

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

OPTICALLY ACTIVE ALPHA-PINENES¹

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Since there is some doubt regarding the purity of α -pinenes obtained from natural sources, and likewise regarding the purity of derivatives prepared from them, we have obtained pure products by the method devised by Lynn,² that is, by the preparation of the nitroso chlorides of the active pinenes, recrystallization of these compounds to insure their purity and finally decomposition of the nitroso chlorides with dimethylaniline to set free the pinenes. In this preparation we have found that the presence of small amounts of water aided in the formation of the nitroso chloride. In fact, we were able to obtain only traces of the desired product previous to this discovery. Lynn in a private communication informed us that in some runs the nitroso chloride precipitated and in others it did not precipitate. Apparently water catalyzes the reaction. The hydrochlorides of pure dextro, levo and inactive pinenes were prepared and their optical rotations observed. The rotations of the active pinenes were equal and opposite in sign. Methods used in the preparations and results observed are given below in the experimental part.

Preparation of Dextro and Levo α -Pinenes.—Dextro α -pinene was obtained from Port Orford cedar oil by the method previously outlined,³ that is, by fractionation of the oil and distillation over sodium. Levo α -pinene was obtained from Douglas Fir balsam. The method of purification was identical with that used for the dextro compound. The constants observed for the levo compound were b. p. 155–156°, $[\alpha]_D^{20}$ -42.6° , n_D^{20} 0.4676; d_{20} 0.8598. It is of interest to note that there is an almost unlimited supply of Douglas Fir balsam available.

α -Pinene with a low specific rotation was obtained from American turpentine oil. It was used for the preparation of the inactive nitroso chloride by the method outlined by Wallach.⁴

Active Nitroso Chlorides.—These compounds were prepared by the method outlined below. The method is given in some detail since the exact conditions for the preparation of such compounds have not been published up to this time.

To 40 cc. of *l*- α -pinene, 40 cc. of methyl alcohol (10% water by volume) and 40 cc. of ethyl nitrite were added. The mixture was placed in a wide-mouthed bottle closed with a stopper bearing a thermometer and mechanical stirrer, and was kept at a temperature of -20° during the addition of the theoretical amount of hydrochloric acid. The hydrochloric acid solution was prepared by passing hydrogen chloride gas into 90% methyl alcohol until an approximately 5 *N* solution was obtained. It was found to be advisable to introduce the alcohol-acid solution below the surface of the liquid and to cool the addition tube through which the acid flowed in order to prevent local super-

¹ From the thesis submitted by R. C. Thielke in partial fulfilment of the requirements for the degree of Master of Science, 1931.

² Lynn, *THIS JOURNAL*, 41, 361 (1919).

³ Thurber, *Ind. Eng. Chem.*, 19, 739 (1927).

⁴ Wallach, *Ann.*, 253, 251 (1889).

heating. A period of approximately two and one-half hours was required for the addition. After all of the acid had been added the reaction mixture was allowed to stand for a short time and was then filtered to remove the inactive derivative which had precipitated.

The filtrate was immediately cooled to -20° and another 200 cc. of cold 90% methyl alcohol added to it. The mixture was then allowed to stand for twenty-four hours, the temperature being maintained at -20° to insure complete precipitation of the active nitroso chloride. Some crystals usually appeared almost immediately after the addition of the cold 90% alcohol. The crystals were removed by filtration and were purified by recrystallization from a 1:2 mixture of chloroform and methyl alcohol.

Dextro pinene nitroso chloride was prepared from *d*-pinene in a similar manner. However, pinene from Port Orford cedar oil does not yield an inactive nitroso chloride, so that the removal of this product is dispensed with. The yield varied with the type of pinene used but was always very low, usually about 2 g. per run.

Properties of Pinene Nitroso Chlorides.—The active nitroso chloride decomposes at room temperature to a brown oily mass in a period of about three weeks. At -20° the compound is stable for a much longer period of time. Some attempts were made to determine the molecular weights, by the freezing point method, of both the active and inactive nitroso chlorides. Definite results could not be obtained but rather high molecular weights were indicated. The active nitroso chlorides are considerably more soluble than the inactive in such solvents as benzene. We expect to make a study of the molecular weights of these compounds at some later time. After recrystallization the following constants were observed.

Nitroso chloride....	<i>dl</i> -	<i>d</i> -	<i>l</i> -
M. p., $^{\circ}$ C.....	115	89.5	90.0
$[\alpha]_D^{20}$ (in benzene) ..	0.0	+396.2	-366.8

These compounds are somewhat unstable near their melting points and different observers may obtain widely varying melting points, depending upon the rate of rise of temperature of the melting point bath.

Optically Active Pinene from the Nitroso Chloride Derivative.—The method described by Tilden was used.⁵ Twenty grams of α -pinene nitroso chloride was warmed with a mixture of 24 g. of dimethylaniline and 60 cc. of 95% ethyl alcohol. The liberated pinene was recovered by steam distillation and was then washed and purified by refluxing over metallic sodium; yield, 8 g. While this is not a large amount of material to work with we were able, by using small-sized apparatus, to determine the physical properties of the pinenes and to prepare their hydrochlorides and determine their properties. The physical properties of the pinenes synthesized are tabulated below.

		B. p., $^{\circ}$ C. (760 mm.)	$[\alpha]_D^{20}$	$[\alpha]_D^{20}$ (in alc. soln.)	d_{20}	n_D^{20}
Regenerated	<i>dl</i> - α -pinene	155-156	0.00	0.00	0.8592	1.4664
Regenerated	<i>d</i> - α -pinene	155-156	+51.14	+53.91	.8591	1.4663
Regenerated	<i>l</i> - α -pinene	155-156	-51.28	-54.04	.8590	1.4662

A tube 2.95 cm. long and holding 1 cc. of liquid was used for the direct determination of the specific rotation, while a 10-cm. tube was used for the determinations in 4% alcohol solution. Apparently the solvent increased the rotation numerically to a slight degree. The main point, however, is that the rotations are equal and opposite in sign within the limits of experimental error. The samples were considered to be pure and were used for the preparation of the hydrochlorides.

⁵ Tilden, *J. Chem. Soc.*, 85, 759 (1904).

α -Pinene Hydrochloride.—The hydrochloride was prepared by saturating 3-cc. samples of pinene with dry hydrochloric acid gas, at a temperature of from 10–15°. Thereafter the mixture was kept at -5° for one hour. The product was then filtered with suction and recrystallized from five times its weight of absolute methyl alcohol. The alcohol was removed by suction filtration and the melting points and specific rotation were determined immediately. These properties are tabulated below.

	M. p. (corr.), $^\circ\text{C}$.	$[\alpha]_D^{20}$ (1% alcohol solution)
<i>dl</i> - α -Pinene hydrochloride	132	0.00
<i>d</i> - α -Pinene hydrochloride	132	+33.52
<i>l</i> - α -Pinene hydrochloride	132	-33.24

The chief point of interest here is that the optical rotations are again equal and opposite in sign within the limits of experimental error. When samples were allowed to stand in the air for even very short periods of time the melting points were somewhat lower. Undoubtedly this accounts for the wide range of melting points (118–133°) reported in the literature.

Summary

1. Samples of pure *d*- α -pinene, *l*- α -pinene and *dl*- α -pinene were prepared and their physical properties determined. 2. The conditions necessary for the formation of active α -pinene nitroso chloride were worked out. 3. It was found that when methyl alcohol is used as a solvent a small amount of water must be present to bring about the formation of the active nitroso chloride. 4. The hydrochlorides of dextro, *dl* and levo α -pinene were prepared and their properties studied. 5. Contrary to reports in many texts and journal articles these compounds exhibit a normal behavior, that is, *dl*- α -pinene yields an inactive hydrochloride and the active pinenes yield active hydrochlorides whose rotations are equal and opposite in sign. 6. A study of the molecular weights of the nitroso chlorides will be made later.

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