NATHAN SUGARMAN[1] and PHILLIP M. DAUGHERTY
Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Ga.

Oxidation of Alpha-Pinene

INTEREST in the esters of pinic acid (2,2-dimethyl-3-carboxycyclobutylacetic acid) for uses as lubricants and plasticizers (*8*) has led to a search for economic methods for producing pinic acid from α-pinene. The method of Delépine (*2*) involving oxidation with buffered potassium permaganate to pinonic acid (2,2-dimethyl-3-acetylcyclobutylacetic acid), followed by oxidation with calcium hypochlorite to yield pinic acid, has been utilized on a small pilot plant scale by Loeblich, Magne, and Mod (*6*). The yield of pinonic acid reported was 44.5% and the over-all yield of pinic acid was 25%. Attention has recently been given to the ozonolysis of α-pinene. Fisher and Stinson (*4*), using low temperatures and low concentrations of ozone in acetic acid, methanol, or nitromethane, obtained after decomposition of the ozonides yields of pinonic acid of about 40 to 60%. Holloway, Anderson, and Rodin (*5*), working with both diluted and highly concentrated ozone, obtained yields of pinonic acid ranging from 14 to 68%.

Work was undertaken under a Research and Marketing Act Contract to study the use of peroxides and nitrogen-containing compounds as oxidants in the conversion of α-pinene.

The first portion of this article summarizes the screening experiments carried out under phase I of the project. The oxidants studied were hydrogen peroxide, sodium peroxide, calcium peroxide, zinc peroxide, nitric oxide, nitrogen dioxide, dinitrogen trioxide, nitrogen pentoxide, nitrosyl chloride, and nitric acid. The peroxide oxidations were liquid-phase reactions, whereas the nitrogen oxide oxidations were carried out in the vapor phase.

As a result of the screening experiments, hydrogen peroxide was selected for further study. The second part of this article describes the work done with hydrogen peroxide oxidation of α-pinene and with further oxidation of neutral products to acids.

Products from the reactions were separated into neutral and acidic portions by ether extractions of alkaline and acidic solutions. The neutral portions were fractionated and the fractions subjected to classification tests. The acid portions were subjected to chromatographic analyses for the estimation of known acidic constituents.

Oxidation with Peroxides and Nitrogen-Containing Oxidants

Hydrogen Peroxide. The experiments with hydrogen peroxide as the oxidant for α-pinene were based upon the Milas reaction (*7*). *Tert*-butyl aclohol was used as the reaction solvent in which the α-pinene and 90% hydrogen peroxide were dissolved. The catalysts used were either dissolved or dispersed in the reaction mixture.

The general method for carrying out the oxidations is described for Experiment 5.

Five hundred milliliters of *tert*-butyl alcohol were used to dissolve 174 grams of 88% hydrogen peroxide (approximately 4 moles). Five grams of anhydrous sodium carbonate were added to neutralize the phosphoric acid stabilizer for the peroxide and to remove water. The liquid was filtered through a plug of glass wool into a reaction flask equipped with a condenser and stirrer. To the flask were added 68 grams (0.5 mole) of α-pinene and 0.67 gram of chromium trioxide. The solution had a deep blue color due to the presence of perchromate ion.

The temperature was maintained while stirring at around 30° C. for 18.5 hours, at which time the deep blue color had changed to purple. Heating was continued for 4 hours at 55° C. The color of the solution became green, indicating that all of the peroxide had been consumed.

After distilling out the *tert*-butyl alcohol, the product was made alkaline and extracted with ether to remove neutral material. The aqueous residue was acidified and again extracted with ether to recover the acidic products.

The reaction conditions employed for the various runs are indicated in Table I. The temperatures were not strictly controlled during the reaction period because of the erratic behavior caused by the exothermicity of the reactions.

The crude acidic products were analyzed by the partition chromatographic method described by Baldwin, Loeblich, and Lawrence (*1*). Although up to ten or more acids were found to be present, only the percentages of pinic, pinonic, and pinononic acids in the crude product are given in Table I. None of the other acids were present in predominant amounts. The yields of neutral and acid products are also given in Table I.

The neutral products were fractionally distilled and the fractions subjected to classification tests for hydroxyl, glycol, carbonyl, and methyl ketone groups. The neutral fractions were not examined in detail, but a study of several of the fractions indicated the presence of hydroxypinocamphone, pinene glycol, and, in case of the tungstic oxide catalyzed reactions, pinol glycol.

One of the neutral fractions from Experiment 5 was oxidized with neutral potassium permanganate and yielded a mixture of acids containing 27.5% pinonic acid and 7.9% pinic acid. This indicated that the neutral products did indeed contain precursors of pinic and pinonic acids.

Referring to Table I, in all cases except with the selenium dioxide catalyst the proportion of neutral products formed was greater than that of the acids. Even with large excesses of hydrogen peroxide (Experiments 5 and 17) the neutral products were preponderant.

The acidic products which were recovered contained little and in several cases no pinic acid (2,2-dimethyl-3-carboxycyclobutylacetic acid). In all cases pinonic (2,2-dimethyl-3-acetylcyclobutylacetic acid) and pinononic (2,-2-dimethyl-3-acetylcyclobutanecarboxylic acid) acids were present. The major portion of the acids, however, consisted of a mixture of unknown acids.

Metallic Peroxides. Those used were sodium peroxide (Baker's C.P.), zinc peroxide (Becco 55%), and calcium peroxide (Becco 60%). The use of each of these oxidants involved a heterogeneous reaction. The reaction products were worked up and examined as described under hydrogen peroxide. The conditions of reaction and the results obtained are summarized in Table II. A variety of acids, mostly unidentified, other than those listed, were present in the crude acidic products in small percentages of each.

With sodium peroxide and sodium hydrogen peroxide, aqueous solutions of the reagents were agitated with 0.5 mole of α-pinene in the reaction flask.

---

[1] Present address, North American Rayon Corp., Elizabethton, Tenn.

Table I. Oxidations with Hydrogen Peroxide

Expt. No.	Catalyst[b]		Molar Ratio		Time, Hr.	Temp., ° C.	Yield, %[a]		Ratio		Acid Content of Crude Acids, %		
	Kind	Concn., %	H_2O_2:Pinene				Neutrals	Acids	Neutrals:Acids		Pinic	Pinonic	Pinononic
4	CrO_3	0.12	1	1	15.0	28	50	8.3	6	1	1.3	16.4	2.4
5	CrO_3	0.99	8	1	18.5 4.0	30 55	45.6	13.7	3.3	1	2.0	13.5	6.3
17	CrO_3	0.45	9	1	48 3	20–30 50–60	60.0	30.6	2.0	1	6.9	8.4	5.9
16	WO_3	0.18	2	1	2 13	28 85	59.5	16.4	3.7	1	0.0	8.8	3.2
18	WO_3	0.18	1	1	1.5 20.0	80 85	48.8	13.1	3.7	1	0.0	8.9	2.9
15	SeO_2	0.37	4.5	1	24	85	50.7	55.1	0.9	1	0.0	8.3	1.7

[a] Based on amount of pinene not actually recovered and which presumably entered into reaction.
[b] Per cent catalyst based on weight of pinene used.

In these reactions, no recoverable acidic products were produced. In both cases, 80% of the original pinene was recovered unchanged.

In the reaction with zinc peroxide, 275 grams of the finely divided powder were suspended in 400 grams of α-pinene in a 1-liter round-bottomed flask. The mixture was heated at 130° to 140° C. for 45 hours. After working up the reaction products, it was found that only 6% of the α-pinene underwent conversion. Neither pinic nor pinonic acid appeared in the recovered acid products. The neutral product contained dipentene, indicating isomerization probably caused by the presence of the zinc compounds.

The calcium peroxide oxidation was carried out by forming a slurry of 180 grams of peroxide in 750 ml. of water and adding 68 grams of α-pinene. The mixture, vigorously stirred, was heated at 90° C. for 32 hours by which time all the peroxide had been consumed. While a better over-all conversion was obtained with this oxidation, high yields of neutrals and acids were not obtained. The acid fraction contained pinic and pinonic acids, and the neutral material responded to classification tests for glycols, methyl ketone, and carbonyl groups, indicating the presence of possible precursors of pinic and pinonic acids.

Nitrogen-Containing Oxidants. The vapor-phase oxidations of α-pinene with the nitrogen-containing oxidants were carried out in a specially constructed borosilicate glass apparatus.

The reactor consisted of a piece of 40-mm. i.d. tubing, 45 cm. in length. It was maintained in a position slightly inclined from the horizontal with the inlet end being higher than the outlet end. At each end of the reactor tube was a thermometer well for measuring inlet and outlet temperatures. Just beyond the inlet thermometer was a tube for introducing the oxidant vapor. Preceding the inlet end, the reactor was attached through an adapter to a boiling flask for vaporizing α-pinene. The outlet end of the reactor tube was attached to a condenser which discharged into a collection flask.

The inlet adapter tube served as a pinene-vapor preheater. Both it and the reactor were heated by wrapped coils of Nichrome wire.

The rate of flow of α-pinene through the reactor was controlled by adjusting the voltage input to the boiling flask heater. Rates of flow of the α-pinene ranged from 4.8 to 14.5 grams per minute for the various experiments.

The gaseous oxidants were metered from the cylinders through Flowrators and entered the reaction chamber at room temperature. The gas flows varied from 160 to 380 cc. per minute. For the nitric acid experiments, nitrogen gas was bubbled through hot fuming nitric acid (specific gravity of 1.50) to carry vapor to the reaction zone.

For several experiments at higher temperatures, the pinene boiler was replaced by a train of three gas-washing bottles immersed in a temperature-controlled heating bath of oil. Nitrogen gas was passed through the train of gas-washing bottles containing pinene, thus picking up pinene vapor and carrying it to the reaction zone.

The condensed product stream was passed directly into an aqueous solution of sodium bicarbonate or sodium hydroxide in order to neutralize quickly the acids formed.

Table II. Oxidation of α-Pinene with Metallic Peroxides

Expt. No.	Peroxide	Molar Ratio		Experimental Conditions	Yields Based on Pinene Consumed, %		Ratio		Acid Content of Crude Acids, %		
		Oxidant:Pinene			Neutrals	Acids	Neutrals:Acids		Pinic	Pinonic	Pinononic
6	$NaHO_2$	4	1	Heterogeneous reaction. Aqueous solution of oxidant 12 Hr. at 28–29° C. 4 Hr. at 50–60° C.	...[a]	0.0	...	...	...	...	...
7	Na_2O_2	4	1	Heterogeneous reaction. Aqueous solution of oxidant 24 Hr. at 28° C.	21.4[a]	0.0	...	...	...	...	...
8	ZnO_2	1	2	Heterogeneous reaction. Solid ZnO_2 suspended in pinene 45 Hr. at 130–140° C.	117.0[b]	10.2	11.4	1	0.0	0.0	4.9
12	CaO_2	3	1	Heterogeneous reaction. Aqueous slurry of oxidant 32 hr. at 90° C.	40.0[c]	6.0	6.7	1	4.7	13.6	9.6

[a] 80% of original pinene recovered unchanged.
[b] 94% of original pinene recovered unchanged.
[c] 26.4% of original pinene recovered unchanged.

Table III. Oxidation of α-Pinene with Nitrogen-Containing Oxidants

Expt. No.	*Oxidant*	*Molar Ratio*		*Temp., ° C.*	*Yield Based on Pinene Consumed, %*		*Ratio*		*Acid Content of Crude Acids, %*		
		Pinene:Oxidant			*Neutrals*	*Acids*	*Neutrals:Acids*		*Pinic*	*Pinonic*	*Pinononic*
10	NO	8.2	1	150	29.0	0.8	35	1	0.0	3.5	0.0
11	NO	8.2	1	230	6.0	0.5	12.5	1	0.9	3.2	5.0
13	NO_2	6.6	1	155	9.8	1.8	5	1	4.3	2.2	3.9
24	NO_2	8.2	$1(N_2)^a$	215	2.5	5.5	0.45	1	5.1	5.5	0.0
14	N_2O_3	5.6	1	160	16.5	2.0	8.5	1	4.9	0.0	0.0
25	N_2O_3	13.0	$1(N_2)^a$	200	4.1	1.2	3.4	1	14.3	6.7	0.0
19	N_2O_5	7.0	1	165	0.0	2.0	...	...	3.8	4.7	3.8
21	N_2O_5	17.0	$1(N_2)^a$	235	2.0	7.6	0.3	1	3.6	7.3	0.0
37	NOCl	3.7	$1(N_2)^a$	150	...	3.1^b	...	...	4.1	8.1	2.3
38	NOCl	3.7	$1(N_2)^a$	250	...	3.7^b	...	...	1.5	9.9	3.0
39	HNO_3	2.7	$1(N_2)^a$	175	...	2.5^b	...	...	0.3	0.0	4.0
40	HNO_3	2.7	$1(N_2)^a$	195	...	0.75^b	...	...	0.9	1.5	3.9

[a] **N_2 signifies nitrogen-diluted vapor.**
[b] **Yield based on total pinene through reactor.**

The neutral products obtained directly through ether extraction were too unstable to distill or fractionate. It was necessary to reflux the product in sodium hydroxide solution in order to stabilize the neutrals, presumably through the hydrolysis of nitrate or nitrite groups. Refluxing in methanol solution was effective only for nitric oxide reaction products.

Data obtained for these experiments are presented in Table III.

The yields of neutral and acidic products, which were calculated on the assumption that all of the unrecovered pinene had entered into reaction, were very small. However, because of some loss of unreacted pinene, these values may be somewhat too low.

From the values for the ratio of neutral to acid products, it appears that, in general, the higher temperatures favor the formation of increased proportions of acids. In all cases except one, the percentage of pinic acid in the acidic products was low, being less than 7%. In the exceptional case, the dinitrogen trioxide run at 200° C., the pinic acid content was 14.3%.

With nitrosyl chloride, 8 to 10% pinonic acid, and 1.5 to 4.0% pinic acid were found in the crude acids. While the crude acid products obtained with the other nitrogen-containing oxidants containing a variety of unknown and known acids derived from rearrangement and degradation of the pinonic acid structure, the nitrosyl chloride oxidation yielded surprisingly low amounts of these materials.

The neutral products contained nitrogen-containing compounds, but these appeared in the higher boiling fractions. The main (largest) fractions from the several oxidations did not contain nitrogen. Many of the fractions gave positive tests for alcohol and carbonyl groups, but only a few showed a positive glycol test.

In the nitrogen oxides oxidations, the molar ratios of pinene to the oxidants were high. Runs using an excess of oxidant were not made.

Hydrogen Peroxide Oxidations of α-Pinene

The hydrogen peroxide oxidations were carried out essentially as described in the first portion of this article. In most cases, *tert*-butyl alcohol was used as the reaction solvent in which the α-pinene and 90% hydrogen peroxide were dissolved. The catalysts used—chromium trioxide, tungstic oxide, sodium tungstate, sodium vanadate, and osmium tetroxide—were either dissolved or dispersed in the reaction mixture. Approximately 0.5 gram of catalysts—as metallic oxide—was used per mole (136 grams) of α-pinene. For 1 mole of α-pinene, the reaction volume was approximately 600 ml.

The experimental data for the hydrogen peroxide oxidations are shown in Table IV. The reaction products were separated into acid and neutral fractions. The acid fractions were analyzed by the chromatographic method of Baldwin, Loeblich, and Lawrence (*1*). Analyses of the acid products are presented in Table V.

Uncatalyzed oxidations at two different temperatures were carried out (Experiments 26 and 27). The different temperatures were achieved by using different alcohols—*tert*-butyl and *tert*-amyl—at the reflux temperature. Increasing the temperature from approximately 85° C. to around 100° C.

Table IV. Experimental Data on Hydrogen Peroxide Oxidations

Expt. No.	*Catalyst*	*Solvent*	*Temp., ° C.*	*Time, Hr.*	*Mole Ratio*		*Yield Based on Pinene Reacted, %*		*Ratio*		*Unreacted Pinene, %*
					Peroxide:Pinene		*Neutrals*	*Acids*	*Neutrals:Acids*		
26	None	*t*-Butyl alcohol	82–87	112	1	1	59.9	6.2	9.6	1	...
27	None	*t*-Amyl alcohol	100–104	21.3	1	1	69.0	9.6	7.2	1	...
28	CrO_3	*t*-Butyl alcohol	5	287	1	1	83.7	6.5	12.9	1	32.3
29	CrO_3	*t*-Butyl alcohol	30	28	1	1	62.7	8.9	7.0	1	46.6
30	WO_3	*t*-Butyl alcohol	30	374	1	1	92.0	1.9	48.4	1	20.1
31	WO_3	Heterogeneous Aqueous pinene	70	70	1.5	1	41.3	12.4	3.3	1	66.1
32	WO_3	Heterogeneous Aqueous pinene	70	13	2.5	1	15.5	6.2	2.5	1	52.5
33	Na_2WO_4	*t*-Butyl alcohol	70	14	1	1	72.8	12.2	5.9	1	42.9
34	CrO_3	*t*-Butyl alcohol	27.5	19.75	2	1	71.7	7.3	9.8	1	57.0
35	$Na_3VO_4 \cdot H_2O$	*t*-Butyl alcohol	26–40	54.75	1	1	60.2	7.5	8.0	1	...
36	OsO_4	*t*-Butyl alcohol	24 36–37	15 439	2	1	62.9	22.5	2.8	1	...

Table V. Analyses of Acid Products from Hydrogen Peroxide Oxidations

Expt. No.	Composition of Crude Acids, %						
	Pinonic	Nopinic	Pinic	Terpenylic	Norpinic	Hydroxy-pinic	P.E.V.[a] 430[b]
26	5.6	5.6	...	2.1	...	...	4.6
27	4.4	6.2	...	3.0	...	...	8.3
28	18.9	6.1	1.7	1.3	0.6	...	4.8
29	15.8	5.5	2.6	2.9	...	...	13.9
30	12.1	3.9	0.7	1.8	...	...	4.6
31	5.5	5.0	...	9.3	...	1.9	19.4
32	4.9	4.6	...	7.0	...	...	16.7
33	12.3	4.2	0.7	3.0	...	...	10.6
34	10.0	0.9	1.6	3.7	...	2.7	7.7
35	7.4	...	0.4	2.9	0.3	...	...
36	30.4	...	0.3	0.6	...	...	...

[a] P.E.V. = peak effluent volume (*1*).

[b] Percentage calculated assuming unknown acid had molecular weight of pinonic acid.

decreased the time of reaction (disappearance of peroxide) from 112 to 21 hours. The increased temperature also resulted in a lower ratio of neutral to acid products—i.e., a greater proportion of acids was produced. The values for the yields are probably too low since only a part of the unreacted pinene was accounted for, and the calculations were made on the basis that all of the remainder had reacted. Pinic acid was not found in the acidic products and the amounts of pinonic acid were low.

Experiments 28 and 29 were designed to show the effect of temperature on the rate of reaction and the products formed using a fixed amount of chromium trioxide catalyst. At the relatively low temperature of 5° C., a combined yield of neutrals and acids of 90.2% was obtained in a reaction time of 287 hours. The acids contained 18.9% pinonic acid, 1.7% pinic acid, and 4.8% of the P.E.V. (peak effluent volume) 430 (unknown) acid. At the higher temperature, the reaction proceeded much more rapidly, but the total yield of products was less (71.6%). The higher temperature also increased the proportion of acidic material formed, but the differences in pinonic and pinic acid contents were not great. However, there was a significant increase of the P.E.V. 430 acid from 4.8 to 13.9%.

The effect of increasing the ratio of hydrogen peroxide to pinene is shown in Experiment 34 which is comparable to Experiment 29. With the higher ratio of peroxide (2:1), the combined yield of neutrals and acids was somewhat greater, but the percentages of pinonic and pinic acids in the crude acids were less, having dropped from 15.8 to 10.0%, and from 2.6 to 1.6%, respectively.

Experiments 30 and 33 represent homogeneous reactions with a tungsten compound catalyst. The catalyst in Experiment 30 was added as tungstic oxide, but that in Experiment 33 was added as a water solution of sodium tungstate. In spite of the long reaction period of Experiment 30, an apparent yield of 92% neutral products and 1.9% acids was obtained, with only 20% of pinene unreacted. At the higher temperature of 70° C. (Experiment 33), the combined yield was lower (85%), the yield of acids was higher and the amount of unreacted pinene was greater. This seems to follow the pattern of the chromium trioxide–catalyzed oxidations at different temperatures. The pinonic and pinic acid contents of the acids from the two experiments are similar, whereas the amount of P.E.V. 430 acid was more than doubled at the higher temperature.

Experiments 31 and 32 were attempts to carry out a heterogeneous reaction using hydrogen peroxide in the aqueous phase at two different concentrations. The total yields of products were low in both cases, more than half of the pinene was unreacted, and the proportions of acids formed were greater than in the other tungsten-catalyzed reactions. Pinic acid was absent from the acidic products in both cases, and the amount of P.E.V. 430 acid was 19.4% in one case and 16.7% in the other.

The use of sodium vanadate as cata-

Table VI. Acid Dichromate Oxidations—Experimental Conditions and Yields

Expt. and Oxidation No.	Grams of $Na_2Cr_2O_7 \cdot 2H_2O$ per Gram Neutrals	Amount of H_2SO_4 per Gram Neutrals[a]		Material Recovered		Fraction of Detected Acids, %		
		Vol., ml.	Concn., %	Yield, %	Total Acids detected, %	Containing four-membered carbon ring[b]	With ruptured ring[c]	Of unknown structure
A[d]	1.78	4.70[e]	63	92.0	65.8	71.8[f]	9.0	19.2
B[d]	1.78	4.70	63	92.0[g]	91.7	64.8[h]	8.5	26.7
C[d]	1.78	4.70	50	108.5	78.0	85.3[i]	7.7	7.0
18[j]-1	1.75	4.66	63	89.1	34.8	14.5[k]	48.7[l]	36.8
27-1	3.55	8.00	50	42.0	56.1	27.1	25.7	47.2
28-1	1.75	4.70	63	17.0[g]	92.8	20.9	35.0	44.1
28-2	3.55	8.00	50	46.0	49.7	20.9	36.7	42.4
28-3	1.78	4.50	50	74.0	26.6	29.6	33.7	36.7
29-1	1.78	4.70	50	132.0	36.8	36.2	16.3	47.5
29-2	3.55	8.00	50	76.0	47.0	28.0	32.2	39.8
30-1	1.78	4.70	50	71.5	14.1	12.2	34.5	53.3
30-2	3.55	4.70	50	88.5	11.7	13.3	33.5	53.2
30-3	3.55	8.00	50	71.0	52.2	10.1	35.1	54.8
33-1	3.55	8.00	50	80.0	39.0	20.3	41.3	38.4
34-1	3.55	8.00	50	76.0	17.4	45.0	22.5	32.5
34-2	1.78	4.5	50	106.0	21.4	48.1	22.8	29.1

[a] Diluted with 5 ml. of water per gram of neutrals.

[b] Except as noted these acids consisted of varying quantities of pinonic, pinononic, pinic, and norpinic, none of which was present in predominating amounts.

[c] Except as noted, the major acid was found to be terpenylic.

[d] Hydroxypinocamphone.

[e] Acid added over period of 1.5 hr.

[f] Pinonic content = 33.6; pinic = 8.0.

[g] Acidic material only, with neutrals removed. Yields of neutrals: A = 0.5%; 28-1 = 52.5%.

[h] Pinonic content = 46.8; pinic = 5.4.

[i] Pinonic content = 59.7; pinic = 1.4.

[j] Fraction boiling 118°–120° C. at 4 mm.

[k] Mainly pinononic acid.

[l] Main acid was terebic.

lyst did not lead to any better results than those obtained using the chromium trioxide catalysts.

As a final experiment with hydrogen peroxide oxidation, osmium tetroxide was used as a catalyst. The crude acids obtained contained 30.42% of pinonic acid. This is the highest pinonic acid content of the acids obtained from an experiment. Also the crude acid mixture contained fewer other detectable acids, and these were present in very small amounts.

Oxidation of Neutral Products

Acid-Dichromate. The neutral products obtained from the hydrogen peroxide oxidations were presumed to be precursors of the desired pinic and pinonic acids on the basis of previous experiments involving fractionation and characterization of the fractions. Rather than to subject the neutral products obtained to fractionation, it was proposed to oxidize these materials to acids. The acid analyses could then be utilized as criteria for the occurrence of easily oxidizable pinic and pinonic acid precursors in the neutral products.

The oxidation of hydroxypinocamphone with sodium dichromate and sulfuric acid has been reported to yield 75% of pinonic acid (*3*). Hence this oxidation was applied to samples of neutral product as well as samples of hydroxypinocamphone.

In a typical oxidation experiment, a 20-gram sample of the neutral material and 100 ml. of water containing 35.6 grams of crystalline sodium dichromate were placed in a reaction flask fitted with a reflux condenser and a dropping tube. The mixture was heated to boiling and 94 ml. of 50% sulfuric acid solution were added over a period of 2 hours to the refluxing mixture.

Using this oxidation method, the yield of pinonic acid from hydroxypinocamphone fell far short of 75%, the best yield obtained being roughly 60% (Table VI). In all cases, the products from the dichromate oxidation of the neutral products from the hydrogen peroxide oxidations of α-pinene contained only small percentages of pinonic acid (0.3 to 7.8%). Furthermore, the amounts of open-chain acids such as terpenylic (3.4 to 26.9%) were in most cases several times that of pinonic. From these results, it would seem that a great part of the neutral products had already become rearranged through opening of the four-membered ring during the peroxide oxidations.

Neutral Permanganate. Oxidation with a neutral potassium permanganate solution was applied to a sample of neutral product (Experiment 28) which had also been oxidized by the acid-dichromate method. Of the recovered acids, there were included 16.0% pinonic acid, 4.0% pinic acid, 18.0% pinononic acid, and 18.3% terpenylic acid. Although 16.0% of pinonic acid appeared in the crude acids, the weight ratios of pinononic and terpenylic acids to pinonic were both 1.1:1. The comparatively high ratio for terpenylic acid would indicate that the neutral product from the hydrogen peroxide oxidation already contained considerable quantities of rearranged neutral material. Hence, the high yields of terpenylic acid from the dichromate oxidations were not entirely due to acid degradation during this oxidation.

Hypochlorite. Since pinonic acid can be oxidized with sodium hypochlorite to produce pinic acid, the use of this oxidant with neutral materials was studied. Two runs were made with hydroxypinocamphone. In the first run, the detected acids in the acidic material recovered were pinonic 10.9%, pinic 2.0%, pinononic 19.4%, and norpinic 2.6%. In the second run with a greater excess of hypochlorite, pinonic acid was not found, but pinononic, pinic, and norpinic acids were present in 10.6, 4.5, and 3.8%, respectively. These results indicate that, with the hypochlorite, chlorination takes place on the α-methylenic group as well as on the methyl group in hydroxypinocamphone.

Hypochlorite oxidation of neutral material from a sodium tungstate-catalyzed hydrogen peroxide oxidation (Experiment 33) was carried out. Pinononic, pinic, and norpinic acids (7.5, 10.0, and 10.8%, respectively) were formed, but no pinonic acid was found. Any pinonic acid formed during the oxidation was apparently further oxidized to pinic acid.

Conclusions

Oxidations of α-pinene with sodium peroxide, sodium hydrogen peroxide, zinc peroxide, and calcium peroxide yielded either no or very small amounts of pinic and pinonic acids.

The acidic products from the oxidations with nitrogen oxides as performed are complex mixtures of acids with neither pinonic acid nor pinic acid predominating. With the possible exception of dinitrogen trioxide at 200° C., oxidations with nitrogen oxides under the conditions reported do not yield enough pinic or pinonic acids to be useful.

The vapor-phase oxidation of α-pinene with nitrosyl chloride yields pinic and pinonic acids in low yields, but with surprisingly small amounts of rearranged and unknown acids.

The oxidation of α-pinene with hydrogen peroxide in *tert*-butyl alcohol catalyzed with the compounds of chromium, tungsten, vanadium, and osmium yields a greater proportion of neutral products than acid products. The mixture of acidic products from hydrogen peroxide oxidation contained pinonic, pinononic, and pinic acids, with the amount of pinonic acid being the greatest of the three.

The osmium tetroxide catalyst yields a less complex mixture of acid products than the other catalysts used. Pinonic acid was the main acid produced.

None of the catalyzed hydrogen peroxide oxidations studied appears to be capable of yielding pinonic and pinononic acids in sufficient quantities to be economically feasible.

Further oxidation of the neutral products with permanganate results in a mixture containing pinonic, pinononic, pinic, and norpinic acids, with the pinonic acid predominating. The neutral products from the peroxide oxidations while containing considerable amounts of materials retaining the four-membered ring also contain rearranged neutral products yielding open-chain acids upon further oxidation. The acid-dichromate oxidations under the conditions described are not satisfactory for converting neutral products to pinonic and pinic acids in high yields. Sodium hypochlorite oxidation of hydroxypinocamphone and of neutral products from hydrogen peroxide oxidation give high yields of pinononic and norpinic acids due to α-methylenic chlorination.

Acknowledgment

The authors wish to acknowledge with appreciation the cooperation of the Southern Utilization Branch, the technical assistance and advice of Gordon S. Fisher and others at the Naval Stores Station, Olustee, Fla., under the direction of E. L. Patton, and the cooperation of suppliers who furnished the samples of materials.

Literature Cited

(1) Baldwin, Doris E., Loeblich, Virginia M., Lawrence, Ray V., *Anal. Chem.* **26**, 760–2 (1954).

(2) Delépine, M., *Bull. soc. chim., France* **3**, 1369–82 (1936).

(3) Fisher, Gordon S., Naval Stores Station, Olustee, Fla., private communication.

(4) Fisher, Gordon S., Stinson, J. S., IND. ENG. CHEM. **47**, 1569–72 (1955).

(5) Holloway, F., Anderson, H. J., Rodin, W., *Ibid.*, **47**, 2111–13 (1955).

(6) Loeblich, V. M., Magne, F. C., Mod, R. R., *Ibid.*, **47**, 855–8 (1955).

(7) Milas, N. A., others, *J. Am. Chem. Soc.* **58**, 1302–4 (1936); **59**, 2342–4 (1937); **59**, 2345–7 (1937); **61**, 1844–7 (1939); **62**, 1841–3 (1940); Brit. Patent **508,526**; U. S. Patent **2,223,807**; *Ibid.*, **2,395,638**; *Ibid.*, **2,402,566**; *Ibid.*, **2,414,385** (1947).

(8) Murphy, C. M., O'Rear, J. G., Zisman, W. A., IND. ENG. CHEM. **45**, 119–25 (1953).

RECEIVED for review October 12, 1955
ACCEPTED May 2, 1956
Work done under Research and Marketing Act Contract No. A-1s-33820, U. S. Dept. of Agriculture.