heating requires great care and considerable experience in order to avoid an undue amount of breakage. They must be heated *over*, not on the side of a burner, the marked side toward the flame. It is our opinion that a muffle should be used where a large amount of slides are to be marked, using a strip of zinc (m. p. 412° C.) and a Seger cone 022, to indicate the temperature limits. Since a muffle furnace was not available, we were unable to carry out this experiment. The marked slides, after being thoroughly dried, may be sent to some shop where glass firing is done and finished there for a nominal charge.[1] JOSEPH C. BOCK.

[CONTRIBUTION FROM THE WISCONSIN PHARMACEUTICAL EXPERIMENT STATION.]

OPTICALLY ACTIVE PINENE NITROSOCHLORIDE AND SYNTHETICAL ACTIVE PINENE.

BY E. V. LYNN.

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The nitroso compounds, characterized by the group —N = O, were first prepared by Cahours,[2] in 1842. The discovery by Tilden,[3] in 1875, that they could be prepared by addition to unsaturated compounds, and the subsequent improvement in the method by Wallach,[4] in 1888, first placed these nitroso compounds in the important position they have since occupied.

Although a blue coloration generally accompanies the commencement of the reaction, the compounds which result are, in most instances, colorless. The latter have been shown to be isonitroso compounds,[5] characterized by the group =N—OH, or bisnitroso compounds,[6] $R'—N_2O_2—R'$. Since the blue substances which have been isolated[7] are shown to be true nitroso in character, and since they readily change to the isomers[8]

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[1] A semi-permanent marking medium can be obtained by mixing a pigment (lead oxid, lampblack, etc.) with a good spar varnish, canada balsam or collodion varnish (banana liquid). It will resist the ordinary cleaning and has been found useful for marking stock bottles and similar containers.

[2] *Ann.*, **41**, 76–77 (1842).

[3] *J. Chem. Soc.*, [2] **13**, 514–518 (1875); *Ibid.*, **31**, 554–561 (1877); *Pharm. J.*, [III] **8**, 188–191 (1878).

[4] *Ann.*, **241**, 241–254 (1888); **253**, 249–267 (1889).

[5] Goldschmidt, *Ber.*, **18**, 1729 and 2220 (1885); Kremers and Urban, *Am. Chem. J.*, **16**, 395–404 (1894); Meyer, *Ber.*, **21**, 1291–1295 (1888); Kremers and Mead, *Am. Chem. J.*, **17**, 607–611 (1895).

[6] Kremers, *Inaug. Diss.*, Göttingen, **1890**; Baeyer, *Ber.*, **28**, 639–652 (1895).

[7] Wallach, *Ann.*, **241**, 312 (1887); Baeyer, *Ber.*, **27**, 436–454 (1894); Thiele, *Ibid.*, **27**, 454–456 (1894); Chapman, *J. Chem. Soc.*, **67**, 780–784 (1895); Piloty, *Ber.*, **31**, 218–220 (1898); Kremers and Schreiner, *Pharm. Arch.*, **2**, 273–300 (1899); Schmidt, *Ber.*, **35**, 3373 and 3727 (1902); Piloty and Steinbock, *Ibid.*, **35**, 3101–3117 (1902); Schmidt, *Ibid.*, **36**, 1765–1768 (1903).

[8] Kremers and Schreiner, *Pharm. Arch.*, **2**, 273–300 (1899).

mentioned above, it is assumed that the initial blue color indicates the formation of true nitroso compounds.

Whenever these true compounds may be expected because of the reagents employed, they seldom crystallize out, but in most instances, isonitroso or bisnitroso compounds are obtained. That side reactions likewise take place is not at all surprising; indeed this is to be expected by one who has worked at all extensively with these compounds and the reaction mixtures from which they are obtained.

Sometimes the crystalline products are formed with almost theoretical yield (nitrosothymol 100%, limonene nitrosochloride 80%), but mostly they are obtained in smaller amounts (pinene nitrosochloride 0 to 50%). The capacity for reaction which these crystalline compounds manifest is so great that chemists quite generally have been content to follow the lines of least resistance, and have given their time and attention to them, paying but little heed to the mixtures from which they arise. It is true that Wallach[1] has isolated pinol and cymene from pinene nitrosochloride mother liquor, and that Kremers and Hanf[2] have found a compound, analogous to pinol, in that from limonene nitrosochloride, but in both cases it was the decomposed liquid which was examined.

In 1891 Kremers[3] observed a wide difference in yield of nitrosochloride from pinene of different sources and, in 1892, showed[4] that the yield varies inversely with the optical rotation of the pinene, a result which has been confirmed in the present work and by many other investigators.[5] In order to account for this variation we must consider the facts that: (1) the nitrosochloride obtained is always inactive; (2) an increase in optical rotation of the pinene diminishes the yield; (3) the mother liquor remains blue for some time; (4) there is frequently a wide difference in solubility between the inactive and active modifications of nitroso derivatives.[6] With these facts in mind, it was but natural for us to suppose that it is the nitrosochloride from the inactive pinene which crystallizes out. A pinene which is naturally inactive gives the largest yield, and this inactivity and consequent increase in amount of product can also be brought about by mixtures of levo and dextro pinenes.[7]

All attempts, however, to obtain derivatives of the active nitroso-

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[1] Wallach, *Ann.*, **253**, 249–267 (1889); **336**, 8 (1904).

[2] Kremers and Hanf, *Proc. Wisconsin Pharm. Assoc.*, **1893**, pp. 47–49.

[3] *Ibid.*, **1891**, pp. 39–41 and 41–43.

[4] *Ibid.*, **1892**, pp. 66–70 and 72–73.

[5] Fox, *Thesis*, Univ. of Wisconsin, **1903**; Tilden, *J. Chem. Soc.*, **85**, 759–764 (1904); Gildemeister and Köhler, *Wallach Festschr.*, **1909**, p. 432; Schimmel & Co., *Report*, April, **1910**, p. 164; Lynn, *Thesis*, Univ. of Wisconsin, **1910**; Brandel (1903), Unpublished results; Baudt (1910), Unpublished results.

[6] Kremers, *Inaug. Diss.*, Göttingen, **1890**.

[7] Kremers and Smith, *Proc. Wisconsin Pharm. Assoc.*, **1892**, p. 72–73.

chloride from the mother liquor gave negative results. Even the mixing of fresh mother liquors from dextro and from levo pinene gave no precipitate of inactive nitrosochloride.[1]

Later, Tilden[2] investigated the cause of this variation of yield with optical activity of the pinene and came to a very different conclusion. Since Baeyer[3] had suggested that the crystalline nitrosochloride is a bis-nitroso compound, Tilden decided that the poor yield with pinene of high rotation is due to the destructive effects of the heat generated in the inversion of one-half of the product as soon as formed. On this basis, however, a difference in external conditions should alter the amount of nitrosochloride obtained, which is contrary to experience.

New Method for Preparing Pinene Nitrosochloride.

It was assumed, therefore, that the persistent blue color of the mother liquor is due to optically active pinene nitrosochloride in solution. Since the presence of acetic acid and of water in Wallach's method[4] might easily alter this active compound, making it impossible of isolation, the method was modified by elimination of the acetic acid and by substitution of alcoholic hydrogen chloride for the aqueous hydrochloric acid. The method now used to prepare pinene nitrosochloride is as follows:

Equal volumes of pinene, ethyl nitrite, and absolute alcohol are mixed and cooled in a freezing mixture. A solution of hydrogen chloride in absolute alcohol is added, in amount corresponding to the theoretical requirements for the pinene used. A thermometer is held in the reaction mixture and the temperature maintained below —5° by constant agitation and regulation of the addition. The hydrogen chloride solution may be added quite rapidly, but the temperature regulation is essential until the filtration is completed. After standing about one-half hour the crystals are filtered off. In the preparation of larger quantities, the absolute alcohol used as a solvent may be replaced by 95% alcohol.

The yield is slightly better than by the old method, but the principal advantage is that the reaction is easier to control. If the alcohol is omitted, the mother liquors can be kept for days without noticeable change in color, at least in the dark and if slightly deficient in acid. In fact, one filtrate was preserved with a blue-green color at 0° for over three weeks.

Optically Active Pinene Nitrosochloride.

The filtrates from the above method, after the further addition of one to two volumes of alcohol, were exposed to temperatures below —10°. After a longer or shorter time, depending upon the temperature and upon the optical rotation of the pinene used, crystals separated in the form of

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[1] Gildemeister and Köhler, *Wallach Festschr.*, 1909, p. 432.

[2] *J. Chem. Soc.*, **85**, 759–764 (1904).

[3] *Ber.*, **28**, 639–652 (1895).

[4] *Ann.*, **245**, 241–254 (1888); **253**, 249–267 (1889).

colorless, transparent needles or cotton-like needles, the latter from samples containing more alcohol. The product was purified by washing with cold alcohol. The best yield, as might be expected, was from pinene of high rotation. Thus, a pinene from *Chamaecyparis lawsoniana* (Murr.) Parlatone, with a specific rotation of +47.7°, gave no trace of inactive,[1] but about 15% yield of the active nitrosochloride. In this case the crystals separated in a few minutes.

I. Subs., 0.5862 g.; AgCl, 0.4180 g.
II. Subs., 0.4213 g.; AgCl, 0.3009 g.
III. Subs., 0.5787 g.; at 21° and 732 mm., 36.9 cc. moist N.
IV. Subs., 0.6001 g.; at 20° and 732 mm., 40.1 cc. moist N.
V. Subs., 0.2670 g.; H_2O, 0.1975 g.; CO_2, 0.5863 g.

		Found.				
	Calc.	I.	II.	III.	IV.	V.
C..................	59.55	...	...	..	..	59.88
H..................	7.94	...	...	..	..	8.20
C..................	17.61	17.64	17.66	..	..	...
N..................	6.95	...	...	6.93	7.21	...

It is, therefore, certain that the explanation for the poor yield of inactive nitrosochloride with pinene of high rotation lies in the previous non-isolation of nitrosochloride from the active pinene present.

The new compound has a melting point of 81 to 81.5°, and an optical rotation of ±322° in alcohol or chloroform solution, the direction being the same as that of the pinene employed. The levo variety was obtained from Oregon or Canada balsams and the dextro from commercial American turpentine oil.

The active nitrosochloride is appreciably soluble in almost every solvent tried, a fact which explains partially why it was not discovered earlier. It is insoluble in water, soluble in 200 parts of alcohol or 50 parts of heptane at 20°, and very soluble in pinene, chloroform, ether, acetone, ethyl acetate, pyridine, ethyl nitrite, benzene, and fatty oils, but less so in methyl or amyl alcohol. The solution in heptane or chloroform is blue at or above room temperature, but becomes colorless at 0°.

The crystals are more unstable than the inactive form but keep fairly well if spread out on paper or if in an open bottle at 0°. Very small amounts may be recrystallized, but in larger quantity, above 0.1 g., the solution usually turns red even at low temperatures. At its melting point, the compound decomposes with evolution of gas and with the formation of the same red liquid obtained by decomposition of the mother liquors.

Like the inactive modification, it reacts readily with benzylamine,[2]

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[1] Compare Schorger, *J. Ind. Eng. Chem.*, **6**, 631 (1914).

[2] Wallach, *Ann.*, **252**, 130 (1889).

with piperidine,[1] with alcoholic alkali[2] to form nitrosopinene, and with aniline.[3] The product with benzylamine is precipitated by water in the form of needles, melting point 144–145°. By slow evaporation from alcohol it can be obtained in large prisms. The rotation is ±92° in 2.5% acetone solution.

Subst., 0.3050 g.: Moist N, 28.0 cc. at 21° and 739 mm.
Calc. for $C_{10}H_{16}NONHC_6H_5$: N, 10.28. Found: 10.39.

The piperidine base crystallizes from water, in which it is appreciably soluble, in roset clusters, melting point 84° C., specific rotation ±50°.

The reaction product with sodium ethylate is precipitated by water as a heavy oil, but all attempts to get it in the crystalline state failed. Curiously, the oil appears to be inactive. By boiling under a reflux condenser with hydrochloric acid, hydroxylamine was undoubtedly formed from the oil, as shown by the reaction of the product with Fehling's solution.

Optically Active Pinene.

Inactive pinene nitrosochloride reacts with aniline to form inactive pinene and aminoazobenzene.[3] In like manner, the active nitrosochloride readily reacts with aniline in alcohol solution. The resulting red liquid, upon distillation with steam, gives active pinene, boiling point 155–159°, n_D 1.470, specific rotation (in 4% alcoholic solution) ± 53.75°. Dextro pinene is obtained from dextro pinene nitrosochloride. In view of the maximum rotation observed for natural pinene[4] (+51.52°) the value found for the artificial product is about what would be expected. Aminoazobenzene is also formed in this reaction, the free base separating from the steam distillation residue in the form of orange-colored needles, melting point 126–127°.

As is well known, dextro pinene has always given an inactive hydrochloride, while levo pinene gives a levo hydrochloride. Since regenerated optically active pinene had never before been obtained, it seemed of interest to test the product in this case. Lack of material prevented trying the levo, but the dextro pinene gave feathery crystals of a hydrochloride which was inactive and had a melting point of 118°.

The Gas Evolved.

The formation of active pinene nitrosochloride, however, does not yet wholly explain the poor yield. Even assuming that there is still some of this active compound in solution, it would not nearly account for the theoretical requirements. With inactive pinene the yield is never over 56% of the hydrocarbon employed, or 50% of the theory. There must, there-

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[1] Wallach, *Ann.*, **245**, 251 (1888).

[2] Tilden, *J. Chem. Soc.*, [2] **13**, 514–518 (1875).

[3] Wallach, *Ann.*, **252**, 132 (1889); **258**, 343 (1890).

[4] Schorger, *J. Ind. Eng. Chem.*, **6**, 631 (1914).

fore, be one or more other reactions, equivalent to about one-half of the pinene.

In the preparation of pinene bisnitrosochloride by any method, the disappearance of the blue color and the precipitation of crystals is accompanied by an evolution of gas. This gas is formed quickly in Wallach's method, but more slowly in the one here used. Its formation is independent of temperature and light, except as to rate; bright light increases remarkably the rapidity of evolution, as does also a rise in temperature. On the other hand, the gas is formed regardless of exclusion of light, and at temperatures as low as —30°, although the rate is decreased.

No attempt appears to have been made to identify or explain the formation of this gas, although Tilden[1] has ventured the opinion that it is nitrous oxide, from the reaction of hydroxylamine (formed by hydrolysis) and nitrosyl chloride.

$$NOCl + NH_2OH \longrightarrow N_2O + HCl + H_2O.$$

Examination of the gas, however, shows that it is more or less pure nitrogen. Its presence would seem to indicate reduction of some nitroso compound. Furthermore, it has been found that the amount of nitrogen formed is approximately equal to that unaccounted for by nitrosochloride formation. It would appear that some other reaction takes place, equal in amount to that which gives the nitrosochloride and possibly dependent on the latter.

I. One cc. pinene, 4 cc. of 1.8 0.1 *N* alcoholic hydrogen chloride, and one cc. of 90% ethyl nitrite (0.77 g.), corresponding to 120.9 cc. nitrogen at 20° and 740 mm., gave 59.5 cc. nitrogen measured under the same conditions.

II. 25 cc. pinene, 35 cc. of 28% alcoholic hydrogen chloride, and 20.5 g. of ethyl nitrite, corresponding to 3245 cc. nitrogen at 20° and 739 mm., gave 1630 cc. nitrogen under the same conditions.

III. The gas did not burn nor support combustion, gave no precipitate with lime-water, and no color with ferrous sulfate. After washing with water, which removed 6.6% by volume, probably alcohol vapor, the residue was passed over heated copper, which was not thereby oxidized, and there was no decrease in volume of the gas. It was, however, absorbed by heated magnesium and the product gave ammonia with water.

The Mother Liquor.

A preliminary examination of the mother liquor, after gas has ceased to develop, shows a very complex composition. Of course, it still contains active nitrosochloride and one is, therefore, not surprised to learn that decomposition sets in at comparatively low temperatures. After extraction with water to remove the alcohol, a portion of the mother liquor

[1] Tilden, *J. Chem. Soc.*, 85, 759–764 (1904).

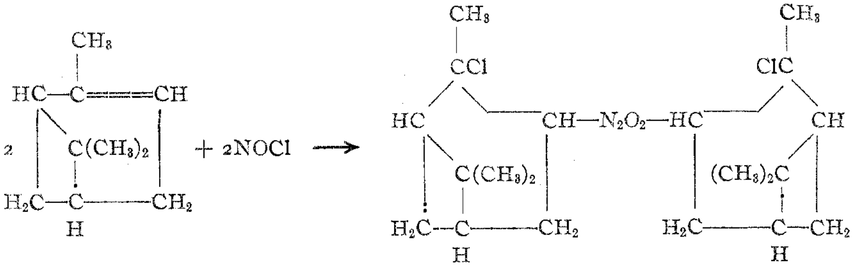
was reduced with zinc and acetic acid. The product was diluted and precipitated with ammonia, giving a yellow, amorphous substance which was not further examined.

Another portion of the mother liquor, after extraction with water, was distilled with steam, during which process, a large amount of gas was given off, part of it being nitric acid. The oily distillate was fractionated several times:

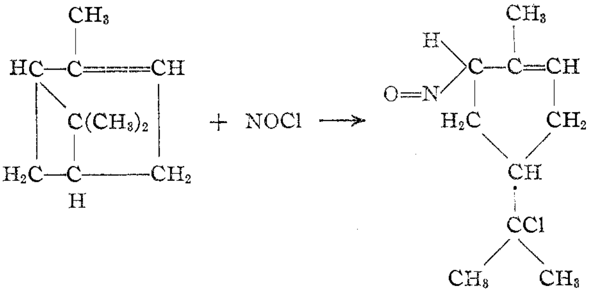
Up to 180°,	9 cc.,	ethereal odor, yellow color.
180 to 185°,	18 cc.,	slight camphoraceous odor.
185 to 200°,	75 cc.,	camphoraceous odor.
200 to 210°,	70 cc.,	camphoraceous odor.
210 to 222°,	40 cc.,	tarry odor.
222 to 250°,	40 cc.,	pyridine-like odor.
Residue,	4 cc.,	black, tarry mass.

All of the fractions above 200° contained some ammonium chloride, which was also found in the condenser and flask. The pyridine odor of fraction 222–250° was removed by extraction with dil. hydrochloric acid. Pinol could not be identified in the first two fractions, either by its nitrosochloride or by its dibromide.

The reaction of pinene with nitrosyl chloride is complicated by the fact that the latter not only may be added at the double bond



but, on the basis of the reactions of pinene with other reagents, such as hydrogen chloride, it may also be utilized to break the smaller cycle



A further possibility, which may now be considered probable, is that of condensation:

$$C_{10}H_{16} + NOCl \longrightarrow C_{10}H_{15}NO + HCl.$$

A study of the menthene-nitrosyl chloride reaction, which would eliminate the first complication, might throw considerable light on that of pinene. A reaction which may prove still more fruitful, however, has been found in that of nitrosyl chloride on *n*-heptane. In the latter substance we have eliminated both the double bond and the cycle and, hence, have but the possibility of condensation to study in its relation to nitrosyl chloride.

Summary.

1. The variation in yield of pinene nitrosochloride with the optical rotation of the pinene was thought due to the formation of optically active pinene nitrosochloride.

2. Wallach's method for preparing this compound was modified by eliminating acetic acid and using alcoholic hydrogen chloride.

3. Optically active pinene nitrosochloride was isolated and converted to active benzylamine and piperidine bases and to active pinene.

4. The gas given off during the preparation of pinene nitrosochloride is nitrogen, in amount equal to half of that added.

5. The mother liquor was briefly examined. As products nitric oxide, ammonium chloride, a substance reducible to a base, and a basic substance boiling at 220° have been isolated.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE WISCONSIN PHARMACEUTICAL EXPERIMENT STATION.]

A NEW REACTION OF PARAFFIN HYDROCARBONS.

BY E. V. LYNN.

Received November 4, 1918.

During the course of some experiments with nitrosyl chloride the writer, by request, prepared a saturated solution of this gas in normal heptane for the use of Prof. Kremers. The solution so prepared was accidentally set in the sunlight for a day. When next observed the reddish brown color had changed to blue and there was a precipitate of white, feathery crystals. The latter was found to be ammonium chloride. In a short time the blue color also disappeared, leaving the heptane colorless; and at the same time a heavy oil precipitated.

The reaction was so unusual that it was examined on a larger scale. The heptane from *Pinus Jeffrey* was kindly placed at the disposal of the writer by Mr. D. C. L. Sherk. It had been specially purified, so that 500 cc. had a boiling range of 0.28°. This was saturated (about 3%) with nitrosyl chloride prepared according to Tilden.[1] The reddish brown solution was preserved in the dark for weeks without any apparent change. In the sunlight, however, the color gradually changed to blue with a simultaneous precipitation of ammonium chloride. The blue color

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[1] *J. Chem. Soc.*, [2] 13, 514–518 (1875).