_{10}H_{16}, 40 \\ C_{2}H_{5}OH, 98 \\ H_{2}SO_{4} \\ 136 \\ C_{10}H_{16}, 46 \\ C_{2}H_{5}OH, 49 \\ H_{2}SO_{4} \\ 136 \\ C_{10}H_{16}, 92 \\ C_{2}H_{5}OH, 49 \\ H_{2}SO_{4} \\ 136 \\ C_{10}H_{16}, 92 \\ C_{2}H_{5}OH, 49 \\ H_{2}SO_{4} \\ 136 \\ C_{10}H_{16}, 92 \\ C_{2}H_{5}OH, 49 \\ H_{2}SO_{4} \\ 136 \\ C_{10}H_{16}, 92 \\ C_{2}H_{5}OH, 49 \\ H_{2}SO_{4} \\ 136 \\ C_{10}H_{16}, 92 \\ C_{2}H_{5}OH, 49 \\ H_{2}SO_{4} \\ 100 \\ H_{2}SO_{4} \\ H_{2}SO_{4}$	-8 -10 -4	3 8 2 4	15 15 0	* 83 6	75 0 0	237 111.3 112.5	$ \begin{array}{c} 10 \\ 26 \\ 6.5 \\ 16 \\ 16 \\ 7 7 7 7 7 $	84.3 66.7 30 9.3	17 8 3	4 0 0	25 24 67
⁵ Allowed	136 $C_{10}H_{16}$, 46 C_2H_5OH , 49 $H_2SO_4^{-3}$ to come to room temperature and heat	0 ed to 65-	1 70° (30 D. for 1	3 hour.	0	48.7	74.5	24	0	U	U

It was identified by means of its physical constants and the melting point of its nitrosochloride (107–108° C.).

The terpin hydrate settled out of the aqueous layer after the removal of the oil, on standing for 3 to 4 days. It was recrystallized from acetone containing a little water.

The terpinolene fraction, after several distillations had the following average values: boiling point, 184-187° C. at 760 mm.; d_4^{20} , 0.8583; n_D^{26} , 1.48017. These values were almost constant for the various runs. They check fairly well with the best values given in the literature. Semmler and Schossberger (19) gave: boiling point 67-68° C. at 10 mm.; d^{20} , 0.8520-0.8547; n²⁰, 1.48228-1.48484. Henry and Paget (13) gave: boiling point, 186° C.; d¹⁵₁₅, 0.8633; n²⁰_D, 1.4883.

The terpinolene was further identified by means of its tetrabromide. The bromination was carried out in a cold ether-amyl alcohol solution, and yields of 50 to 60 per cent were obtained. In most cases the separation of the tetrabromide occurred readily. In some few cases the addition of a little ethyl alcohol facilitated the separation. After recrystallization from ethyl alcohol it usually melted at 115-116° C., the value given in the older literature. After repeated recrystallization from alcohol, the least soluble form was obtained which melted at 122° C. Henry and Paget were the first to show that the recrystallization of the tetrabromide yielded two forms. The first to come out melted at 122° and the second melted at 119° C.

At times, tests for α -terpinene (nitrosite, melting point 155° C., 22) were obtained in the fractions at 174-183° C., but the results were not consistent and duplicate runs often gave negative results.

The presence of dipentene was established by means of its tetrabromide, melting point 124-125° C. It was the main constituent of the 174-178° fraction and was found in smaller amounts in the fractions 170-174° and 178-183° C. The limonene tetrabromide was not isolated at any time.

p-Cymene was usually found in small amounts in the 174-178° C. fraction. It was obtained from this fraction by repeatedly shaking with concentrated sulfuric acid and finally steam-distilling; the terpene hydrocarbons were polymerized and hence not volatile in steam (2,6-dinitro derivative, melting point 54° C., 7).

The lower fractions (except 156-161° C., mostly pinene) consisted definitely of mixtures. Various types of fractionating columns were tried but in no case was separation possible. The values for some of the intermediate fractions are as follows:

° C.	d28	n_D^{26}				
156-161	0,8509 - 0.8512	1.4658 - 1.4743				
174-178	0.8480-0.8476	1.4734 - 1.4740				
178-183	0.8472 - 0.8474	1.4743 - 1.4765				

The fractions from 156-180° C. were dextrorotatory but varied from run to run, indicating the probable presence of pinene, limonene, or both. Repeated tests were made for camphene and cincole but always with negative results.

The polymer formed gave rather uniform values for physical constants, varying over a very small range: boiling point, 166-168° C. at 8 mm.; d²⁶, 0.9198; n²⁶_D, 1.50843. It appeared to be the same dimer reported by Dulou (10), Carter, Smith, and Read (8), and Brooks and Humphrey (7).

Vapor-Phase Isomerization

Thorium oxide was the only catalyst studied in this series of Thorium oxide was the only catalyst studied in this series of experiments. Eighteen grams of 20-mesh pumice were impreg-nated with 6 grams of thorium oxide. The pumice was added to a nitric acid solution of the thorium, the solution slowly evapo-rated, and the residue gently heated until no more oxides of nitrogen were given off. A 4-inch (10.2-cm.) catalyst bed was held in place by perforated porcelain plates, in a 26-mm. (in-side diameter) Pyrex tube. A regulated stream of nitrogen was held through the heated nineare and the mixture was then bubbled through the heated pinene, and the mixture was then passed through a preheater and over the catalyst. Pyrolysis effects increased at higher temperatures, and it was found necessary to operate within fairly definite temperature limits (380-425° C.). The condensate was worked up by repeated fractionation, either at normal pressure or in vacuum.

The presence of unchanged pinene was established by means of physical constants and the formation of the nitrolbenzylamine (melting point 122-123° C.). Dipentene was present in large amounts as indicated by the good yields (55-65 per cent) of dipentene tetrabromide from the 170-180° C. fractions.

The presence of appreciable amounts of camphene in the lower fractions was shown by the Bertram-Walbaum method (5). For example, 20 grams of the 158-165° C. fraction from run 1 was treated with sulfuric acid (0.8 cc. in 1.2 cc. water) and 50 cc. of glacial acetic acid. The mixture was heated to 50-60° C. for 3 hours, then saponified and steamdistilled. This treatment yielded 13.7 grams of crude isoborneol (phenylurethane, melting at 137-138° C.).

Terpinolene tetrabromide could not be obtained from any of the fractions, and the tests for α -terpinene were likewise negative. All of the fractions were dextrorotatory, indicating the possible presence of pinene, limonene, or both.

When the condensate was fractionated entirely at normal pressure considerable polymerization occurred and more polymer formed with each fractionation. When the fractionation was carried out in vacuum, the excess polymerization was avoided and low-boiling fractions with unusually low densities were obtained (Table II, run 4). The low densities indicated the possible presence of an unsaturated open-chain hydrocarbon, but no derivatives could be prepared and fractionation appeared to be impossible.

	TABLE	II. V.	apor-Pha	se Ison	(ERIZ	ATION	Ŧ
Run No.	Pinene Used	Bath Temp.	Catalyst and Preheater Temp.	Nitrogen Rate	Ti	me	Steam- Volatile Condensate
1	Grams 344	°C. 170	° C. 390	Liters/ min. 0.78	$\frac{Hr}{2}$	Min. 45	Grams 273
23	430 Same as 2, without	160	420	0.78	ĩ	15	340
4	catalyst 430	160 170	420 420	0.78 0.78	3 3	30 30	361 350
		A	nalysis of .	Run 1			
	Fraction ° C.	d_{4}^{20}	n_{\perp}^2	0	$[\alpha]_{D}^{22}$	s	team Dist. %
	$158-165^{a}$ 165-170 170-175 175-180	$0.8445 \\ 0.8445 \\ 0.8421 \\ 0.8420$	1.47 1.47 1.47 1.47 1.47	751 772 783 790	+10. +14. +18. +21.	1 4 8	22.1 18.8 21.8 33.0
		A	nalvsis of H	Run 2		-	
	$\begin{array}{c} 158 - 165 \\ 165 - 170 \\ 170 - 175 \\ 175 - 180 \end{array}$	0.8400 0.8401 0.8420 0.8438	$1.47 \\ 1.47 \\ 1.48 \\ $	760 788 311 322	+ 8.9 +13.9 +18.7 +22.5	9 0 7 2	21.7 18.0 27.1 29.6
		A	nalysis of .	Run 3			

The steam-volatile oil after several fractionations yielded 60 per cent of fairly pure pinene, whose constants checked the starting point quite well. The rest of the oil appeared to be a mixture of pinene and dipentene. Poor yields of dipentene tetrabromide were obtained on the higher boiling fractions.

	Ar	alysis of Run	4	
Fraction at 10 Mm.	Yield	d ²⁰	$n_{\rm D}^{24}$	$[\alpha]_{\rm D}^{26}$
• C.	Grams			
51-2 52-3 53-4 54-54.5 56-58 58-58.5 58.5-59 59-60 60-65	$16.1 \\ 49.6 \\ 27.7 \\ 47.3 \\ 17.5 \\ 23.2 \\ 26.3 \\ 25.8 \\ 43.6 \\ 14.7 \\ $	$\begin{array}{c} 0.8307\\ 0.8275\\ 0.8255\\ 0.8255\\ 0.8256\\ 0.8356\\ 0.8356\\ 0.8301\\ 0.8273\\ 0.8317\\ 0.8555 \end{array}$	1.4783 1.4780 1.4777 1.4776 1.4787 1.4780 1.4788 1.4788 1.4795 1.4819 1.4853	+7.4 +8.9 +8.9 +10.2 +11.1 +10.8 +11.6 +12.1 +13.1 +12.4
65 - 71	14.9	0.8468	1.4922	+11.5

00-(1 14.9 0.8468 1.492 +11.5 ⁶ Twenty grams of the 158-165° C. fraction yielded 13.7 grams of orude isoborneol by the Bertram-Walbaum method. ^b The fractionation in vacuum proved less efficient than at normal pres-aure, All of the fractions from 54-71° C. gave tests for dipentene in spite of the low density. The lower fractions, 51-54° C., contained appreciable amounts of campinene but not as much as the 158-165° C. fraction from run 2; 98 grams gave 19.8 grams of orude isoborneol by the Bertram-Walbaum method.

TABLE III. HYDRATION											
Run No. Reagents Grams	Temp. ° C.	Tim Add <i>Hr</i> .	e of ition Min.	Total Hr.	Time Min.	Steam- Volatile Oil Grams	Polymer Grams	Terpinolene Grams	Terpineol Grams	Terpine Hydrate Grams	Recovered Pinene Grams
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5 3 0 3 3 3 3 3 3 3 3 -	4 2 2 4 3 4 3 1 in eac	0 15 15 20 0 45 30 20 30 20 30 case.	5 12 5 7 5 8 6 6 10	30 0 30 30 30 20 0	124 112 103 121 48.4 24.4 26 46 45 66.8	2.9 2.4 7 3 20 3.1 6 9 8.8 3	28.7 10.2 13.5 5.1 8.1 3 0 4 2.9 M	24.8 38.4 40.6 44.3 10.8 3 2.5 7 5.1 ostly unchs	2 9.6 1.6 57.8 30 34.5 98.5 100.5 inged pine	17.5 20 0 25 0 15 13.6 0 5.2 me

Because of space limitations only a few of the more important runs are included here.

Acid Hydration

The pinene was added slowly, with vigorous stirring, to the cold acid solution. In the case of the terpineol runs, the reaction mixture was treated as described under the acid isomerizations. The terpineol fraction was separated and purified by repeated vacuum distillation (boiling point 95-98° C. at 10 mm.; d_4^{20} , 0.9361; n_4^{20} , 1.4805).

The mixture was fractionated at normal pressure. Fairly pure terpinolene was isolated in every case and identified through its tetrabromide. Dipentene was also found in every case as indicated by its tetrabromide. Chemical tests failed to disclose the presence of any other hydrocarbons.

In the case of the terpin runs, the reaction mixture was poured into 100 to 200 cc. of ice water and allowed to stand overnight in the cold to facilitate the precipitation of the terpin hydrate. The latter was filtered with suction, washed with a little cold acetone, and recrystallized from hot acetone containing a little water (melting point 115-117° C.).

Small amounts of borneol or isoborneol separated during the vacuum distillation and sometimes during the steam distillation. It only appeared in those runs where alcohol was not used. It was identified by its melting point (200-203°C.) and phenylurethane (melting point 137-139° C.).

Discussion of Results

The action of concentrated sulfuric acid on pinene is vigorous and difficult to control. Preliminary runs were made at temperatures ranging from 0° to -60° C. These runs were very unsatisfactory, and polymerization appeared to be the major reaction. In the presence of ethyl alcohol (ethylsulfuric acid being the probable isomerizing agent) the reaction proceeded much more smoothly although temperature control remained the most important factor. As Table I indicates, some hydration usually occurred in these runs. In the presence of larger amounts of alcohol (run 4) the reaction became much slower and considerable amounts of unchanged pinene were recovered. In run 5, where the temperature was finally raised to 65-70° C., a fair amount of terpinolene was obtained. Terpinolene has been reported to be unstable and easily isomerized and polymerized.

The catalytic vapor-phase isomerization was of interest, chiefly because of the possibilities indicated. A more complete examination of various catalysts would undoubtedly lead to better yields of camphene.

Mulsey (14) passed pinene vapors over aluminum oxide at 310-425° C. At 410° he reported a large proportion of dipentene, a little limonene, no camphene, and probably some α -terpinene and terpinolene.

Arbuzov (1) studied the isomerization of α -pinene over hot reduced copper and through tubes filled with fragments of Suprax glass. In addition to dipentene, he obtained an aliphatic hydrocarbon (C₁₀H₁₆, b. p. at 16 mm., 87-87.5° C.).

The best yield (26 per cent) of the latter was at 340-350° C. This compound was allo-ocimene. Arbuzov concluded that temperature rather than the nature of the catalyst played the important role and probably this hydrocarbon was always formed when pinene was heated above 300° C.

Although it is possible that the results obtained might be explained by the presence of *allo*-ocimene, there was no positive evidence on which to base such a conclusion. It was not possible to isolate such a hydrocarbon, and it was extremely doubtful that the physical constants for the various fractions gave much indication of its presence. When the pinene was passed through the Pyrex tube without the catalyst, other conditions being the same, there was no indication of the presence of an unsaturated open-chain compound.

The hydration experiments (Table III) were, as a rule, easier to control because it was simpler to maintain a uniform low temperature. But here also temperature control appeared to be the most important factor; if the temperature was allowed to rise appreciably, considerable polymerization oc-The best yields of terpineol resulted when ethyl curred. alcohol was used; the absence of ethyl alcohol, other conditions being the same, facilitated the formation of terpin hydrate. It was surprising that no terpin hydrate separated when 50 per cent sulfuric acid was used (Table III, run 10) even though stirring was maintained for 10 hours.

Aschan (3) reported a 53.2 per cent yield of terpin hydrate by the use of 45 per cent sulfuric acid and stirring at 1° C. for 10 hours. Ono (15) reported a yield of 83 grams of terpin hydrate from 100 grams of pinene. He used 45 per cent sulfuric acid and stirred for 15 hours at 0° C.

The present experiments indicated a slow reaction where 50 per cent sulfuric acid was used.

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