

## PRIMARY DOCUMENTS

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

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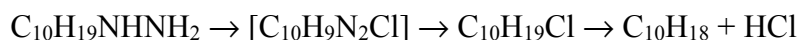
Translated by Vladislav Suntsov and David E. Lewis

### 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.

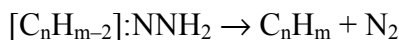
Working on this question 11 years ago (1), I settled on this explanation of the process: I can only explain the transformation of the hydrazine to saturated hydrocarbons during oxidation in alkaline medium by formation of an intermediate product of this type:  $[\text{C}_n\text{H}_{m-1}]\cdot\text{N}=\text{NH}$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

hydrazines of the type,  $R-NH-NH_2$ , in comparison to secondary hydrazines  $\begin{matrix} R \\ \diagdown \\ N-NH_2 \\ \diagup \\ R \end{matrix}$ , 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:  $R-N(OH)-NH_2$ . Loss of water will lead to a product,  $R-N=NH$ , which decomposes with the formation of saturated hydrocarbons and nitrogen according to the following equation (2)



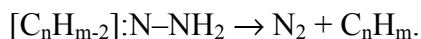
The data I obtained recently while studying alkylidenehydrazines  $(C_nH_{m-2}):N-NH_2$  convince me that the views presented on the mechanism of the oxidation of primary hydrazines in alkaline medium are correct.

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

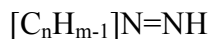


Thus the catalytic decomposition of alkylidenehydrazines leads to the formation of the very products that are obtained in the oxidation of primary hydrazines with an alkaline solution of potassium ferricyanide.

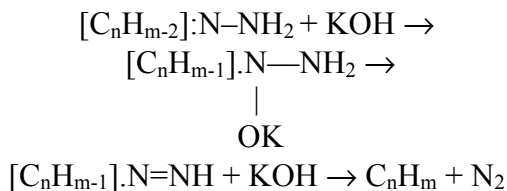
If we assume that in the last reaction, the alkylidenehydrazine is formed as the first intermediate, one would have to assume that the alkylidenehydrazine would decompose in an aqueous alkaline solution at low temperature (below 100°) according to this equation:



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. 1,3-methylcyclohexylidenehydrazine [*Now known as 3-methylcyclohexanone hydrazone* —translators]
2. Thujiylidenehydrazine [*thujone hydrazone*]
3. Camphylidenehydrazine [*camphor hydrazone*]
4. Fenchylidenehydrazine [*fenchyl hydrazone*]
5. 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. $\text{CH}_3\text{C}_6\text{H}_9\text{:NNH}_2$ .

12 grams of 1,3-methylcyclohexylidenehydrazine were decomposed, as indicated above, by heating in the presence of 2 grams of potassium hydroxide. The distillate is washed with hydrochloric acid (1 vol. HCl and 1 vol. H<sub>2</sub>O) to remove the base entrained by the products of the reaction, followed by sodium hydroxide and is then dried over calcium chloride. Five grams of methylcyclohexane are produced. Yield: 54%.

Boiling point of the alkane product is 101° at 757 mm.

Specific gravity.

Weight of the substance at 20° = 2.4371 g.

Weight of water at 0° = 3.1670 g

$$d_{0}^{20} = 0.7695$$

Refractive index  $n_{\text{D}}^{20} = 1.4230$ ;

$$R^2 = 32.36. \text{ Calculated for } \text{C}_7\text{H}_{14} \text{ } R^2 = 32.22. (4)$$

## 2. Catalysis of thujylidenehydrazine C<sub>10</sub>H<sub>16</sub>:N-NH<sub>2</sub>.

From 20 grams of thujylidenehydrazine (1 gram KOH), 12 grams of washed and dried (with calcium chloride) thujane were obtained. Yield: 70%.

Properties of the hydrocarbon:

Boiling point 157.5° at 759 mm.

Specific gravity.

Weight of the substance at 20° = 2.5879 g

Weight of water at 0° = 3.1670 g

$$d_{0}^{20} = 0.8172.$$

Refractive index  $n_{D}^{20} = 1.4406$ .

$R^2=41.56$ . Calculated for thujane 43.93; higher by 0.62.

Rotation:  $\alpha = +30.86$ ;  $[\alpha]_D = +37.55^\circ$ .

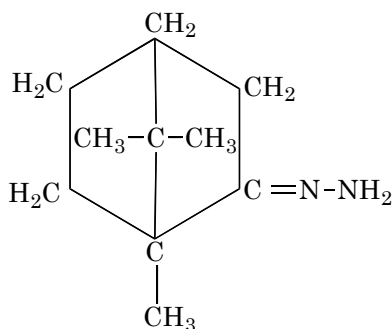
A second experiment gave thujane with the same properties: boiling point 157-157.5° at 759 mm.

$d_{0}^{20} = 0.8171$ ;  $n_{D}^{20} = 1.4400$ ;  $R^2=44.54$ ;

$\alpha = +30.68$ ;  $[\alpha]_D = +37.55^\circ$ .

The thujane produced by oxidation of thujylhydrazine has a smaller rotation.

## 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)  $-0.52^\circ$ ; 5)  $-1.28^\circ$ ; 6)  $-1.93^\circ$ ; 7)  $-2.35^\circ$ ; 8)  $-2.83^\circ$ ; 9)  $-3.14^\circ$ ; 10)  $-3.36^\circ$ ; 11)  $-3.72^\circ$ ; 12)  $-3.94^\circ$ ; 13)  $-4.28^\circ$ .

After distillation of the alcohol on the water bath, the camphylidinenhydrazine 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  $143^\circ$  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 ( $18.5^\circ$ , 750 mm)

$C_{10}H_{18}N_2$  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  $C_{10}H_{16}:NNH_2 + HCl$  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  $180^\circ$ .

Determination of N

Weighed 0.2012 g; 24.1 cc N ( $19^\circ$ , 757 mm)

$C_{18}H_{18}N + HCl$  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:

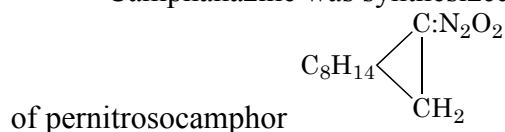
Solvent: absolute alcohol

Concentration: 0.7998 g in 10 cc of solution;

$\alpha = +3.34^\circ$ ;  $[\alpha]_D = +41.76^\circ$ .

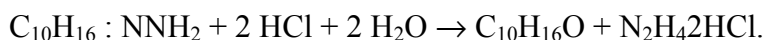
### Camphanazine $C_{10}H_{16}:N-N:C_{10}H_{16}$

Camphanazine was synthesized by A. Angeli and V. Castellana (5) during the reduction



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°).

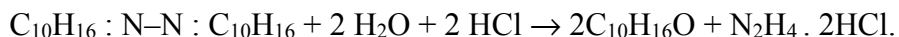
Determination of nitrogen:

Weighed: 0.1865 g: 15.4 cc N  
(23°, 780 mm)

C<sub>10</sub>H<sub>32</sub>N<sub>2</sub> 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 plane 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<sub>3</sub>OH;

concentration: 0.3542 g in 10 cc of solution,

$\alpha = -1.32^\circ$ .  $[\alpha]_D = -37.27^\circ$ .

4. Solvent C<sub>2</sub>H<sub>5</sub>OH;

concentration: 0.5769 g in 10 cc of solution,

$\alpha = -1.11^\circ$ .  $[\alpha]_D = -19.25^\circ$ .

5. Solvent CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH;

concentration: 0.5501 g in 10 cc of solution,

$\alpha = -0.78^\circ$ .  $[\alpha]_D = -14.18^\circ$ .

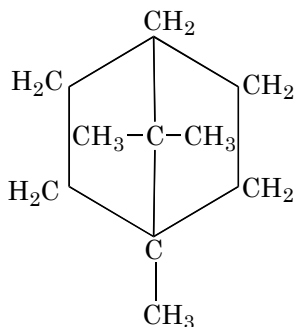
Rotation in benzene and absolute alcohol mixtures:

90% C<sub>6</sub>H<sub>6</sub> + 10% C<sub>2</sub>H<sub>5</sub>OH;  $[\alpha]_D = -47.80^\circ$ .

57.4% C<sub>6</sub>H<sub>6</sub> + 42.6% C<sub>2</sub>H<sub>5</sub>OH;  $[\alpha]_D = -30.15^\circ$ .

16.3% C<sub>6</sub>H<sub>6</sub> + 83.7% C<sub>2</sub>H<sub>5</sub>OH;  $[\alpha]_D = -25.39^\circ$ .

### Camphane from Camphylidinehydrazine



The main alkane of the camphor group, camphane, was first prepared in the pure state by Kachler and Schnitzer (6) by the reduction of bornyl chloride with sodium metal in boiling benzene solution. The hydrocarbon, which the investigators named hydrocamphor, had the following properties: corrected melting point 152°; corrected boiling point 157-158°, not optically active. Later investigators of the preparation of camphane also used the reduction of pinene hydrohalides. The properties of camphane synthesized by this method are very close to those given by Kachler and Schnitzer:

Camphane from pinene hydrochloride: corrected melting point 155°, corrected boiling point 159° (Rosenberg); corrected melting point 155°, corrected boiling point 160-162° (Semmler) (7).

Camphane from pinene hydriodide: corrected melting point 153-154°, corrected boiling point 160° (Aschan) (8).

The method of producing hydrocarbons described on previous pages made it possible to convert camphor to camphane by the decomposition of camphylidinehydrazine.

In a Wurtz flask, 2 g of potassium hydroxide and 30 g of camphylidinehydrazine are placed. Upon heating the mixture, nitrogen is produced and camphane is distilled into a receiver



flask. Because the melting point of camphor closely coincides with the boiling point of the hydrocarbon, the take-off tube of the flask during the operation is held at a temperature close to the boiling point of camphane, which causes significant loss of the hydrocarbon.

After preliminary grinding, the solid distillate was washed with hydrochloric acid in order to remove camphylidenehydrazine, then washed again with water and dried between two porous plates. The yield of hydrocarbon was 10 g.

From hot methanol solution, camphane crystallizes in aggregates resembling snowflakes, and as hexagonal plates when crystallized from a mixture of alcohol and ether. On storage in an evacuated sealed tube the hydrocarbon quickly sublimes, forming regular hexagonal crystals on the walls of the tube.

Camphane melts at 158-159°, solidifies at 157°, boils at 160-161° at 763 mm, and is not optically active.

Analysis.

Weighed	0.1231 g:	0.3935 g CO <sub>2</sub> ;	0.1433 g H <sub>2</sub> O
C <sub>10</sub> H <sub>18</sub>	Calculated	% C –	86.87.
		H –	13.13
	Found	% C –	87.18
		H –	13.02.

The hydrocarbon does not react with bromine or fuming nitric acid (1.52), and the latter even when heated.

#### 4. Conversion of Fenchone to Fenchane.

In collaboration with A. Proskuryakov

A sample of fenchone was obtained from Kalbaum; melting point: +5°,  $\alpha$ +59.28°;  $d_{15} = 0.949$  (wt. Vest. (9)).

A solution of 100 g of fenchone and 100 g of 50% hydrazine hydrate in 250 cc of ethanol was boiled for 80 hours on a heated water bath with a reflux condenser. Despite the continuous boiling no more than 30% of the fenchone reacted with hydrazine. The ethanol was distilled from the salt bath, and the residue was diluted with water. The fenchylidenehydrazine was extracted from the oily supernatant layer (a mixture of fenchylidenehydrazine and fenchone) by shaking and cooling in presence of hydrochloric acid (1 vol. fuming HCl + 1 vol. water); from the residue, 70 g of fenchone was isolated.

The fenchylidenehydrazine was isolated from the hydrochloric acid solution with potassium hydroxide. The oily base liberated was dried with fused potash by upon heating on a water bath. The yield is 10 g of fenchylidenehydrazine.

Fenchylidenehydrazine, carefully dried with potash was decomposed by slow distillation with dry potassium hydroxide (2 g). During the distillation, nitrogen is produced, and the

thermometer reads 215-220°. The residue in the flask crystallizes on cooling. This crystalline solid is fenchanazine  $C_{10}H_{16}:N-N:C_{10}H_{16}$ , and will be described later.

The resulting liquid distillate was washed with hydrochloric acid (1:1) and water, and the remaining hydrocarbon, after a washing with base, was distilled with steam. This yielded 4 g of the hydrocarbon, which was purified by refluxing over sodium and distillation.

Fenchane boils at 151.5° at 763 mm and is a volatile liquid with a slight camphor odor.

Analysis:

Weighed	0.1077 g:	0.3433 g CO <sub>2</sub> ;	0.1265 g H <sub>2</sub> O
C <sub>10</sub> H <sub>18</sub>	Calculated	% C –	86.87
		H –	13.13
	Found	% C –	86.93
		H –	13.14

Specific gravity

Weight of the compound at 20° - 0.7532 g

Weight of water at 4° = 0.9047

$$d_{4}^{20} = 0.8326$$

Refractive index  $n_{D}^{20} = 1.4463$

Molecular refraction  $R^2$  44.23

Calculated for bicyclic C<sub>10</sub>H<sub>18</sub>  $R^2 = 43.93$

Rotation:

Solvent – 95% alcohol

concentration: 0.7380 g in 10 cc of solution;

$$\alpha = -1.22^\circ. \quad [\alpha]_D = -16.53^\circ$$

Fenchane is completely inert to potassium permanganate; it does not react with bromine or fuming nitric acid, even upon heating.

2 cc of fenchane were heated in a sealed tube with 20 cc of fuming hydriodic acid for 8 hours at 210°. The properties of the hydrocarbon remained almost the same.

Boiling point: 150-151° at 757 mm.

Specific gravity

Weight of the compound at 20° = 0.7502 g

Weight of water at 4° = 0.9047 g

$$d_{4}^{20} = 0.8292$$

Refractive index  $n_{D}^{20} = 1.4460$ ;  $R^2 = 44.40$

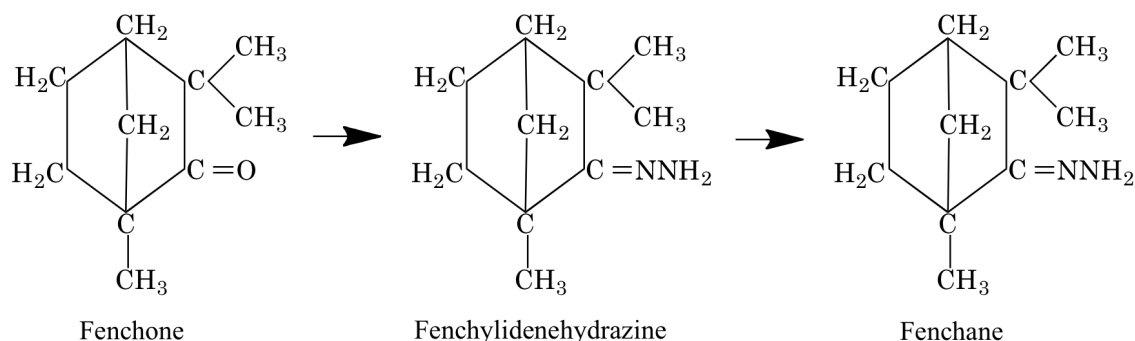
Rotation:

Solvent – alcohol;

concentration: 0.7334 g in 10 cc of solution;

$\alpha = -1.20^{\circ}$ .  $[\alpha]_{D} = -16.36^{\circ}$

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:



### Fenchazine $C_{10}H_{16}:N-N:C_{10}H_{16}$

As noted previously, this substance is obtained in the residue after the decomposition of camphylidenehydrazine. The solid was washed with water, pressed dry on a porous plate and purified by crystallization from hot methyl alcohol, in which it is soluble with difficulty. Upon cooling, the azine forms rectangular shards. Upon slow evaporation of the benzene-azine solution, large (1 cm) irregular quadrilateral shards are formed. Melting point:  $106^{\circ}$ .

Determining N.

Weighed 0.1639 g: 14.1 cc N ( $20^{\circ}$ , 748 mm)

$C_{10}H_{16}:N-N:C_{10}H_{16}$ .calculated % N – 9.31

Found % N – 9.66

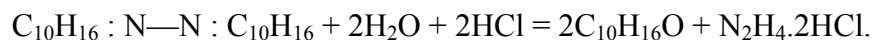
Rotation:

Solvent – benzene;

concentration: 0.5284 g to 10 cc solvent;

$\alpha = +11.25^{\circ}$ ;  $[\alpha]_{D} = +212.90^{\circ}$ .

Upon heating on a water bath with fuming hydrochloric acid, fenchazine decomposes into fenchone and hydrazine hydrochloride, which establishes the structure of this compound.



### 5. Catalysis of Cyclohexylidenehydrazine

25 g  $\text{C}_6\text{H}_{10} : \text{NNH}_2 + \text{H}_2\text{O}$  was decomposed in small portions in the presence of 2 g of potassium hydroxide. A highly basic distillate was produced, which proved to be a mixture of cyclohexane and cyclohexanol; the alkaline reaction is explained by the presence of free hydrazine (hydrate). On diluting the distillate with water, a hydrocarbon separated. The yield of hydrocarbon, which was washed with hydrochloric acid and dried with potassium hydroxide, was 8 g. The cyclohexane obtained boils at  $81^\circ$  at 759 mmHg; melting point  $4.5\text{--}5^\circ$ .

Specific gravity

Weight of the compound at  $20^\circ = 0.7039$  g.

Weight of water at  $4^\circ = 0.9047$  g.

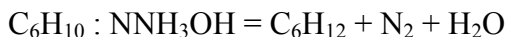
$$d_{\frac{20}{4}} = 0.7781$$

Refractive index  $n_{\frac{20}{D}} = 1.4262$ ;

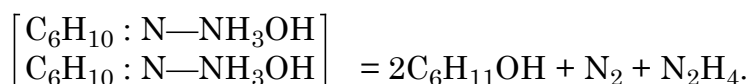
$$R^2 = 27.68. \text{ Calculated for } \text{C}_6\text{H}_{12} - R^2 = 27.62.$$

Cyclohexanol was isolated from the acidic washing water by distillation. The distillate was saturated with potash; the cyclohexanol that separated was dried with fused potassium carbonate. Yield: 8 g. of cyclohexanol. The alcohol boiled at  $161^\circ$  and 763 mm and crystallizes upon storing at room temperature. The evaporation of the acidic liquid left after the distillation of cyclohexanol produced 2 g of hydrazine hydrochloride.

Going from cyclohexylidenehydrazine hydrate to cyclohexanone represents the normal degradation reaction of alkylidenehydrazines:



The conversion of the hydrate to cyclohexanol may be explained using the following scheme:



Tomsk, March 7, 1911

## 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. П. 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. Molecular refraction. The definition currently used is  $R = \frac{(n^2 - 1)}{(n^2 + 2)} \frac{M}{\rho}$ ; it has the advantage that it is almost independent of the density, temperature and aggregation state of the compound, and that it can be predicted on the basis of simple addition of the contributions from bonds, atoms or groups. We do not know why Kizhner reports  $R^2$ . See M. Born and E. Wolf, *Principles of Optics*, 4th ed. (Pergamon Press: Oxford, 1970), pp. 88-90.
5. 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.
6. "Referate," *Ber. deutsch. chem. Ges.*, **1880**, *13*, 2230-2245; Referate 6260. Cited in the original as Ber. 13, 6160, 2236 (1880). [We believe that the name of the second author is in error; see J. Kachler and F. V. Spitzer, "Ueber Hydrocamphen," *Ber. deutsch. chem. Ges.*, **1880**, *13*, 615-616. —translators]
7. F. W. Semmler, "Borneol und Isoborneol," *Ber. deutsch. chem. Ges.*, **1900**, *33*, 774-778. Cited in the original as Ber 33, 777.
8. O. Aschan, "Ueber Camphan," *Ber. deutsch. chem. Ges.*, **1900**, *33*, 1006-1010. Cited in the original as Ber 33, 1009.
9. [This is the abbreviation of a proper noun, which we believe to be Westinghouse. We believe it may describe a particular type of pycnometer, but have no evidence for this interpretation other than the context. —translators]