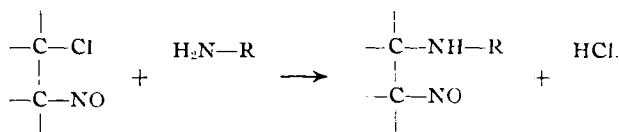


CONTRIBUTIONS TO THE KNOWLEDGE OF FOREST PRODUCTS.

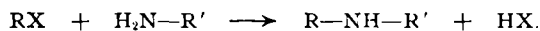
II. THE ACTION OF PHENYLHYDRAZINE ON PINENE-NITROSO-CHLORIDE.

BY ROLAND E. KREMERS.

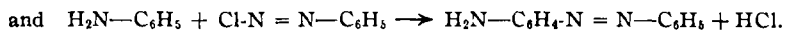
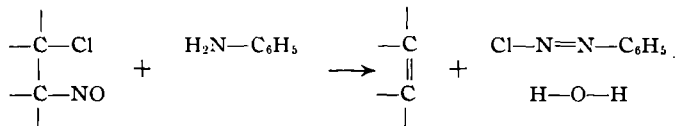
The following is a preliminary discussion of a new reaction involving nitrosochlorides. After Wallach had improved the technique of preparing nitrosochlorides from unsaturated compounds, the reaction became one of the most important of those used to isolate and to identify certain terpenes and related compounds.¹ But it was soon found that the resulting nitrosochlorides had decomposition points that lay close together. Hence more advantageous compounds were sought and were presently found in the nitrolamines prepared according to the general reaction:



On the whole the reaction appears to be general since such a variety of compounds as ammonia, methyl-amine, allyl-amine, aniline, and naphthylamine—to select only types from the list—have at one time or another been involved successfully in nitrolamine reactions. And indeed this was in a measure to be expected since they but illustrate a fundamental type reaction of organic chemistry, *i. e.*, the formation of secondary or tertiary amines from primary or secondary amines and a halogen substitution product:



If there are variations from this type reaction, it is only reasonable to assume that they are in some way due to the peculiar structure of the molecule involved. Such instances Wallach finds in pinene-nitrosochloride, methylindene-nitrosochloride, and tetrahydrobenzol-nitrosochloride. In the case of pinene nitrosochloride it is generally stated that aliphatic amines, secondary heterocyclic amines as piperidine, and aromatic amines as benzylamine, react normally, but that aromatic amines of the type aniline and toluidine react atypically to regenerate the hydrocarbon. Thus:



In the course of his experiences with nitrosochlorides, the writer has often wondered as to the real cause for this difference. Finally a certain skepticism developed which led to a closer scrutiny of the facts in the original literature. At present it must be admitted that the difference between the conditions under which aniline has been allowed to react upon pinene-nitrosochloride as compared with those for benzylamine or piperidine is not sufficiently great to warrant an *à priori* conclusion that the above generalization is more apparent than real. Meanwhile

¹ For the chemistry of the nitrosochlorides, see O. Wallach, "Die Terpene u. Campher," 2nd ed.

it was noted that bases derived from hydrazine had not been employed. Since hydrazines can be alkylated just as amines, the idea presented itself to try out this reaction. The choice of phenylhydrazine as the representative with which to start was prompted partly by the desire to see whether it would react as an "aromatic amine" or as an amine that does not come within this pale. The outcome of these speculations when tested in the laboratory is outlined below. For a preparation of pinenenitroschloride the writer is indebted to Mr. J. C. Seabright.

The following substances were mixed in an acetylation flask.

Pinene-nitroschloride	5 Gm.
Phenylhydrazine, Kahlb.	5 cc
Alcohol, 95 p.c.	10 cc

The flask was then set over a wire gauze and warmed very cautiously by a small flame; the mixture was frequently shaken. After the reaction had set in it was allowed to complete itself. This procedure is analogous to Wallach's preparation of limonene-nitrolanilide. As the reaction progressed the pinene-nitroschloride disappeared and larger plate-like crystals were formed. The reaction mixture was allowed to cool which caused it to set to a crystal-mass. The precipitate was filtered out by suction, washed with a little 95 percent alcohol until free from all traces of yellow color, and pressed between filter paper to dry: product A.

The filtrate, which now contained the other products in alcoholic solution, was precipitated by the addition of water. Only a slight odor of pinene could be detected in the oil. Hydrochloric acid was next added in excess to keep in solution basic material on the supposition that an excess of phenylhydrazine was present. The oil which did not dissolve was extracted with ether and separated. After evaporation of the ether an oil, mixed with well defined crystals, was obtained: product B.

The acid solution thus freed from insoluble matter was then made alkaline with an excess of ammonium hydroxide. An oil precipitated which soon crystallized: product C.

The crystalline material in product B was separated by suction filtration and blotted between filter paper. The compound was readily soluble in cold alcohol, but was found to crystallize out very well during the spontaneous evaporation of such a solution containing a few drops of petroleum ether of b. p. 40-60° C. Yellowish crystals, m. p. 147-48° C.

Product C comprised more material than B. It was recovered by suction filtration and, after being washed with water, was dried for two days between filter paper. It was readily soluble in cold alcohol but largely insoluble in petroleum ether b.p. 40-60° C. It was accordingly thoroughly washed with petroleum ether containing a few drops of alcohol. This gave a product composed of but faintly yellowish, hard prisms. M. p. 148-50°. Analyzed according to the Dumas method, 0.1610 Gm. of substance yielded 23.8 cc of N₂ at 24° C. and 744.5 mm. pressure, equivalent to 16.21 percent N₂.

N₂ calculated for C₁₆H₂₃ON₃ = 15.38 p.c.

N₂ calculated for C₁₆H₂₁N₃ = 16.47 p.c.

Product A was finally obtained in the form of beautiful pearly, lustrous plates, m. p. over 220° C. It was readily soluble in water. These facts suggested that it was phenylhydrazine-hydrochloride, which was proved as follows:

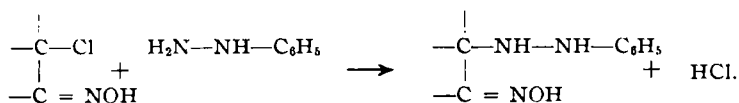
Product A	2.5 Gm.
Sodium acetate, fused,	2.5 Gm.
H ₂ O, q. s. to dissolve, solution filtered.	
Furfural	1.5 Gm.

An instantaneous reaction took place on the addition of the furfural. The reaction product was flocculated by shaking. The compound was purified by recrystallization from dilute alcohol; m. p. 95° C. Furfural-phenylhydrazone melts at 96° C. Therefore product A is phenylhydrazine-hydrochloride.

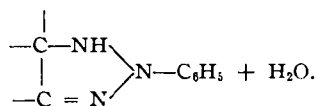
With these data before us, it is possible to consider critically the various alternatives presented by what we know of the chemistry of pinene-nitrosochloride.

The three probable courses of the reaction, to judge by the behavior of pinene-nitrosochloride toward other reagents, are: 1, nitrolamine formation; 2, elimination of hydrochloric acid with the formation of nitrosopinene; and 3, elimination of nitrosyl-chloride with regeneration of pinene. That any appreciable part of the reaction should have proceeded according to number 3 is most improbable because pinene was not regenerated and because the action of nitrosyl-chloride on phenylhydrazine should yield other products than phenylhydrazine-hydrochloride. Both reactions 1, and 2, fulfil the requirement that phenylhydrazine-hydrochloride should be formed as a byproduct. Reaction 2, can likewise be disregarded as a major factor because nitrosopinene was not formed; it melts at 130-31° (Wallach) as compared with products B and C which melt close to 150° C.

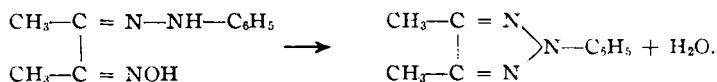
By this process of elimination, the presumptive evidence favors reaction 1. But there remains the discrepancy in the percent of nitrogen present. If we accept the statement that the colorless bimolecular nitrosochlorides are not true nitroso, but iso-nitroso, compounds, our generalized reaction can be formulated:



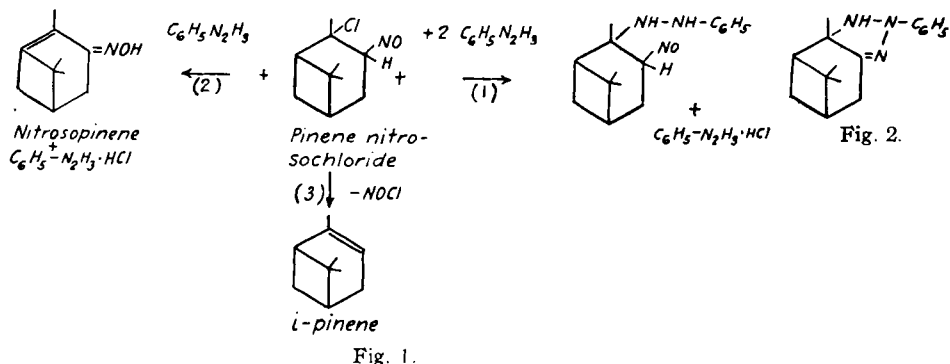
If subsequently ring closure takes place due to dehydration, we should have:



A partial analogy for this can be found in the formation of osotriazols from hydrazoximes of orthodiketones.



There is therefore established a very strong probability that product C is a compound having the structure



It will be necessary to adduce further proof, especially in the way of reactions of this new compound, before giving it a name or attempting to decide with certainty just what structure is actually present. This work is being extended to other nitrosochlorides.

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CONTRIBUTIONS TO THE KNOWLEDGE OF FOREST PRODUCTS.

III. IDENTIFICATION OF PHENOLS AS 3,5-DINITROBENZOIC-ACID ESTERS.¹

BY R. C. BROWN AND ROLAND E. KREMERS.

Introduction.—In the course of an investigation of some cohobated aqueous distillates, one of us became interested in the use of 3,5-dinitrobenzoic acid as a reagent for identifying the lower saturated alcohols.² By means of it a solid characteristic derivative of methyl alcohol was readily obtained.³ Encouraged by this fact, the same reagent was used in the course of some as yet unpublished work on guaiacol. From this it was but a step to the thought of applying this acid as a reagent in the identification of phenols as a group.

Theoretical Considerations.—The phenols, like the alcohols, are hydroxy substitution products of hydrocarbons. The chief difference is that the rest of the molecule has an "acidifying" effect on the fundamental properties of the —OH group. Hence it is that the reactions involving the —OH group of phenols differ in degree rather than in kind from the reactions of the alcohols. For the same reason, practically all general methods of identifying alcohols have been tried with phenols with suitable modifications.

Of these the most important is perhaps the formation of phenylurethanes from phenylisocyanate. The method itself is excellent and the resulting products apparently are uniformly crystalline. However, it is not in general use, probably due to the cost of the reagent and its instability. The benzoic acid esters, prepared by the Schotten-Baumann reaction, are most generally used, but have a

¹ Based on part of a thesis submitted by R. C. B. to the Graduate Faculty of Vanderbilt University in partial fulfillment of the requirements for the degree of M.S., June 1922.

² Univ. of Wis. Pharm. Expt. Sta., Circular 11, Oct. 1920.

³ See Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 68.