

tals has indicated oxidation of the sulfur atoms.¹⁵ The above results are consistent with a mechanism involving (1) the consumption of three moles of periodate to cleave the contiguous hydroxyl bearing carbon chain to give two moles of formic acid and two of glyoxal diethyl mercaptal, (2) the consumption of four moles of periodate to give two moles of glyoxal diethyl sulfoxide, (3) the spontaneous decomposition of the latter to give two moles of formic acid and two of formaldehyde diethyl sulfoxide and (4) slow oxidation of the latter to formaldehyde diethyl sulfone.

D-Mannohexodialdose (VI).—Diisopropylidene-D-mannohexodialdose (5 g.) was heated at 100° for 40 minutes with 50% acetic acid (20 ml.) the solvent was removed by distillation, and the thick sirup obtained was dissolved in water (5 ml.). This solution was poured into absolute ethanol (50 ml.). The amorphous material that precipitated was collected and dried. It sintered at 150–160° and turned brown. The specific rotation at 20° was +47.7° (*c* 1, water).

Anal. Calcd. for C₈H₁₀O₆: C, 40.3; H, 5.6. Calcd. for C₈H₁₀O₆·0.5H₂O: C, 38.5; H, 5.9. Found: C, 38.9; H, 5.9.

D-Mannohexodialdose was not fermented by a bakers yeast that fermented D-mannose readily.

2,3,4,5-Diisopropylidene-D-mannitol (VII).—A solution of I (1.0 g.) in water (25 ml.) was treated with 0.3 M sodium metaperiodate (15 ml.). After one hour most of the periodate

(15) C. Huebner, R. Pankratz and K. P. Link, *THIS JOURNAL*, **72**, 4811 (1950).

had been consumed, and sodium borohydride (0.38 g.) was added to reduce the aldehyde groups. After one hour, the solution was extracted four times with chloroform (25 ml. each portion). The combined chloroform extract was washed once with water (10 ml.), then the organic layer was concentrated to a thick sirup which began to crystallize. It was recrystallized from benzene, to give 2,3,4,5-diisopropylidene-D-mannitol (0.7 g.) with m.p. 90–92°, and $[\alpha]_D^{20} +13.4^\circ$ (*c* 3, chloroform).

Anal. Calcd. for C₁₂H₂₂O₆ (262): C, 55.0; H, 8.4. Found: C, 55.3; H, 8.4.

Deacetonation of VII was accomplished by refluxing 0.25 g. in 0.5 N hydrochloric acid for five minutes. After removal of the solvent by distillation, the D-mannitol was crystallized from a mixture of water and ethanol. It melted at 164–165°, and the m.p. was not depressed when the substance was mixed with authentic D-mannitol. The specific rotation, +29.4° (*c* 4.5), in the presence of two parts of sodium borate decahydrate, compares well with the literature value +28.6° (*c* 10) determined under similar conditions.

Anal. Calcd. for C₆H₁₄O₆ (182): C, 39.5; H, 7.7. Found: C, 39.8; H, 7.8.

Acknowledgment.—The authors wish to express their gratitude to the Nutrition Foundation, Inc., for the generous support of this work.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, SOUTHERN REGIONAL RESEARCH LABORATORY¹]

Peroxides from Turpentine. II. Pinane Hydroperoxide²

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RECEIVED MARCH 16, 1953

The preparation of *cis-l*-pinane-2-hydroperoxide from β -pinene is described. The β -pinene was converted to *cis-l*-pinane by hydrogenation and fractional distillation of the product. The *cis-l*-pinane was oxidized at about 90° for 20 hours to give an oxidate containing about 50% of pinane hydroperoxide. The pure *cis-l*-pinane-2-hydroperoxide was isolated by a combination of distillation and precipitation of the sodium salt. Its structure was proved by reduction to the known *cis*-pinalol-2.

In the first paper of this series⁴ it was reported that pinane could be oxidized with oxygen to give a hydroperoxide which is a very good polymerization catalyst, but the hydroperoxide was not isolated or identified. The purpose of the present paper is to describe the preparation of a pure pinane hydroperoxide and to present evidence that it is *cis-l*-pinane-2-hydroperoxide.

Since there are four stereoisomers of pinane there should also be four stereoisomers for each position isomer of pinane hydroperoxide. In order to minimize the problem of stereoisomerism, the pinane used in this investigation was prepared from *l*- β -pinene by hydrogenation under conditions which were expected to give the *cis* isomer. The crude pinane obtained after simple distillation to remove the catalyst had the properties indicated in Table I. These properties are in very good agreement with those reported by Lipp⁵ for *cis*-pinane.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented in part before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

(3) Southern Regional Research Laboratory, New Orleans, Louisiana.

(4) G. S. Fisher, L. A. Goldblatt, I. Kniel and A. D. Snyder, *Ind. Eng. Chem.*, **43**, 671 (1951).

(5) A. Lipp, *Ber.*, **56**, 2096 (1923).

He reported n_D^{20} 1.4624, d_4^{20} 0.8562 and $[\alpha]_D -18.9$ for *cis-l*-pinane prepared from impure *l*- α -pinene and n_D^{20} 1.4624, d_4^{20} 0.8566 and $[\alpha]_D +23.08$ for *cis-d*-pinane. Fractionation of this crude pinane through an efficient distillation column at 20 mm. yielded a series of fractions of substantially constant boiling point, refractive index and density, but whose optical rotation increased throughout the distillation. Properties of typical fractions from this distillation are also given in Table I. The nature of the low rotating impurity will be discussed further in connection with the oxidation studies.

TABLE I

PHYSICAL PROPERTIES OF β -PINENE AND DERIVED PINANES

	n_D^{20}	d_4^{20}	$[\alpha]_D$	Total <i>cis</i> -tillate, %
β -Pinene	1.4787	0.8723	-21.3°	..
Crude pinane	1.4624	.8571	-22.7°	..
Fraction 16	1.4622	.8563	-21.6°	10
36	1.4624	.8567	-22.9°	40
47	1.4624	.8569	-23.2°	60
56	1.4626	.8565	-23.6°	78
63	1.4624	.8567	-23.8°	90

In order to determine whether this variation in optical rotation of the pinane would affect the op-

tical rotation and other properties of the hydroperoxide produced from it, portions of fraction 10, $[\alpha]_D -21.4$, fraction 44, $[\alpha]_D -23.2$ and fraction 64, $[\alpha]_D -23.8$, were oxidized to a peroxide content of about 50% and stripped to remove unreacted pinane. As shown in Table II nearly identical peroxide concentrates were obtained from all fractions; however, the pinanes recovered from the oxidates showed even greater variation in optical rotation than did the original pinanes. Apparently, the low-rotating impurity is more resistant to oxidation than is the *cis*-pinane.

TABLE II

EFFECT OF OPTICAL ROTATION OF PINANE ON THE PROPERTIES OF PINANE HYDROPEROXIDE

Fraction no.	Pinane hydroperoxide				Recovered pinane $[\alpha]_D$	
	$[\alpha]_D$	n^{20}_D	d^{25}_4	Assay, %		
10	-21.4°	1.4896	1.028	-20.5°	87	-20.3°
44	-23.2°	1.4884	1.018	-20.6°	92	-22.3°
64	-23.8°	1.4889	1.027	-20.6°	86	-23.7°

^a The observed peroxide number times 100 divided by 11,760.

In order to confirm this observation and at the same time obtain a fairly concentrated sample of the low rotating impurity, fractions 11 to 21 were combined, oxidized for about 20 hours at 90–95°, and stripped in the usual manner. The recovered pinane was then reoxidized and the process was repeated for a total of five oxidations. The properties of the various peroxide concentrates and recovered pinanes obtained by this procedure are given in Table III. The resistance of the impurity

very good agreement with those obtained for the final recovered pinane V.

As would be expected for such a pair of diastereomers, the infrared absorption spectra of *cis*-pinane (fraction 63) and recovered pinane V (presumably *trans*-pinane) are very similar.⁷ Several bands occurring in the *cis* form are shifted to about 0.1 μ longer wave length in the *trans* form, and bands at 10.2 and 11.6 μ are present in the *cis* form but absent in the *trans* form.

Preparation of Pure Pinane Hydroperoxide.—

Since nearly identical peroxide concentrates were produced from all of the fractions of pinane investigated, a heart-cut from the distillation was used for the preparation of the pure pinane hydroperoxide. The properties of the pinane, the oxidate prepared from it, and the peroxide at various stages of purification are given in Table IV. Although it is possible to obtain peroxide contents of more than 70% by direct oxidation of the pinane at about 90°, oxygenated by-products which interfere with subsequent purification are also produced. Hence, the oxidation was stopped when about 50% of the pinane had been converted to the hydroperoxide. Simple vacuum stripping gave a concentrate which contained about 90% of pinane hydroperoxide. The impurities consisted of small amounts of acids, aldehydes and ketones, including at least one relatively high-boiling positive rotating impurity. These various by-products were not further investigated. The two most common methods of purifying tertiary organic hydroperoxides are distillation and regeneration from the sodium salt. Preliminary experiments showed

TABLE III

SUCCESSIVE OXIDATION AND STRIPPING

Pinane charged: 291 g., n^{20}_D 1.4623, d^{25}_4 0.8534, $[\alpha]_D -21.5^\circ$. Oxidation conditions: 20–25 hours at 90–95°

Oxidation no.	P.N. ^a crude	Concentrated peroxide				Recovered pinane			
		P.N. ^a	Wt., g.	n^{20}_D	d^{25}_4	$[\alpha]^{20}_D$	n^{20}_D	d^{25}_4	$[\alpha]^{20}_D$
I	5700	10,860	155	1.4905	1.027	-20.4°	1.4621	0.8534	-20.4°
II	6000	10,940	49	1.4905	1.027	-20.7	1.4620	.8540	-19.1
III	2450	9,700	5	1.4894	...	-19.9	1.4617	.8542	-18.4
IV	1210	9,850	2	1.4877	...	-18.5	1.4619	.8530	-18.0
V	1040	10,040	1	1.4884	...	-17.7 ^b	1.4619	.8518	-18.1

^a Peroxide number in milliequivalents per kilogram. ^b In methanol (10%). All others neat.

to oxidation and the selectivity of oxidation of *cis*-pinane is shown by the low rate of oxidation in the last two or three oxidations as compared with the first two oxidations. The optical rotation of the recovered pinane, after decreasing markedly in the first two oxidations, became relatively constant. The refractive indices and densities of the recovered pinanes were only slightly lower than those of the original pinane. The great similarity between the boiling points, refractive indices and densities of the impurity and *cis*-pinane strongly suggests that the impurity is *trans*-pinane. The physical constants reported in the literature for *trans*-pinane vary widely and it is likely that all such materials contained *p*-menthane as well as some *cis*-pinane. The most reliable values are probably those reported by Schmidt⁶ for *trans-d*-pinane prepared from *trans-d-d*-pinene. He reports d^{20} 0.8558, n^{20}_D 1.4618 and $[\alpha]_D +20.4$, which values are in

that although distillation of the peroxide concentrate did not result in any obvious purification, it did greatly improve the purification that could be achieved by way of the sodium salt. Distillation of the regenerated pinane hydroperoxide then served to remove the last of the positive rotating

TABLE IV

PREPARATION OF PURE PINANE HYDROPEROXIDE

	Peroxide no.	n^{20}_D	d^{25}_4	$[\alpha]^{20}_D$
Pinane	...	1.4624	0.8528	-23.2°
Oxidate	6,700
Concentrate (I)	10,780	1.4884	1.018	-20.6°
(I) Distilled ^a (II)	10,870	1.4893
(II) Regenerated ^b (III)	11,680	1.4895	1.019	-21.8°
(III) Distilled ^c	11,750	1.4898	1.021	-27.4°

^a 57 to 60° at 0.1 mm. ^b From sodium salt. ^c 56° at 0.04 mm.

(6) H. Schmidt, *Chem. Ber.*, **80**, 520 (1947).

(7) R. T. O'Connor, private communication.

impurity and traces of the sodium salt to give substantially pure *l*-pinane hydroperoxide. About 50% of the peroxide present in the oxidate was isolated as the pure pinane hydroperoxide.

Proof of Structure.—The reactions used in establishing the structure of the pinane hydroperoxide are indicated in Fig. 1. It was found that the hydroperoxide could be reduced to the known pinanol-2 melting at 79° by reduction either with sodium sulfide in alkaline solution or with $\text{PtO}_2\text{-H}_2$ in ethyl acetate. During hydrogenation one mole of hydrogen was absorbed per mole of hydroperoxide. Since an authentic sample of the pinanol-2 was not available for comparison, its identity was verified by hydrolysis to *cis*-terpin. Direct treatment of the pinane hydroperoxide with 5% aqueous sulfuric acid followed by neutralization and extraction also gave *cis*-terpin. Comparison of the yield of *cis*-terpin directly from the pinane hydroperoxide with that obtained from pure pinanol-2 indicates that at least 75% of the pinane hydroperoxide is the 2-isomer.

Since inversion would not occur during the hydrogenation of the pinane hydroperoxide to the alcohol, the pinane-2-hydroperoxide will have the same stereo configuration as the alcohol produced from it. The stereo configuration of the pinanol-2 melting at 79° has not been rigorously established, but it is generally considered to be the *cis* form, having the methyl group and the dimethyl substituted carbon of the cyclobutane ring on the same side of the cyclohexane ring. The diastereomer melting at 59° is also known. The assignment of structure to the two forms is based on the Auwers-Skita⁸ rule which proposes that in the cyclohexane series the stereoisomer with the higher density and higher index of refraction is the *cis* isomer.

Consideration of the steric factors involved in the production of the two isomers would also lead to this same assignment of configuration. The isomer melting at 59° is produced from nopinone by means of the Grignard reaction. In a recent paper⁹ a rule was proposed to predict the stereochemical direction of asymmetric induction in reactions of acyclic systems in which a new asymmetric center is created adjacent to an old. In essence this rule states that the predominant form will be the one produced by entry of the new substituent from the least hindered side of the molecule. Extension of this rule to the addition of methyl Grignard to nopinone would call for the methyl group to enter the molecule chiefly at the side farthest from the dimethyl group and thus yield *trans*-pinanol-2. Similarly, the formation of the *cis*-isomer by oxidation either with oxygen or with potassium permanganate would be expected since the entering oxygen or hydroxyl radical should find it easier to approach the pinane molecule or free radical from the side farthest from the dimethyl group. Hence, the assignment of structure to the alcohols seems to have a firm theoretical basis. The pinane hydroperoxide must be predominately *cis-l*-pinane-2-hydroperoxide since it yields *cis-l*-pinanol-2 in good yield.

(8) K. Auwers, *Ann.*, **420**, 84 (1919); A. Skita, *Ber.*, **53**, 1792 (1920).

(9) D. J. Cram and F. A. Abd Elhafez, *This Journal*, **74**, 5828 (1952).

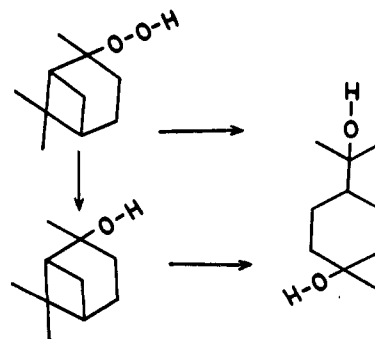


Fig. 1.—Reactions of pinane-2-hydroperoxide.

Further information as to the purity of the pinane hydroperoxide was obtained by comparison of the infrared spectra¹⁰ for the pure *cis*-pinanol-2, pure *trans*-pinanol-2,¹¹ and the crude alcohol produced by hydrogenation of the pure pinane hydroperoxide. The spectra of *cis*-pinanol-2 and the crude alcohol are essentially superimposable. Strong bands occurring at 9.70 and 11.41 μ in the *trans*-pinanol are absent in the pinanol from the pure pinane hydroperoxide. Hence, the pinane hydroperoxide isolated in the manner described previously is substantially pure *cis-l*-pinane-2-hydroperoxide. It is noteworthy that the crude pinanol produced by hydrogenation of peroxide V (see Table III) has an infrared spectrum which is qualitatively identical with that for *cis*-pinanol-2 except for the presence of a strong ketone band at 5.85 μ in the impure pinanol. This implies that *trans*-pinane also yields the *cis*-pinane-2-hydroperoxide. Since the free radicals initially produced from *cis*- and *trans*-pinane would both assume the same planar configuration at the 2-carbon atom, the formation of the same hydroperoxide or mixture of hydroperoxides from both forms of pinane is to be expected.

Rate of Decomposition and Activation Energy.—A brief investigation was undertaken to establish the rate and order of the thermal decomposition of pure pinane hydroperoxide. The results of this study are given in Table V. Difficulty was experienced in getting reproducible results and this is reflected in the high standard deviations reported. However, the distribution of values was reasonably normal. Samples run with and without diluent indicated that the decomposition is first order in the early stages but that an autocatalytic reaction also becomes significant in the latter stages. Hence,

TABLE V
DECOMPOSITION RATES FOR PINANE HYDROPEROXIDE

Temp., °C.	Samples, no.	K^a	Standard dev.
110	17	0.020	0.005
120	30	.053	.010
130	13	.117	.024

^a Moles of pinane hydroperoxide decomposed per mole present per hour.

(10) The infrared spectra were obtained by members of the Analytical, Physical, Chemical and Physics Division, Southern Regional Research Laboratory, New Orleans, La., using a Beckman I R-2-T recording infrared spectrophotometer with rock salt optics. All samples were measured in chloroform solution against chloroform in the same 0.4-mm. cell at concentrations of 45 to 80 g./l.¹

(11) Kindly supplied by Dr. J. P. Bain.

the rate constants calculated for samples in which more than about half the peroxide decomposed are not included in the calculations. Calculation of the activation energy by the Arrhenius equation gives $E = 27$ kcal./mole.

Experimental

Materials.—The *l*- β -pinene used in this investigation was obtained by fractional distillation of gum turpentine through an efficient column (*ca.* 100 plates). From the physical properties given in Table I the purity was estimated at better than 95%. Suitable fractions from several distillations were combined and redistilled just before being used. All other reagents were commercial products which were used without purification.

Pinane.—*l*-Pinane was prepared by hydrogenation of β -pinene n_{20}^D 1.4787, d_{20}^{25} 0.8723, $[\alpha]_D -21.3^\circ$, in a rocker type hydrogenator at 20 to 100 atmospheres and 100 to 140° using 1% nickel in the form of a commercial catalyst containing 16% nickel with filter-aid as the support and coconut oil as the carrier. The theoretical amount of hydrogen was absorbed in about 4 hours. Bulb to bulb distillation at 20 mm. pressure to remove the coconut oil gave a substantially quantitative yield of pinane n_{20}^D 1.4624, d_{20}^{25} 0.8571, $[\alpha]_D -22.7^\circ$. This material was distilled through a 100-plate Podbielniak column at 20 mm. pressure and a reflux ratio of from 50:1 to 100:1. Over 90% of it distilled at about 60°. The physical properties of selected fractions taken during the distillation are given in Table II.

Oxidation.—All oxidations were carried out in reactors immersed in a constant temperature oil-bath and equipped with a fritted glass gas inlet (usually as a false-bottom in the reactor), a thermometer, and a moisture-trap condenser assembly to return any vaporized pinane to the reactor and retain any aqueous by-products. A strong flow of oxygen through the inlet tube was maintained to provide adequate agitation of the sample.

Peroxide Content.—The peroxide content was determined by a modification of the Wheeler iodimetric method¹² using a sample containing between 0.1 and 2.0 milliequivalents of peroxide and a 5-minute reaction time. Peroxide content is expressed as PN = milliequivalents of peroxide per kilogram. Values obtained by this method were found to check with those obtained by the method of Wagner,¹³ and by the polarographic method of Willits.¹⁴ The theoretical PN for pinane hydroperoxide is 11,760.

Preparation of Pure Pinane Hydroperoxide.—*cis-l*-Pinane (218 g., 1.58 moles, n_{20}^D 1.4624, d_{25}^{25} 0.8528, $[\alpha]_D -23.2^\circ$) was oxidized at 95° for 20 hours and gave a crude oxidate (220 g., PN = 6680) containing 0.74 mole of peroxide. This was stripped at 0.1 mm. using water vapor as the carrier gas and a maximum pot temperature of 65°. The residue in the still consisted of 122 g. of colorless peroxide (PN = 10,780, n_{20}^D 1.4884, d_{25}^{25} 1.018, $[\alpha]_D -20.6$, acid no. 3.3) equivalent to 0.66 mole.

Part of this peroxide (72.5 g., 0.39 mole) was shaken with 0.19 g. of solid NaOH (theoretical amount to neutralize acidic component) and distilled bulb to bulb at approximately 0.1 mm. with the NaOH present.

Fraction	Dist. temp., °C.	Pres. sure, mm.	n_{20}^D	Peroxide no.	Wt., g.
1	54	0.1	1.4886	10,200	5.5
2	57	.1	1.4893	10,870	50.1
3	60	.1	...	11,250	5.0
Residue	6,030	7.0

Fractions 2 and 3 (0.30 mole of peroxide) were combined and diluted with 600 ml. of pentane. The sodium salt of the peroxide was prepared by cooling the solution in an ice-bath and adding 25 g. of 50% NaOH in increments of 2-3 g. with vigorous shaking after each addition. The temperature was kept below 10° during the addition and held at this temperature for an hour. The supernatant liquid was decanted from the precipitated salt, and the precipitate was

washed with two portions of cold pentane. Water and benzene were added and the salt was regenerated with carbon dioxide. The regenerated peroxide was recovered by benzene extraction. After filtration and evaporation of the benzene with vacuum, 31.9 g. of peroxide, PN = 11,680 (0.19 mole, n_{20}^D 1.4895, d_{25}^{25} 1.019, $[\alpha]_D -21.8^\circ$) was obtained. The pentane filtrate and washings were treated with 12 g. of NaOH and worked up by the same procedure to give an additional 10.0 g. of peroxide (0.06 mole).

The 31.9 g. of this peroxide was distilled bulb to bulb at 0.04 mm. A first cut of 2.7 g., PN = 11,280, n_{20}^D 1.4897, was removed and the remainder was distilled to give 23.9 g. of pinane hydroperoxide, PN = 11,750 (theory 11,760), (0.14 mole, n_{20}^D 1.4898, d_{25}^{25} 1.021, $[\alpha]_D -27.4^\circ$).

Reduction of Pinane Hydroperoxide to Pinanol-2 (2-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptane).—The peroxide (5 g., PN = 11,680) was shaken thoroughly with a solution of Na₂S and NaOH (6.0 g. of Na₂S·9H₂O, 1 g. of NaOH and 0.5 ml. of 1% soap solution in 30 ml. of H₂O). Heat was evolved. The solution was then heated at 80° for 1 hour. Twenty-five milliliters of H₂O was added, a Dean-Stark trap was inserted and the solution was refluxed. The alcohol which collected in the trap was removed from time to time and the heating was continued until no more alcohol was formed. The combined alcohol layers, which had solidified on standing, were dissolved in pentane, washed with water and dried over Na₂SO₄. Evaporation of the pentane and drying gave 4.00 g. (88% yield) of semisolid alcohol. After several recrystallizations from pentane the alcohol melted at 78.0-79.2°, $[\alpha]_D -19.1^\circ$ (*c*, 8.0% in hexane). Lipp⁵ reported m.p. 79° for methylpinol (pinanol-2).

Pure pinane hydroperoxide (0.6428 g.) was dissolved in 10 ml. of ethyl acetate and hydrogenated in a quantitative hydrogenator¹⁵ using 25 mg. of PtO₂ as a catalyst. Hydrogenation was complete in 1 hour, 0.996 mole of hydrogen per mole of hydroperoxide being absorbed. Filtration and evaporation of solvent gave a crude product melting at 65-70°.

Hydrolysis of Pinanol-2.—Hydrolysis was carried out essentially according to the method of Wallach.¹⁶ One gram of pinanol-2 was shaken with 500 ml. of 5% H₂SO₄ for about 4 hours. The resulting solution was extracted with two 15-ml. portions of pentane to remove unhydrolyzed material. The aqueous layer was neutralized with base and extracted with ethyl acetate in a continuous extractor for 2 hours. On evaporation of the ethyl acetate 0.79 g. of semi-solid product was obtained. Recrystallization from 50 ml. of H₂O gave 0.48 g. of terpin hydrate. Dehydration gave *cis*-terpin, m.p. 104.2-105.2° (mixed melting point with authentic *cis*-terpin, 102.5-105.4°). To determine losses which might be expected in this recrystallization, 0.8 g. of known terpin hydrate was recrystallized in exactly the same manner. This left 0.18 g. in the mother liquor. Hence, 1 g. of pure pinanol-2 gave 0.66 g. of terpin hydrate.

One gram of crude alcohol from pure pinane hydroperoxide gave 0.55 g. of terpin hydrate.

One gram of pinane hydroperoxide gave 0.47 g. of terpin hydrate when hydrolyzed in the same manner.

Decomposition of *cis-l*-Pinane-2-hydroperoxide.—About 0.1-g. samples of pure pinane hydroperoxide were weighed into small constricted tubes. The tubes were flushed with nitrogen, sealed and placed in the constant temperature bath. After the desired length of time had elapsed (typically two to three hours), the tubes were removed, quenched and the peroxide number of the product determined. Similar results were obtained when the samples were sealed *in vacuo* but much lower apparent decomposition rates were obtained when other samples were sealed with air in the tubes. In some cases pinane was added as a diluent. The rate constants reported include values obtained both with and without dilution.

Acknowledgment.—The authors wish to express their appreciation to Mr. R. T. O'Connor, Analytical, Physical Chemical, and Physics Division, Southern Regional Research Laboratory, for his kind cooperation in obtaining the infrared spectra and preparing them for publication.

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