

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.<sup>1</sup> 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

<sup>1</sup> *J. Chem. Soc.*, [2] 13, 514-518 (1875).

quickly disappeared and the resulting turbid liquid gradually deposited a yellow oil. At the same time a gas was evolved, apparently from the yellow oil, which had sunk to the bottom. The gas was found to be 75% hydrogen chloride and to contain some (about 2.5%) nitric oxide.

The heptane was separated, saturated with nitrosyl chloride again and the process repeated until 50 g. of oil had been obtained. There was filtered from this oil about 2.5 g. of ammonium chloride.

The oil was submitted to steam distillation, during which process large quantities of hydrogen chloride were given off. The distilled oil weighed 30 g. when separated and dried. It had an intensely fragrant odor, which was retained to a high degree by the aqueous distillate, even when diluted to 6 volumes. The aqueous residue precipitated Fehling's solution, indicating the presence of hydroxylamine.

The dried oil, which dissolved in alcohol but was reprecipitated by water, was fractionated, and the index of refraction of each portion determined.

No.	Fraction. B. p.	Amt. Cc.	$n_D$ .	Odor.
1.....	98-100°	3	1.3198	heptane
2.....	144-150°	15	1.4093	original
3.....	150-154°	5	1.4100	original
4.....	154-160°	3	1.4118	original
5.....	Residue	3	..	decomposition

From the data obtained, it would appear that the oil is mainly a mixture of the three ketones from heptane  $C_7H_{14}O$ <sup>1</sup> with dipropyl ketone predominating.

Since there are no derivatives of the latter by which it could be identified, it was decided to prepare one, if possible. Pure dipropyl ketone, prepared from calcium butyrate by distillation, was submitted to the action of semicarbazide hydrochloride. In a few minutes crystals appeared in the form of feathery plates which recrystallized from heptane or petroleum ether, melted at 125°. These were analyzed according to Rimini.<sup>2</sup>

Subst., 0.3281, 0.2239; moist N; 49.9 cc. at 24° and 740 mm.; 32.9 cc. at 22° and 740 mm.

Calc. for  $C_9H_{17}N_3O$ : N, 16.37. Found: 16.51, 16.10.

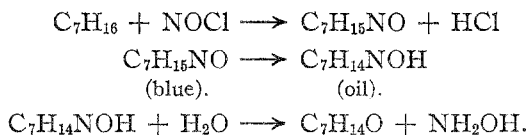
Fraction 2, above, however, gave no semicarbazone when similarly treated. A further examination of this fraction will be necessary to identify it as dipropyl ketone.

The original oil from the reaction of nitrosyl chloride on heptane was undoubtedly decomposed before and during distillation, as evidenced

<sup>1</sup> Methylamyl ketone boils at 151-2°, dipropyl ketone at 144°, ethyl butyl ketone at 147-8° (Beilstein).

<sup>2</sup> *Gazz. chim. ital.*, 34, I, 224-230; *Chem Zentr.*, 1904, 213, 1428.

by the evolution of hydrogen chloride. Leaving the ammonium chloride out of consideration, we may assume the reactions to be



A satisfactory explanation of the reduction of the hydroxylamine to ammonia has not yet presented itself.

It has been found that petroleum ether, b. p. 45-70°, gives apparently the same reaction as does heptane. We may assume, therefore, that any of the liquid paraffin hydrocarbons will react in the same way. The reaction of nitrosyl chloride on these hydrocarbons opens up a field in the chemistry of the paraffins which should be found exceedingly fruitful. The absence of ready reaction with most reagents has hitherto proved an obstruction in the study of the saturated chain compounds, and it is hoped that nitrosyl chloride will be of material aid. Furthermore, there is also the probability of using nitrosyl chloride as a reagent for other classes of compounds, such as benzene and its derivations, the cycloparaffins, heterocyclic compounds, etc. Indeed, there is hardly a limit to the speculative possibilities.

Finally, a further study of this interesting reaction of nitrosyl chloride on heptane and other paraffin hydrocarbons will, doubtless, enlighten us considerably regarding its reaction on pinene and on the other terpenes and related substances.

MADISON, WISCONSIN.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## FOUR-MEMBERED CYCLIC-UREAS. I. HISTORY AND NOMENCLATURE.

BY WILLIAM J. HALE.

Received August 26, 1918.

The four-membered cyclic-urea structure was first proposed by H. Schiff in 1869.<sup>1</sup> Through a comprehensive study of a large number of condensations between urea and various aldehydes it was observed that the product (I) resulting from the action of acetaldehyde upon urea possessed properties slightly different from those products obtained when urea was brought into action with various aromatic aldehydes. When, for example, this ethylidene-urea of Schiff was boiled with aniline alone there followed a decomposition of the molecule into urea and acetaldehyde (the latter through further condensation with excess of aniline separated finally as a form of ethylidene diphenylamine). On the other hand,

<sup>1</sup> *Ann.*, 151, 206 (1869).