

The Reaction between α -Pinene and Acids.

1. α -Pinene and Sulphuric acid.

By

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As is well known α -pinene gives terpinhydrate¹ by the catalytic action of dil. sulphuric acid. Recently O. Aschan² reported to have thus obtained terpinhydrate as the main hydration product (about 80% yield) with a small quantity of transterpine. The details of this experiment are, however, not given in the abstracts, and much seems not to have been studied about the influence of external conditions upon the reaction. So I have taken up the problem to study it more fully and, if possible, to clear up the true nature of the catalytic hydration.

EXPERIMENTAL PART.

α -Pinene obtained by repeated distillation of American turpentine oil having the following physical properties was used in the experiment.

Boiling point	155-156°
Specific gravity	0.8544 (24°)
Optical rotation	+37.81
Refractive index	1.4682 (21°)

¹ F. W. Semmler, Die ätherischen Oele, Bd. II., 203 (1906).

² Journ. chem. Soc., Abstracts i, 336 (1919).

1. PRELIMINARY EXPERIMENT.

100 grams of α -pinene were mixed with 300 grams of sulphuric acid (about 43%), and the mixture was vigorously shaken for about 15 hours at 18–20°C. After separating the crystalline substance from the reaction product by filtration, the filtrate was neutralized with sodium carbonate. The crystalline substance first separated and solid matter isolated by neutralization were mixed together and washed several times with petroleum ether. The crystalline mass thus purified, after having been dried in air, was crystallized from alcohol, whereupon needles, melting at 116–117° were obtained. The yield was about 31.5 grams. The crystals were proved to be terpinhydrate by a direct comparison with a pure specimen.

The oily liquid portion (about 66 grams) obtained after neutralization of sulphuric acid by soda and separated from terpinhydrate gave the following physical characters:

Specific gravity	0.8737 (22°)
Optical rotation	+5.25
Refractive index	1.4773 (21°)

50 c.c. of the oil were subjected to distillation under atmospheric pressure, and the following fractions were collected:

155–160°	3.1 c.c.
160–165°	1.8 c.c.
165–180°	39.9 c.c.
Above 180°	4.8 c.c.

The principal distillate (B.P. 165–180°) was found to have the following physical properties.

Specific gravity	0.8685 (17°)
Optical rotation	almost inactive
Refractive index	1.4751 (21°)

This fraction was redistilled on metallic sodium under atmospheric pressure, and a fraction boiling at 175–178° was collected and examined.

Specific gravity	0.8572 (17°)
Optical rotation	±0
Refractive index	1.4745 (21°)

It was analysed with the following results :

0.1123 gr. substance gave 0.3628. gr. CO₂ and 0.1209 gr. H₂O

	Found	Cal. (C ₁₀ H ₁₆)
Carbon	88.09%	88.15%
Hydrogen	12.03%	11.85%

A solution of this fraction (5.4 c.c.) in three times its volume of a mixture consisting of 2 parts of amyl alcohol and 3 parts of ether was cooled with a freezing mixture, and into it a solution of bromine (2.8 c.c.) in an amyl-alcohol-ether mixture was added gradually. 2 or 3 drops of water were then added, and the reaction mixture was allowed to stand overnight in an open beaker, when a large crop of white crystals was produced. On recrystallizing them from petroleum ether crystals melting at 124° and having all the properties of dipentenetetrabromide were obtained.

2. QUANTITATIVE INVESTIGATION.

To learn the influence of various conditions upon the reaction following experiments were conducted :

(1) Influence of the concentration of sulphuric acid.

α -Pinene	100 grs.
Sulphuric acid	300 grs.
Time	5 hours.
Temperature	17-20°

Table I.

Concentration of sulphuric acid	Terpin-hydrate	Oily part				Distillation test (50 c.c.)			
		gr.	sp. gr.	optical rotation	refractive index	155-160°	160-165°	165-178°	above 178°
%	gr.		(24°)		(22°)	c.c.	c.c.	c.c.	c.c.
10	no formation	99.3	0.8584	+31.80	1.4693	47.1	2.6	(above 160°)	
20	trace	99.2	0.8582	+31.03	1.4694	40.5	7.4	1.6	(above 165°)
30	1.4	99.0	0.8610	+21.37	1.4696	33.4	11.9	3.8	(above 165°)
40	13.2	87.7	0.8624	+15.98	1.4697	28.3	13.2	6.8	0.9
45	32.0	68.3	0.8727	+14.35	1.4700	9.4	13.8	21.0	4.7
50	17.5	82.6	0.8626	+12.75	1.4728	7.8	7.7	28.5	4.9

(2) Influence of amount of sulphuric acid.

α -Pinene	100 grs.
Time	5 hours.
Temperature	17-20°

Table II.

α -Pinene	Sulphuric acid (45%)	Terpin-hydrate	Oily part				Distillation test (50 c.c.)			
			gr.	sp. gr.	optical rotation	refractive index	155-160°	160-165°	165-178°	above 178°
gr. 100	gr. 100	gr. 19.8	81.4	(24°) 0.8700	+14.83	(22°) 1.4687	c.c. 26.2	c.c. 18.7	c.c. 3.0	c.c. 1.8
100	200	29.5	70.9	0.8737	+14.90	1.4690	9.7	15.8	18.9	3.3
100	300	32.0	68.3	0.8727	+14.35	1.4700	9.4	13.8	21.0	4.7
100	400	13.2	88.6	0.8759	+10.72	1.4738	8.0	11.9	25.3	3.2
100	500	10.7	91.7	0.8672	+ 8.64	1.4743	5.9	8.4	28.6	5.9

(3) Influence of time of reaction.

α -Pinene	100 grs.
Sulphuric acid (45%)	300 grs.
Temperature	17-20°

Table III.

Time	Terpin-hydrate	Time	Oily part				Distillation test (50 c.c.)			
			gr.	sp. gr.	optical rotation	refractive index	155-160°	160-165°	165-178°	above 178°
hrs. 5	gr. 32.0	gr./hr. 6.4	78.3	(24°) 0.8727	+14.35	(22°) 1.4700	c.c. 9.4	c.c. 13.8	c.c. 21.0	c.c. 4.7
10	48.0	4.8	52.2	(29°) 0.8780	+10.45	1.4708	1.2	9.4	28.9	8.8
15	53.5	3.5	46.4	(29°) 0.8739	+ 5.27	1.4773	*0.7	5.7	26.0	7.0

* Distillation test for 40 c.c.

(4) Influence of temperature.

α -Pinene	100 grs.
Sulphuric acid (45%)	300 grs.
Time	10 hours.

Table IV.

Temperature	Terpin hydrate	Oily Part				Distillation test (50 c.c.)			
		gr.	sp. gr.	optical rotation	refractive index	155-160°	160-165°	165-178°	above 178°
17-20°	gr. 48.4	52.2	(29°) 0.8780	+10.45	(22°) 1.4708	c.c. 1.2	c.c. 9.4	c.c. 28.9	c.c. 8.8
0-(-6°)	82.5	17.7	0.8640	+17.00	1.4683	28.5	7.5	19.0	3.2
0-(-4°)	80.1	20.8	0.8645	+17.38	1.4680				
0-(-7°)	83.0	17.9	0.8640	+17.16	1.4684				

3. ACTION OF SULPHURIC ACID UPON TERPINEOL.

The terpineol used in the experiments was prepared in the manner described below.

200 grams of terpinhydrate were mixed with 350 grams of oxalic acid (about 0.5%), and the mixture was boiled for 5 hours in an oil bath under constant stirring. The upper layer, coloured pale brown, was separated from the oxalic acid solution, washed with a dil. soda solution and then with water and subjected to steam distillation. The oily distillate dried with anhydrous sodium sulphate, was distilled under diminished pressure. The yield was about 85%.

Boiling point	103-107° (12-14 m.m.)
Specific gravity	0.9356 (20°)
Refractive index	1.4822 (21°)

50 grams of terpineol thus prepared were mixed with 200 grams of sulphuric acid (45%), and the mixture, cooled with a freezing mixture, was vigorously shaken for about 8 hours. The crystals obtained, were washed several times with petroleum ether and recrystallized from alcohol. The yield was almost quantitative. The crystals melted at 116-117° and were proved to be identical with terpinhydrate.

4. ACTION OF SULPHURIC ACID UPON DIPENTENE.

Dipentene, showing the following physical properties, was used.

Specific gravity	0.8563 (16°)
Optical rotation	±0
Refractive index	1.4738 (21°)

50 grams of dipentene were treated with 200 grams of 45% sulphuric acid in the manner analogous to that described in the previous article, and crystals proved to be terpinhydrate were obtained.

5. PREPARATION OF TERPINHYDRATE FROM TURPENTINE OIL.

Turpentine oil was distilled on metallic sodium, and a fraction boiling at 155–160° was collected. 100 grams of this fraction were mixed with 300 grams of sulphuric acid (45%), and the mixture cooled with a freezing mixture was vigorously shaken for 10–15° hours.

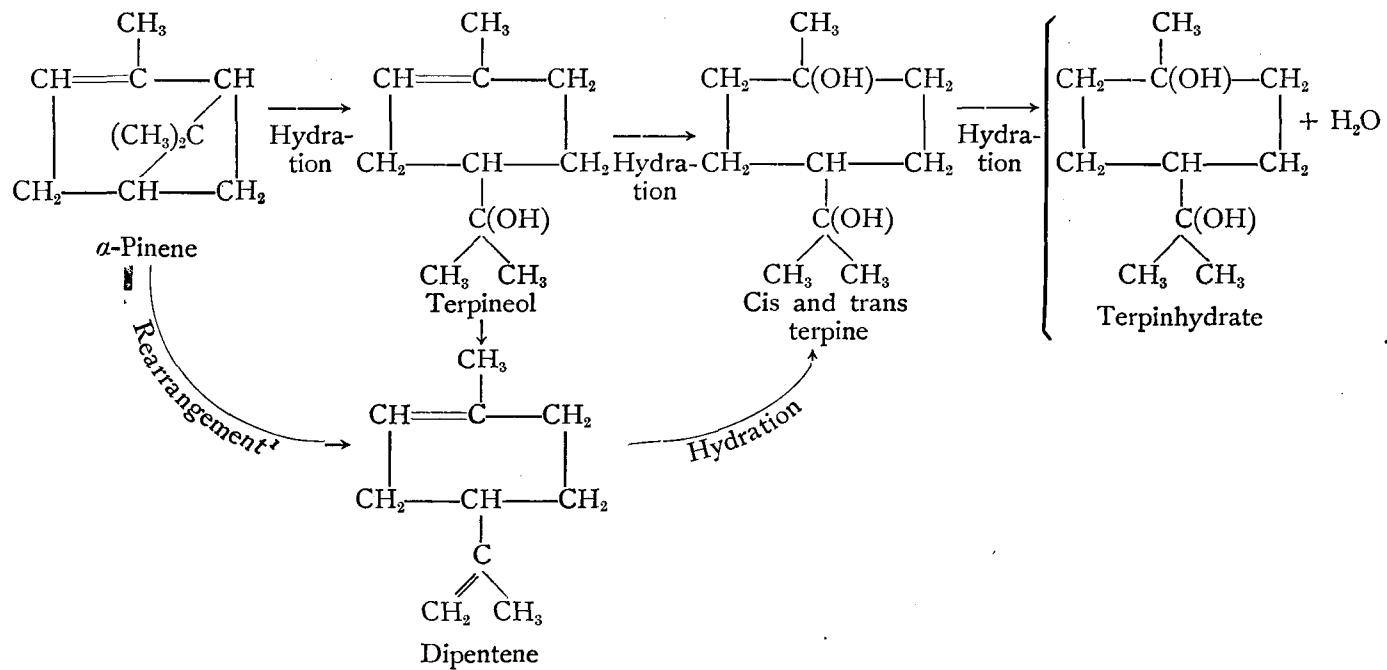
The crystals separated and those obtained by neutralizing the filtrate with crystalline sodium carbonate were mixed together and washed several times with petroleum ether. The white crystals when recrystallized from alcohol, melted at 116–117°. The yield was about 80 grams.

6. MECHANISM OF REACTION.

It is already known that α -pinene changes into terpineol¹ on the one hand and into transterpine² on the other, by the action of sulphuric acid. Now it might be better to regard these transformations and those described above as proceeding continuously from one to another than to consider them all independent. From this point of view I propose the following scheme for the catalytic hydration of α -pinene which takes place through the agency of sulphuric acid:

¹ Flavitzky, Ber. D. chem. Ges., 12, 2354 (1879).

² O. Aschan, loc. cit.



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