homophorone occurred among the products it was either in such negligible amounts as to escape attention or else the ring was closed under the influence of the alkaline condensing agent to form homo-isophorone.

It is further assumed in this paper that the molecular refraction exaltations for mesityl oxide, phorone and isophorone are applicable, within a certain small amount of error, to the homologs of these compounds herein discussed.

Summary

1. The action of sodium ethylate on diethyl ketone has been investigated.
2. Two compounds have been isolated, one a homolog of mesityl oxide, and the other a homolog of isophorone.
3. The important constants of these compounds have been determined.
4. The homomesityl oxide has been shown to possess the structure $(C_2H_5)_2C{=}C(CH_3)COC_2H_5$.
5. The probable structure of the homo-isophorone has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

SYMMETRICAL DICYCLOHEXYL HYDRAZINE AND RELATED COMPOUNDS

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Kizhner reported that he was able to reduce cyclohexylidene-azine by sodium in alcohol.[2] He obtained unsymmetrical dicyclohexyl hydrazine instead of the expected hydrazo compound. The mechanism of this peculiar rearrangement has never been explained.[3]

In view of recent successes in the reduction of azines and other compounds containing the C=N complex, by means of the Skita method of catalytic reduction using colloidal platinum as catalyst,[4] it was decided to attempt also the reduction of the ketazine produced through the interaction of two molecular equivalents of cyclohexanone and one of hydrazine hydrate, to determine whether the reported rearrangement would take place on catalytic reduction.[5]

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[1] Part of the work included in this paper is from a thesis presented by H. H. Harkins in partial fulfilment of the requirements for the degree of Master of Arts at the University of Texas, 1923.

[2] Kizhner and Byelov, *J. Russ. Phys. Chem. Soc.*, **43**, 577 (1911); *C. A.*, **6**, 347 (1912).

[3] Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, **1913**, p. 95.

[4] (a) Lochte, Noyes and Bailey, THIS JOURNAL, **44**, 2556 (1922). (b) Neighbors and Bailey, *ibid.*, **44**, 1561 (1922).

[5] Taipale [*Ber.*, **56**, 1247, 1794 (1923)] reports the results of his work on the reduction of the same type of compounds. Unfortunately most of the work of Taipale,

Cyclohexylidene-azine is readily reduced by the catalytic method of reduction at room temperature, and the product obtained is the expected symmetrical hydrazine. Attempts to isolate Kizhner's unsymmetrical compound from the reduction mixture were unsuccessful. In view of these results, attempts were made to repeat Kizhner's work to obtain a sample of his compound for comparison, but none of his hydrazine could be obtained. Since the original Russian article was not available, our failure may be due to inability to reproduce the conditions under which he worked.

The reduction product, hydrazocyclohexane, is very similar to symmetrical di-isopropyl hydrazine.[6] As it is very easily oxidized even by atmospheric oxygen, it is almost impossible to obtain the base in a high state of purity, especially in view of the fact that its boiling point is about 270°, while the melting point is below room temperature. Salts and derivatives are readily prepared and purified, however.

On oxidation by any weak oxidizing agent, the hydrazo compound is changed almost quantitatively into the corresponding azo derivative, a straw-colored oil, closely resembling 2,2′-azo-bispropane. The melting point of the pure product is 34.5°, practically the same as that of the azine. The azo compound is remarkably stable toward dilute acids; in its preparation by bromine water it is even extracted from the acid solution in which it is formed. On refluxing the compound with a mixture of 1 part of concd. hydrochloric acid and 4 parts of water, hydrolysis is complete within 30 minutes, yielding cyclohexyl hydrazine[2] and cyclohexanone in the usual manner.

When the cyclohexyl hydrazine is purified through its hydrochloride, liberated by concd. sodium hydroxide, extracted with ether, and then treated with one molecular equivalent of cyclohexanone, the corresponding hydrazone is produced. This derivative was not purified and analyzed because it was never obtained in the solid form and because the study of the hydrazone itself was made unnecessary by the isolation of the peroxide of the hydrazone—a new type of aliphatic peroxide. Busch and Dietz[7] isolated the first peroxides of hydrazones, but the compounds studied by them were all peroxides of hydrazones of aromatic hydrazines. The comparative stability of the peroxide was unexpected and experiments are now in progress to determine whether analogous derivatives may be isolated from other aliphatic hydrazones. The complete insolubility in water may explain the stability of the peroxide.

covers the same ground as that reported in the above-mentioned American articles. In a letter to Dr. J. R. Bailey, Taipale mentions the fact that he, too, is working on the reduction of the compound reported on in this communication. Our work was practically completed when the letter arrived in July, 1923, and the communication did not mention any products obtained by the Russian chemist in his work on this compound.

[6] Ref. 4a, p. 2560.

[7] Busch and Dietz, *Ber.*, **47**, 3277 (1914).

Attempts to prepare the unsymmetrical hydrazine through reduction of the nitrosamine of dicyclohexyl amine failed because reduction either did not take place or yielded the secondary amine and ammonia instead of the desired hydrazine. Catalytic reduction failed completely even when the nitrosamine had been carefully purified.

Experimental Part

Cyclohexylidene-azine.—The cyclohexanone from which this compound was prepared was made by reduction of phenol by the Skita method and subsequent oxidation of the alcohol to the ketone by the method of Osterberg and Kendall.[8] A number of attempts were made to prepare the ketone according to the Sabatier-Senderens method usually recommended, but no satisfactory yields were obtained.

In the preparation of the azine one molecular equivalent of hydrazine sulfate was treated in concd. aqueous solution with an excess of sodium carbonate and 2 equivalents of ketone. In this manner a yield of 60–70% of product boiling above 120° (40 mm.) was obtained. In all cases some unchanged cyclohexanone was collected below 120°, and a small amount of cyclohexylidene hydrazine seems to be always present in the higher-boiling fraction.

Reduction of Cyclohexylidene-azine.—When a 20g. portion of the azine is shaken with colloidal platinum and hydrogen under two atmospheres' pressure, reduction takes place rapidly and is complete in less than an hour if enough hydrochloric acid is present to form the hydrochloride. If the amount of solution in the shaker is large so that the rubber stopper comes in contact with the solution or if in any other manner the mixture touches rubber no absorption of hydrogen is observed.

A series of trial reductions was made in an attempt to reproduce Kizhner's work. We used 4, 6, 8 and 12 molecular equivalents of sodium, first in 95% alcohol and then in absolute alcohol, but were able to isolate, in addition to unchanged azine, only traces of our hydrazo compound and small amounts of the monocyclohexyl hydrazine, formed doubtless from the cyclohexylidene hydrazine present in the azine. We had hoped to get at least traces of Kizhner's compound even though we did not know details of his method because his original articles were not available.

Hydrochloride of Hydrazocyclohexane.—The catalyst is precipitated by acetone, filtered off, and the filtrate evaporated in a vacuum after acidification of the solution toward congo red paper. The hydrochloride remains as a white, flaky mass. The salt is soluble in benzene, alcohol or acetone, slightly soluble in water, and insoluble in ether, petroleum ether or ethyl acetate. It may be recrystallized from alcohol or from water. Thus purified, it is obtained as very fine, white needles that are partially volatilized before melting on platinum foil. When the salt is heated in a melting-point tube, however, it melts sharply at 271° (corr.) in a bath of mixed sodium and potassium nitrates.

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[8] Osterberg and Kendall, This Journal, **42**, 2616 (1920).

Analyses. Calc. for $C_{12}H_{25}N_2Cl$: N, 12.05; Cl, 15.26. Found: N, 12.31, 12.48, 12.37; Cl (Mohr), 15.57, 14.91.

OXALATE, $(C_6H_{11}NHNH\text{-}C_6H_{11}COOH)_2$.—This salt is obtained by treating an ether solution of the base with anhydrous oxalic acid. It is insoluble in water and ether, and slightly soluble in the other common organic solvents. Recrystallization from alcohol yields fine, white needles of the pure salt.

Analyses. Calc. for $C_{26}H_{50}O_4N_4$: C, 64.73; H, 10.37; N, 11.62. Found: C, 65.24, 64.40; H, 10.44, 10.26; N, 11.90, 11.71, 12.04.

Nitroso Derivative of the Symmetrical Hydrazine.—A nitroso derivative is readily prepared as a yellow crystalline product, but proved too unstable for purification and was not analyzed.

Symmetrical Dicyclohexyl Hydrazine.—The free base is liberated from the hydrochloride by the action of cold concd. aqueous sodium hydroxide; the hydrazine thus liberated is very easily oxidized so that even the freshly prepared base evolves a trace of the characteristic azo odor. This behavior toward air necessitates working in an atmosphere of nitrogen, but even then the momentary contact with air at various stages in the purification produces a distinct odor of the azo derivative. A sample distilled in a vacuum in a slow stream of nitrogen gave the following constants; m. p., 6–10°; b. p., 260–270° (740 mm.); d_4^{27}, 0.9384; n_D^{33}, 1.4888.

Azocyclohexane.—On the addition of cold bromine water to an aqueous suspension of the hydrochloride of the base, the bromine color is instantly discharged without evolution of gas. The oxidizing agent is added drop by drop, while the mixture is stirred constantly, until the color is no longer discharged rapidly. An excess of bromine must be avoided. The azo derivative is then extracted from the mixture by treatment with 5 to 8 portions of ether or by continuous extraction, the ether solution dried by potassium carbonate, and the ether evaporated in vacuum or in a stream of dry air. The straw-colored oil as it cools solidifies to a very slightly colored mass of thick needles; m. p., 34.5°. When the oxidation with bromine water is carried out carefully without using an excess of bromine the above method gives higher than an 80% yield of the azo derivative. When an excess of bromine water is employed or if the mixture is heated, a large part of the product is changed to a brown tar which cannot be removed readily. For this reason this method was finally abandoned in favor of oxidation by atmospheric oxygen. When the base is liberated, taken up in ether, and a stream of air drawn through the solution, the oxidation to the azo derivative is complete in about 6 hours. The loss due to vaporization is more than made up by the greater certainty of results and the convenience of the method. Since there is no danger of carrying the oxidation too far, the substance obtained by this method is practically free from by-products if a pure hydrochloride is employed in preparing the base.

The compound obtained by either method has a pleasant, sweetish odor somewhat resembling that of 2,2′-azobispropane and 2,2′-azobisbutane. It is perfectly stable at room temperature, but is partially decomposed when an attempt is made to distil at atmospheric pressure. The boiling point under these conditions is about 200°. Purification for analysis was accomplished by evaporating off most of the solvent from an ether solution, spreading the resulting crystals on a cold porous plate and drying them in a desiccator over calcium chloride. Although the compound is soluble in alcohol and insoluble in water, the addition of cold water to a cold alcoholic solution of the substance yields only an emulsion, so that this method cannot be used for purification; d_4^{30}, 0.9191; n_D^{34}, 1.4790; n_D^{20}, 1.4835.

Analyses. Calc. for $C_{12}H_{22}N_2$: C, 74.23; H, 11.34; N, 14.43; mol. wt., 194. Found: C, 74.41; H, 11.34; N, 14.92, 14.75; mol. wt. (f. p. lowering in benzene), 210, 182.

On reduction with 5% sodium amalgam the hydrazo compound is obtained; m. p. and mixed m. p. of hydrochloride, 268° (uncorr.). The same product is obtained by reduction with sodium in alcohol, and by the Skita catalytic method.

No sign of a reaction could be observed when the compound was treated with absolute hydrocyanic acid or with potassium cyanate and glacial acetic acid.

Cyclohexyl Hydrazine.—When one part of the azo derivative is treated with about ten parts of a 1:20 solution of hydrochloric acid, the substance floats as an oil layer which is very slowly decomposed, even when it is heated under a reflux condenser. At the end of an hour, over 80% of the azo derivative was found unchanged in this layer. When, however, a 1:4 solution is used, the hydrolysis proceeds rapidly and is complete at the end of 30 minutes. The ketone layer which remains is separated from the acid layer and the latter thoroughly extracted with ether to remove all the ketone since it causes gum formation in the subsequent operations. The ketone was identified by formation of its acid sulfite derivative, as well as by its odor.

The acid layer is evaporated in a vacuum. The sirupy residue solidifies as it cools. Recrystallized once from alcohol, the hydrochloride melts at 107–110°. Since the compound has been described by Kizhner, it was not analyzed, but the base was further identified by means of its very characteristic phenyl mustard oil derivative, and by means of a benzaldehyde condensation product.

PHENYLTHIOSEMICARBAZIDE.—When phenyl mustard oil is added to an ether solution of cyclohexyl hydrazine, wart-like masses of crystals form throughout the solution. These are recrystallized from alcohol; m. p., 148° (instead of 143°, reported by Kizhner).

Analyses. Calc. for $C_{13}H_{19}N_3S$: N, 16.86. Found (micro; Dumas): 16.35, 16.80.

BENZALDEHYDE DERIVATIVE, $(C_6H_{11}—N—N{=}CHC_6H_5)_2CHC_6H_5$.—When the hydrochloride of cyclohexyl hydrazine is treated with benzaldehyde, or when an ether solution of the base is treated with benzaldehyde and a drop of hydrochloric acid, a voluminous precipitate of white flakes separates. On recrystallization of these from ethyl acetate the compound is obtained as very fine, white needles; m. p., 183° (corr.). During recrystallization of this substance from hot water, the odor of benzaldehyde is noted; when it is heated with dilute acid it is also hydrolyzed to benzaldehyde and cyclohexyl hydrazine.

Analyses. Calc. for $C_{33}H_{40}N_4$: N, 11.38. Found (micro; Dumas): 11.27, 11.58.

Peroxide of Cyclohexanone Cyclohexylhydrazone, $\underbrace{CH_2(CH_2)_3CH_2CH}—NH—\underbrace{N—O—O—C}\underbrace{CH_2(CH_2)_3CH_2}$.—When an ether solution of one molecular equivalent of cyclohexyl hydrazine is mixed with one equivalent of cyclohexanone there is no immediate sign of reaction. When the ether is allowed to evaporate in air, white crystals soon separate along the edges of the solution. Soon after the ether has all disappeared, the residue changes to a solid mass of needles. The product may at first be mistaken for the hydrazone itself, but as evaporation of the ether in a vacuum produces only an oil of slightly pungent odor, while the evaporation in the presence of air yields a solid product melting at 76°, it is evident that the crystalline substance must be an oxidation product of the hydrazone. The oil obtained during evaporation in a vacuum was then exposed to a stream of air and found to change gradually to the same solid product. The new compound is soluble in the common organic solvents, but insoluble in water. Even a trace of the product in alcohol is sufficient to produce an emulsion when water is added. For purification, the substance is dissolved, at room temperature, in a small amount of alcohol, and about 10 volumes of water is added. When this solution is stirred, the product crystallizes from the emulsion as a voluminous precipitate of fine, white needles melting with decomposition at 76°. When the heating is slow the melting point is somewhat lower, sometimes as low as 74°.

When the new compound is left in the open air or even in a desiccator for a few days, it gradually changes to a mixture of colorless oil and a new crystalline compound; m. p., 136–137°. It is only slightly soluble in ether or alcohol. Only small amounts of this crystalline compound were obtained, and neither it nor the oil was identified because of the large amounts of the expensive raw materials required to yield even a gram or two of these final products.

Analyses. Calc. for $C_{12}H_{22}O_2N_2$: C, 63.71; H, 9.73; N, 12.39. Found (freshly prepared samples used for each analysis): C, 63.60; H, 9.72; N, (micro; Dumas), 12.80, 12.48.

The analyses, as well as the method of preparation and behavior of the new compound, indicate that it is the peroxide of the hydrazone. Such compounds have been prepared and studied by Busch and Dietz.[7] Their compounds were peroxides of aromatic hydrazones, however, while ours appears to be the first aliphatic peroxide of this type.

Cyclohexanone Cyclohexylhydrazone.—Attempts to isolate this hydrazone and purify it failed to produce it in solid form. A yellow or straw-colored oil was obtained in every case. The oil shows no similarity to the azo derivative described in this paper. While the azo derivative is perfectly stable in air, the hydrazone is oxidized immediately in the presence of air. In view of the expense connected with the preparation of sufficient amounts of the hydrazone for complete purification and analysis, and in view of the slight interest attached to the hydrazone after the isolation of its peroxide derivative, no attempt was made to purify the oil for analysis.

Attempts to Prepare Unsymmetrical Dicyclohexyl Hydrazine.—After attempts to prepare this hydrazine by reduction of the azine by sodium according to Kizhner, and by the catalytic method of Skita, had failed to yield the desired product, Fischer's method was tried.[9] Dicyclohexyl amine was readily prepared by catalytic reduction of aniline according to the method of Skita[10] and also by the reduction of diphenylamine by the same method. The nitrosamine was prepared in the usual manner. Attempts to reduce the nitrosamine to the hydrazine according to Fischer's method failed. The products obtained were the secondary amine and ammonia. Sodium amalgam, and also zinc and acetic acid in a freezing mixture, yielded the same products. Zinc dust and ammonium chloride effected only a partial reduction after two weeks at room temperature, but the secondary amine was again readily isolated from the reaction mixture. Catalytic reduction failed completely in all cases, even when the nitrosamine had been carefully purified by recrystallization from methyl alcohol.

Summary

1. Cyclohexylidene azine has been reduced to hydrazocyclohexane by catalytic reduction according to Skita. The unsymmetrical hydrazine reported by Kizhner as the product obtained on reduction of this ketazine by sodium in alcohol could not be isolated.

2. Azocyclohexane is readily prepared through oxidation of the hydrazo compound.

3. The corresponding hydrazone has not been isolated in pure form, but the peroxide of it is readily prepared and was identified as the first purely aliphatic compound of this type.

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[9] Fischer, *Ann.*, **199**, 287 (1879).

[10] Skita and Berendt, *Ber.*, **52**, 1519 (1919).