

containing more personal details during his Tomsk period, see: (c) V. D. Yushkovskii, "IV. Iz istorii Tomskogo Politekhnikheskogo Universiteta. Protivostoyanie Tomsk v sud'be professora Kizhnera [From the history of Tomsk Polytechnic University. Confrontation in the fate of Professor Kizhner at Tomsk]," *Izv. Tomskogo Pol-ka. Uni-ta.*, **2002**, 305, 208-221. (d) D. E. Lewis, *Early Russian Organic Chemists and Their Legacy*, Springer, Heidelberg, 2012, pp 105-106. (e) D. E. Lewis, "Disability, Despotism, Deoxygenation—From Exile to Academy Member: Nikolai Matveevich Kizhner (1867-1935)," *Angew. Chem. Int. Ed.*, **2013**, 52, 11704-11712. (f) V. Suntsov and D. E. Lewis, "A Century of Base-promoted Decomposition of Hydrazones: the Early Career of Nikolai Matveevich Kizhner (1867-1935)," *Bull. Hist. Chem.*, **2014**, 39, 43-52.

5. A more modern variant involved replacing the oxygen gas with a mixture of copper oxide and calcium carbonate and lowering the oxidation temperature to 550°C to slow down the combustion process and thus avoid loss of volatile materials and nitrogen: F. Shea and C. E. Watts, "Dumas Method for Organic Nitrogen," *Ind. Eng. Chem. Anal. Ed.*, **1939**, 11, 333-334.
6. M. Born and E. Wolf, *Principles of Optics*, 4th ed., Pergamon Press, Oxford, 1970, pp 88-90.

About the Authors

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PRIMARY DOCUMENTS

25. THE CATALYTIC DECOMPOSITION OF ALKYLIDENEHYDRAZINES AS A METHOD FOR THE PREPARATION OF HYDROCARBONS (ABRIDGED)

N. Kizhner

Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, **1911**, 43, 582-595.

Translated by Vladislav Suntsov and David E. Lewis

Supplemental Material

Introduction

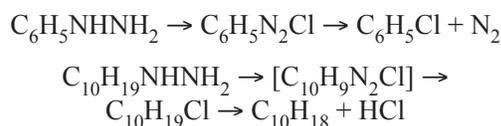
The oxidation of primary hydrazines of the aliphatic and cyclic series, our studies have shown, yields the same products as oxidation of primary aromatic hydrazines. Just as in the last case, the identity of the oxidation

products depends on the conditions under which the oxidation takes place.

During oxidation in an alkaline medium, the hydrazine group is substituted by hydrogen; the reaction proceeds so smoothly that it can be used as a method for producing hydrocarbons. During oxidation in an

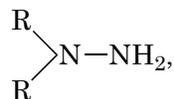
acidic medium, the hydrazine group is replaced by the acid radical. This reaction is common to primary hydrazines of all classes: chlorobenzene is obtained from the oxidation of phenylhydrazine with copper sulfate in hydrochloric acid solution (Gattermann); under the same conditions, menthylhydrazine yields menthyl chloride and menthene, as the products of the decomposition of the first compound (Kizhner).

The sequence of the mechanism by which acidic oxidation of hydrazines occurs is clear: the reaction forms a diazonium salt intermediate, which dissociates in the conditions of the earlier reaction, forming a halo derivative of the hydrocarbon:



The work of E. Fischer confirms the correctness of this view of the process of oxidation of primary hydrazines: careful oxidation of phenylhydrazine sulfate with silver oxide results in formation of benzenediazonium sulfate. E. Fischer has obtained a salt, $\text{C}_2\text{H}_5\text{N}=\text{NSO}_3\text{K}$, of the explosive diazoethanesulfuric acid by the oxidation of potassium ethylhydrazine sulfate, with silver oxide. With regard to the mechanism of the oxidation of hydrazines in alkaline medium, one is limited just to guesses.

Working on this question 11 years ago (1), I settled on this explanation of the process: I can only explain the transformation of the hydrazine to saturated hydrocarbons during oxidation in alkaline medium by formation of an intermediate product of this type: $[\text{C}_n\text{H}_{m-1}]\text{N}=\text{NH}$. I see the probability of the formation of such a substance being easier in the oxidation of primary hydrazines of the type, $\text{R}-\text{NHNH}_2$, in comparison to secondary hydrazines



which points to greater mobility of the hydrogen on the NH group compared to that of hydrogens on the amide group. In this case, the first product of the oxidation of the primary hydrazines could be a substance of this type of structure: $\text{R}-\text{N}(\text{OH})-\text{NH}_2$. Loss of water will lead to a product, $\text{R}-\text{N}=\text{NH}$, which decomposes with the formation of saturated hydrocarbons and nitrogen according to the following equation (2)



The data I obtained recently while studying alkylidenehydrazines ($\text{C}_n\text{H}_{m-2}:\text{N}-\text{NH}_2$) convince me that the

views presented on the mechanism of the oxidation of primary hydrazines in alkaline medium are correct.

When heated in the presence of a small amount of solid potassium hydroxide, alkylidenehydrazines decompose according to following equation:



Thus the catalytic decomposition of alkylidenehydrazines leads to the formation of the very products that are obtained in the oxidation of primary hydrazines with an alkaline solution of potassium ferricyanide.

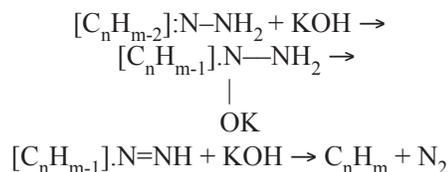
If we assume that in the last reaction, the alkylidenehydrazine is formed as the first intermediate, one would have to assume that the alkylidenehydrazine would decompose in an aqueous alkaline solution at low temperature (below 100°) according to this equation:



However, experience has shown that alkylidenehydrazines can be steam distilled from a concentrated solution of caustic alkali without showing any noticeable trace of degradation. It follows that they cannot be the intermediates in conversion of hydrazines into hydrocarbons. The most likely explanation is the one previously mentioned: the formation of an unstable "diazo" form:



The mechanism of the conversion of alkylidenehydrazines to hydrocarbons can be explained if prior isomerization of the alkylidenehydrazone into an unstable "diazo" form by the action of the caustic alkali is allowed:



Experimental Part

The decomposition of alkylidenehydrazines was usually conducted as follows:

A Wurtz flask is connected to a dropping funnel and a water-cooled condenser; 1 to 2 grams of dry potassium hydroxide are placed in the flask prior to that. After adding a small amount of the alkylidenehydrazine, the mixture is heated on a grid (3) until nitrogen is evolved, after which the reaction continues by itself, and the hydrocarbon is distilled

into the receiver flask. Of all the alkylidenehydrazines studied, the decomposition of cyclohexylidenehydrazine hydrate is the most energetic; if enough of this substrate is used at one time, the reaction may end with an explosion.

Decompositions of the following alkylidenehydrazines are described in this article:

- 1,3-methylcyclohexylidenehydrazine [*Now known as 3-methylcyclohexanone hydrazone*—translators]
- Thujylidenehydrazine [*thujone hydrazone*]
- Camphylidenehydrazine [*camphor hydrazone*]
- Fenchylidenehydrazine [*fenchyl hydrazone*]
- Cyclohexylidenehydrazine hydrate [*cyclohexanone hydrazone hydrate*]

The decomposition of cyclohexylidenehydrazine hydrate is interesting in that, besides producing the normal decomposition product, cyclohexane, it yields cyclohexanol (in almost equal proportions), which is responsible for cleavage of the nitrogen in the form of hydrazine hydrate.

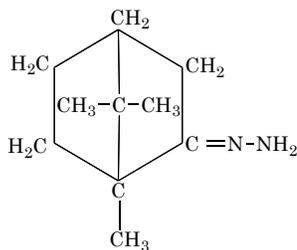
1. Catalysis of 1,3-methylcyclohexylidenehydrazine. $\text{CH}_3\text{C}_6\text{H}_9:\text{NNH}_2$.

... [For the complete experimental details, see the Supplemental material.]

2. Catalysis of thujylidenehydrazine $\text{C}_{10}\text{H}_{16}:\text{N-NH}_2$.

... [For the complete experimental details, see the Supplemental material.]

3. Camphylidenehydrazine and its conversion to camphane:



Camphylidenehydrazine was obtained by continuous boiling of an alcoholic solution of camphor and hydrazine hydrate. Because the conversion of camphor to camphylidenehydrazine is accompanied by a change in the sign of optical rotation, the reaction could be followed with a polarimeter; the rotation was measured after each 11 to 12 hour period of continuous boiling. The reaction

was conducted using 200 g of camphor, 200 g of a 50% solution of hydrazine hydrate, and 750 cc of alcohol; the resulting solution was boiled on a hot water bath for a total of 170 hours. Before boiling the optical rotation of the solution was: $\alpha = +7.23^\circ$.

Here is a table of the rotations measured at indicated time intervals:

1) $+2.60^\circ$; 2) $+1.17^\circ$; 3) $+0.26^\circ$; 4) -0.52° ; 5) -1.28° ; 6) -1.93° ; 7) -2.35° ; 8) -2.83° ; 9) -3.14° ; 10) -3.36° ; 11) -3.72° ; 12) -3.94° ; 13) -4.28° .

After distillation of the alcohol on the water bath, the camphylidenehydrazine is separated from the water, and extracted with ether. The ether is thoroughly dried with fused potassium carbonate. After distilling the ether, the product is distilled under reduced pressure.

Camphylidenehydrazine boils at 143° at 33 mm; upon cooling it crystallizes into a white crystal mass, which melts at $53-55^\circ$.

Determination of N.

| | |
|---|---|
| Weighed: | 0.1709 g; 25.9 cc N (18.5° , 750 mm) |
| $\text{C}_{10}\text{H}_{18}\text{N}_2$ calculated % N – | 16.86 |
| Found % N – | 17.14 |

Rotation in absolute ether solution:

| | |
|--------------------------|--------------------------------|
| Concentration: | 9.9000 g in 100 cc of solution |
| $\alpha = -4.77^\circ$; | $[\alpha]_D = -40.81^\circ$ |

Rotation in 90% alcohol:

| | |
|--------------------------|-------------------------------|
| Concentration: | 5.309 g in 100 cc of solution |
| $\alpha = -1.65^\circ$; | $[\alpha]_D = -32.74^\circ$ |

Camphylidenehydrazine and water form a liquid hydrate, which is soluble in water. Apparently, this leads to reduction in optical rotation when it is in alcohol-water solution.

The hydrochloride $\text{C}_{10}\text{H}_{16}:\text{NNH}_2 + \text{HCl}$ forms a white precipitate when dry hydrogen chloride is passed through a solution of camphylidenehydrazine in absolute ether. The precipitate is washed with absolute ether and vacuum dried at 180° .

Determination of N

| | |
|--|-------|
| Weighed 0.2012 g; 24.1 cc N (19° , 757 mm) | |
| $\text{C}_{18}\text{H}_{18}\text{N} + \text{HCl}$ Calculated % N – | 13.65 |
| Found % N – | 13.82 |

The hydrochloride is easily dissolved in water. The solution may be stored for long periods of time without degrading at room temperature.

Rotation in aqueous solution:

Concentration: 0.8521 g in 10 cc of solution;
 $\alpha = -2.67^\circ$; $[\alpha]_D = -31.33^\circ$.

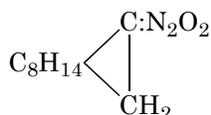
When a solution of camphylidenehydrazine is boiled with excess hydrochloric acid, total hydrolysis to camphor and the salt of hydrazine takes place. The camphor obtained has the following rotation:

Solvent: absolute alcohol

Concentration: 0.7998 g in 10 cc of solution;
 $\alpha = +3.34^\circ$; $[\alpha]_D = +41.76^\circ$.

Camphanazine $C_{10}H_{16}:N-N:C_{10}H_{16}$

Camphanazine was synthesized by A. Angeli and V. Castellana (4) during the reduction of pernitrosocamphor



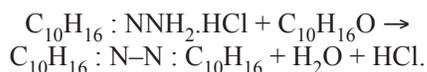
I prepared this compound by hydrolyzing camphylidenehydrazine.

In excess hydrochloric acid, as previously noted, camphylidenehydrazine is completely decomposed into camphor and hydrazine hydrochloride, as follows:



However, if during the hydrolysis of one molecule of camphylidenehydrazine only one molecule of hydrochloric acid is used, in other words, the hydrolysis of camphylidenehydrazine hydrochloride $C_{10}H_{16} : N-NH_2 \cdot HCl$ occurs, a significant amount of camphanazine is formed, in addition to the camphor.

Shown schematically, the process of forming camphanazine under these conditions can be expressed by the equation:



This equation, however, does not explain the actual mechanism of camphanazine formation. This is evident from the fact that camphanazine results from the hydrolysis of camphylidenehydrazine hydrochloride in an aqueous solution, where camphor should be removed from the reaction due to its insolubility in water. In addition, direct experiments have shown that camphor does not react with camphylidenehydrazine even after prolonged boiling in alcohol solution.

A solution of camphylidenehydrazine (80 grams) with an equivalent (1 mol) of hydrochloric acid was boiled on a water bath for a few hours; a copious precipitate, which was a mixture of camphor and camphanazine, deposited. The camphor was removed from the mixture by means of steam; the remainder (22 g) is almost pure camphanazine. The yield is 27%, based on camphylidenehydrazine. If the hydrolysis of the hydrochloride is performed in ethanol solution, instead, the yield does not change.

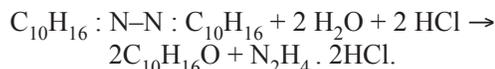
To a solution of 30 g. of camphylidenehydrazine in 200 cc of alcohol were added 15 cc of fuming hydrochloric acid (1 mol). After boiling the solution under reflux on a water bath for three hours, the alcohol and camphor were removed by steam distillation. The residue yielded 7 g of camphanazine (23%).

From ethanol, camphanazine crystallizes as large octahedral crystals or as hexagonal plates. Melting point 185-186° (Angeli's: 185°).

Determination of nitrogen:

| | |
|------------------------------------|---------------------|
| Weighed: | 0.1865 g: 15.4 cc N |
| | (23°, 780 mm) |
| $C_{10}H_{32}N_2$ calculated % N – | 9.33 |
| Found % N – | 9.51 |

On heating with fuming hydrochloric acid on a water bath, camphanazine is decomposed quantitatively according to the equation:



From 13 g of the azine were obtained 12 g of camphor and 4 g of hydrazine hydrochloride salt. By theory, 13.2 camphor and 4.5 g hydrazine hydrochloride should be obtained.

Camphanazine rotates the plane of polarization to the left, but the magnitude of the rotation varies greatly depending on the nature of the solvent.

1. Solvent: benzene;

concentration: 0.5708 g in 10 cc of solution,
 $\alpha = -5.27^\circ$. $[\alpha]_D = -92.33^\circ$.

2. Solvent: ether (abs.);

concentration: 0.4064 g in 10 cc of solution,
 $\alpha = -3.66^\circ$. $[\alpha]_D = -90.66^\circ$.

3. Solvent: CH_3OH ;

concentration: 0.3542 g in 10 cc of solution,
 $\alpha = -1.32^\circ$. $[\alpha]_D = -37.27^\circ$.

4. Solvent $\text{C}_2\text{H}_5\text{OH}$;

concentration: 0.5769 g in 10 cc of solution,
 $\alpha = -1.11^\circ$. $[\alpha]_D = -19.25^\circ$.

5. Solvent $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$;

concentration: 0.5501 g in 10 cc of solution,
 $\alpha = -0.78^\circ$. $[\alpha]_D = -14.18^\circ$.

Rotation in benzene and absolute alcohol mixtures:

90% C_6H_6 + 10% $\text{C}_2\text{H}_5\text{OH}$; $[\alpha]_D = -47.80^\circ$.

57.4% C_6H_6 + 42.6% $\text{C}_2\text{H}_5\text{OH}$; $[\alpha]_D = -30.15^\circ$.

16.3% C_6H_6 + 83.7% $\text{C}_2\text{H}_5\text{OH}$; $[\alpha]_D = -25.39^\circ$.

Camphane from Camphylidenehydrazine

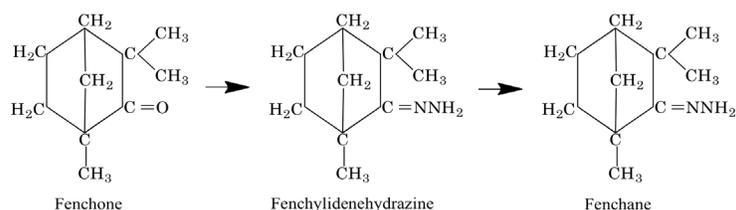
... [For the complete experimental details, see the Supplemental material.]

4. Conversion of Fenchone to Fenchane.

In collaboration with A. Proskuryakov

... [For the complete experimental details, see the Supplemental material.]

The structure of the resulting hydrocarbon is deduced from the structure of fenchone, and if Semmler's formula for the latter is adopted, a description of the transformations can be expressed as follows:



... [For the remainder of this section of the experimental, see the Supplemental material.]

5. Catalysis of Cyclohexylidenehydrazine

... [For this section of the experimental, see the Supplemental material.] Tomsk, March 7, 1911

Supplemental Material

An unabridged translation of this paper can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

References and Notes

1. N. Kizhner, "O prevrashcheniyakh bromaminov pod vliyaniem okisi serebra i gidroksilamina [On the transformation of bromoamines with silver oxide and hydroxylamine]," *Zh. Russ. Fiz.-Khim. O-va.*, **1905**, 31, 1033-1062. Cited in the original as Ж. P. X. O. 31, 1043 (1899).
2. [In some reactions, Kizhner used reaction arrows and sometimes equals signs to separate products from reactants. He sometimes also used equals signs within formulas to indicate a double bond. We use a reaction arrow consistently for the former purpose. —translators]
3. [This appears to be a specific type of heating apparatus, but we are unable to identify it. —translators]
4. A. Angeli and V. Castellana, "Ueber einige Derivate des Kamfers." *Chem. Zentralbl.*, **1905**, II, 623-624. Abstracted article: "Sopra alcuni derivati della canfora," *Atti R. Accad. del Lincei Roma* [5], **1905**, 14, I, 669-677. Cited in the original as Cbl 1905, II, 623.