

their cyclic isomers give the same products in reactions that take place in the presence of acids. In processes involving the use of bases the products obtained from the two types are different.

3. The halogens react very readily with the cyclic compounds. By alternately introducing halogen and eliminating halogen acids it is possible to go step by step from the tetrahydropyridine derivatives to true pyridines.

4. The action of halogen on the open-chained compounds results in a mixture of a great number of open-chained and cyclic bromo compounds. The action can, however, be controlled. Halogenation in the presence of potassium acetate gives only open-chained compounds while the same process in glacial acetic acid gives mainly a true pyridine derivative.

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

SYMMETRICAL DI-ISOPROPYL-HYDRAZINE AND ITS DERIVATIVES. II

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Introduction

Recently, in a preliminary report ² on the reduction of dimethyl ketazine to symmetrical di-*isopropyl*-hydrazine, the latter was prepared and characterized by a few derivatives. Since then certain results have been obtained that round out this investigation and may prove of general interest in connection with the chemistry of aliphatic hydrazines.

The value of catalytic reduction as applied to the C=N complex was pointed out in the preliminary article. The preparation of primary *isopropyl*-hydrazine, by the same method, directly from ³/₄ a mixture of equimolecular amounts of hydrazine and acetone, without an isolation of the acetone hydrazone formed, as described in the present paper, promises a general method of producing mono-alkyl hydrazines in any quantity desired with little labor and a minimum of expense.

It is obvious that the application of catalytic reduction to suitable hydrazones and azines may be expected to furnish a practical method of preparing hydrazino and hydrazo paraffins containing asymmetric carbon atoms. The preparation, from these compounds, of optically active hydrazines and through them, of optically active paraffins, is contemplated as one of the lines of investigation in our continuation of the work that may be expected to develop from the present research.

¹ Abstract of a thesis submitted to the Graduate Faculty of the University of Illinois, by Harry L. Lochte, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² THIS JOURNAL, 43, 2597 (1921).

True to its monobasic nature in other reactions, symmetrical di-*iso*-propyl-hydrazine forms only a mononitroso derivative which, unexpectedly, yields a sodium salt on the addition of a conc. alcoholic solution of sodium hydroxide to its ethereal solution. As far as we are aware, this is the first sodium salt known of a nitroso derivative of a symmetrical, di-substituted hydrazine. Although for the corresponding salts of primary hydrazines 4 different structural formulas have been suggested³ for the salt obtained in the present investigation, only 3 structures are possible, $R-N(NO)-NHR$, $R-N(NO\dot{H})=NR$, and $R-N-N-R$.



The present investigation does not, however, lead to any results that indicate which of the 3 forms predominates under any particular conditions.

A novel reaction of symmetrical di-*iso*propyl-hydrazine is its quantitative conversion to 2,2'-azobispropane, $(CH_3)_2CH-N=N-CH(CH_3)_2$, when its hydrochloride reacts for several days with copper oxide at room temperature. The analytical data and molecular weight obtained prove that this oxidation product has the formula, $C_6H_{14}N_2$. It has a faint straw color and is insoluble in cold dil. alkalis and acids. These properties, together with the fact that it is only very slowly hydrolyzed by dil. acids, point to the azo rather than the isomeric hydrazone structure, $(CH_3)_2C=N-NH-CH(CH_3)_2$.

The only other azo paraffin known is Thiele's azomethane, $CH_3-N=N-CH_3$, a colorless gas at room temperature, but a liquid of very faint straw color below 1.5° . Although the gas explodes violently when mixed with air and ignited,⁴ azomethane is otherwise a fairly stable compound that may be heated to 300° without decomposition. It has never been transformed to the isomeric hydrazone. However, since this is the first member of the series of azo paraffins, we may expect its properties to be only approximately like those of the homologous compounds with 6 or more carbon atoms.

It has been shown⁵ that although certain mixed aliphatic-aromatic azo compounds can often be isolated, they transpose, sometimes even in the solid form, to the isomeric hydrazones. Quite recently, Neighbors and Bailey⁶ have found that their yellow 2-carbonamido-azopropane, NH_2-

³ Voswinkel, *Ber.*, **35**, 1943 (1902). Bamberger and Hausser, *Ann.*, **375**, 316 (1910). Thiele, *Ber.*, **41**, 2807 (1908). Thiele, *Ann.*, **375**, 336; **376**, 242 (1910). Pechmann, *Ber.*, **26**, 1047 (1893). Bamberger and Pemsel, *ibid.*, **35**, 758 (1902). Curtius, *ibid.*, **33**, 2562 (1900). Kizis, *Dissertation* Strassburg, about 1912, exact date not given.

⁴ Thiele, *ibid.*, **42**, 2578 (1909).

⁵ Fischer, *ibid.*, **29**, 794 (1897). Elbers, *Ann.*, **227**, 354 (1885). Thiele, *ibid.*, **376**, 267 (1910).

⁶ Neighbors and Bailey, *THIS JOURNAL*, **44**, 1561 (1922).

$\text{CON}=\text{N}=\text{CH}(\text{CH}_3)_2$, slowly changes in solution or in the dry state to the colorless acetone semicarbazone. Whenever both the hydrazone and the azo forms are possible for a molecule, the latter represents the more stable structure and often is the only form known. In the case of azo-*isobutyric* acid, studied by Thiele,⁷ the azo form exists only as long as the presence of the 2 carbonyl groups in the molecule, $(\text{CH}_3)_2(\text{COOH})\text{C}=\text{N}=\text{N}=\text{C}(\text{COOH})(\text{CH}_3)_2$, prevents a change to the hydrazone form. As soon as one of the carboxyl groups is removed through elimination of carbon dioxide the compound changes over to the hydrazone form, $(\text{CH}_3)_2(\text{COOH})\text{C}=\text{NH}=\text{N}=\text{C}(\text{CH}_3)_2$, which then hydrolyzes to hydrazino-*isobutyric* acid and acetone.

If the azo structure is correct for the oxidation product of our symmetrical hydrazine, then its slow hydrolysis to acetone and *isopropyl*-hydrazine must be preceded by a transposition to acetone-*isopropyl*-hydrazone. Attempts to isolate this product as an intermediate product were fruitless, due, doubtless, to the fact that it hydrolyzes instantly in acid of the strength required to transpose the azo derivative. The conversion of the azo form to the hydrazone form was effected, however, by a different method. When the azo derivative is allowed to stand at room temperature for several weeks over solid sodium or potassium hydroxide, or heated to 180° with solid alkali for 3 to 5 hours, a partial transformation results.

Before the conversion described in the preceding paragraph had been effected, numerous attempts were made to prepare the hydrazone from acetone and *isopropyl*-hydrazine. No definite results were obtained, until the work of Reddelien⁸ on the catalytic action of zinc chloride in the formation of Schiff bases suggested a suitable condensing agent in hydrazone formation. The addition of a very small amount of anhydrous zinc chloride to a mixture of acetone and *isopropyl*-hydrazine causes a violent reaction that has to be slowed down by cooling to prevent volatilization of the acetone. The yield of hydrazone by this method is about 70%. After the properties and reactions of the hydrazone had been studied, attempts were again made to prepare the compound without resorting to zinc chloride as a condensing agent. When anhydrous acetone and *isopropyl*-hydrazine are mixed in molecular amounts and an equal volume of absolute alcohol is added, the hydrazone odor becomes very pronounced, although no heat effect is observed. Fractional distillation of the mixture gives a yield of about 80% of acetone-*isopropyl*-hydrazone, so that this method of preparation is to be preferred to that employing zinc chloride.

In contrast to the azo derivative, acetone-*isopropyl*-hydrazone is a

⁷ Thiele and Heusser, *Ann.*, **290**, 8 (1896).

⁸ Reddelien, *ibid.*, **388**, 170 (1912).

colorless liquid having a stinging menthol odor. Even when it is dissolved in conductivity water, attempted conductivity determinations showed that the hydrazone is extensively hydrolyzed. The ease with which the hydrazone hydrolyzes to acetone and primary *isopropyl*-hydrazine explains the failure of our earlier attempts to obtain a satisfactory yield and doubtless explains also why homologous hydrazones have not previously been prepared.

That the isolation of the true hydrazone establishes beyond doubt the structure of the oxidation product obtained with copper oxide can be readily seen from a glance at the following table. Incidentally, these data reveal characteristic differences between azo and hydrazone compounds. These differences may be of future value in deciding between the two structures in doubtful cases.

TABLE I
 PROPERTIES OF 2,2'-AZOBISPROPANE AND ACETONE-ISOPROPYLHYDRAZONE

	2,2'-Azobispropane	Acetone- <i>isopropyl</i> -hydrazone
Color.....	Light straw.....	Colorless
Odor.....	Nauseatingly sweet.....	Stinging menthol-like
Boiling point.....	88.5°.....	132-134°
Density.....	0.7408.....	0.8225
Mol. wt. (calc. 114).....	110, 119.....	105, 108, 104
Mol. vol.....	154.....	138.7
N_D^{23}	1.3890.....	1.4360
Synthesis.....	Oxidation of	Condensation of
	$(CH_3)_2CH-N \begin{array}{ c } \hline H \\ \hline \end{array} -N \begin{array}{ c } \hline H \\ \hline \end{array} -CH(CH_3)_2$	$(CH_3)_2C=O + H_2N-NH-CH(CH_3)_2$
Behavior towards:		
Water.....	Insol.....	Sol., hydrolysis
Dil. acid.....	Insol.....	Hydrolysis
Dil. alkali.....	Insol.....	Solution
Conc. alkali and heat.....	Partial change to hydrazone.....	No effect noted
Reducing agents (catalytic)	Easily reduced to symmetrical hydrazine	Same
Reducing agents (sodium and alcohol)	Easily reduced to sym. hydrazine	Partially reduced to sym. hydrazine
Oxidizing agents	No effect in case of ordinary weak agents	Decomposition with red coloration

Should the method of preparing aliphatic hydrazones with zinc chloride as a catalyst prove to be of general application, as seems probable, it would obviously furnish the intermediates for preparing mixed hydrazo-paraffins, no representatives of which are known. These could be made through condensation of primary hydrazines with the desired carbonyl compounds, and the hydrazones thus obtained would undoubtedly yield the desired hydrazo compound.

In the course of further work with symmetrical di-*isopropyl*-hydrazine, it was obtained in a high state of purity by performing all possible steps

in the final isolation of the free base in an inert atmosphere. Drying by means of aluminum amalgam as reported in the preliminary article, is the most reliable method so far recorded for dehydration of hygroscopic bases of this type. Metallic sodium may be used as a rapid dehydrating agent, but it is difficult to remove the dried base from the sodium hydroxide formed, without considerable loss in attempting to filter it or to distil it directly without separation of the hydrazine and the sodium hydroxide. Either method gives results far superior to those obtained with barium oxide which has been employed almost exclusively in dehydrating hygroscopic hydrazine bases. If the distillation and collection of the hydrazo base are conducted in an inert gas, it is obtained almost pure, containing less than 2% of its azo oxidation product. To volatilize this small amount of the azobispropane, dry nitrogen is bubbled through the mixture until the index of refraction stays constant over a 15-minute interval. Titration by iodine or hydrochloric acid then shows that the base has a purity of about 99.5%. Owing to the difficulty of performing the titrations without having the base come in contact with the air, the results are probably slightly low.

For some unexplained reason it is often the case that the oxalate of a hydrazine does not give analytical results that correspond to a definite compound,⁹ despite the fact that hydrazines almost invariably form beautifully crystallizing salts with oxalic acid. In the case of the oxalate of symmetrical di-*isopropyl*-hydrazine, it was only after 6 recrystallizations from alcohol that the product showed a constant melting point and gave satisfactory results on analysis.

Experimental Part

Symmetrical Di-*isopropyl*-hydrazine.—Refractive-index determinations on subsequent lots of the symmetrical hydrazine led to doubt as to the purity of the product described in the preliminary article. The base is prepared as described in the first paper, but the isolation and final distillation should be done in an inert atmosphere. Even a small amount of air changes the purity noticeably. Careful distillation of the base that has been dried for as much as 5 days over aluminum amalgam yields a product that has a purity higher than 98% as indicated by iodine or acid titration. In case even higher purity is desired, as in the preparation of samples on which physical constants are to be determined, the last trace of impurity (azo derivative) may be removed by using, as a receiver, a small absorption apparatus of the type described by Noyes.¹⁰ After the distillation has been completed, the stream of dry nitrogen is permitted to continue to bubble through the liquid until the index of refraction remains constant between readings taken at 15-minute intervals. The vaporization of the azo derivative in this manner involves the loss of a small amount of the symmetrical hydrazine, but the loss is not as great as, and the purity is greater than that obtained by any other method tried. A series of iodine titrations showed a purity of this compound of over 99.5%, a result which was confirmed by a series of titrations with hydrochloric acid.

⁹ Harries, *Ber.*, **27**, 2279 (1894).

¹⁰ Noyes, *THIS JOURNAL*, **43**, 1779 (1921).

With the base thus carefully purified, a redetermination of the following physical constants of symmetrical di-isopropyl-hydrazine reported in the first paper gave the following results: boiling point at 750 mm., 124.5°; d_4^{27} , 0.7844, instead of d_4^{31} , 0.7712; n_D^{24} 1.4125 instead of n_D^{23} , 1.4087.

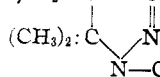
Oxalate of Symmetrical Di-isopropyl-hydrazine.—This salt, prepared in absolute ether solution by addition of 1.2 mols. of anhydrous oxalic acid to 2 mols of the base is one of the most beautiful of the compounds prepared. After 6 recrystallizations from alcohol and drying in a vacuum for 2 hours at 100° in a Storch tube,¹¹ the salt melts at 200°.

Analysis. Calc. for $C_{14}H_{34}O_4N_4$: N, 17.39. Found: 17.51.

Semicarbazide Derivative.—The mass obtained on adding 1 mol. of fresh potassium cyanate to 1 mol. of the hydrochloride of symmetrical di-isopropyl-hydrazine, soon solidifies as it is stirred. After recrystallization, in turn, from alcohol, from a mixture of ether and petroleum ether, and from ethyl acetate, the product melts sharply at 100°.

Analyses. Calc. for $C_7H_{17}ON_3$: N, 26.41. Found: 26.26, 26.18.

1-Benzoyl-3-methyl-5-dimethyl-pyrazoline, $H_2=C-CH_3$



$(CH_3)_2$ — $N-COC_6H_5$.—In the course of a series of attempts to reduce dimethyl-ketazine by means of ordinary reducing agents, after the properties of the symmetrical di-isopropyl-hydrazine had been determined through preparation of the hydrazine by catalytic reduction of the ketazine, benzoyl chloride was employed in attempts to isolate possible reduction products of dimethyl-ketazine. The crystalline product obtained immediately on adding benzoyl chloride to the reduction mixture in any of the cases studied proved to be Hoffman and Frey's benzoyltrimethyl-pyrazoline¹² obtained by benzylation of trimethyl-pyrazoline, formed by rearrangement of ketazine in the presence of acid. The same product is produced when benzoyl chloride is added directly to a solution of ketazine and affords a valuable test for this compound.

Analysis. Calc. for $C_8H_{16}ON_2$: N, 12.96. Found: 12.92.

2,2'-Azobispropane, $(CH_3)_2CH-N=N-CH(CH_3)_2$.—When the dry hydrochloride of symmetrical di-isopropyl-hydrazine is mixed with a 30% excess of dry powdered copper oxide in a stoppered flask, a peculiar sweetish odor is noticeable in about 15 minutes, small globules of moisture appear on the crystals within an hour, after about 12 hours the contents of the flask are distinctly moist, and after 3 to 4 days the mixture is so fluid that it may be poured from the reaction flask as a thick paste. A peculiar phenomenon in connection with this reaction is the formation of large cubical ruby-red crystals on the walls of the flask a day or two after the oxidation begins. If, after the reaction mixture has stood for a week, the contents of the flask are heated slowly in a water-bath, it is observed that at 88.5° the red crystals suddenly change to white cuprous chloride, while, at the same time, 2,2'-azobispropane begins to distil as a colored oil. The colored fraction is followed, at 92–100°, by a fraction of water which collects in the receiver as a lower layer.

Twenty g. of the hydrochloride yields 21 cc. of crude, or 19 cc. of pure product. The calculated yield is 20 cc. After drying overnight with calcium chloride, the oil distils as a faintly straw-colored liquid, boiling at 88.5° at 750 mm. pressure. The odor of the compound is nauseatingly sweet and very characteristic. Oxidation of the hydrochloride and detection of the odor of the azo compound constitutes a very sensitive test for symmetrical di-isopropyl-hydrazine.

¹¹ Storch, *Chem. Zentr.*, 1893, I, 915.

¹² Hoffman and Frey, *Monatsh.*, 22, 760 (1901).

The pure oxidation product is neutral to litmus, insoluble in dil. acids or alkali, but miscible with all common organic solvents. No derivatives could be obtained with aqueous hydrocyanic acid, cyanic acid, or bromine.

Examination for absorption bands in the visible part of the spectrum did not show any absorption except a very small amount at the extreme violet end of the visible spectrum. No attempt was made to examine the compound in ultra-violet light, although the work of Hantsch and Lifschütz¹³ indicates that we may expect absorption in this region.

The index of refraction for sodium light at 23° is 1.3890. Since a number of samples gave the same result, it is obvious that the azo derivative may readily be prepared in a high state of purity. The density, $d_4^{23} = 0.7408$, was determined by a Sprengel type pycnometer.

Although the oxidation product is obtained in best yield by the method described, it may be prepared by means of a variety of oxidation reactions. A convenient method of preparing the azo derivative consists in treating the hydrochloride in a weak solution of sodium hydroxide, with a small excess of copper acetate. On distillation, this mixture gives a yield of 50 to 60% of 2,2'-azobispropane.

No method of obtaining the peculiar ruby-red compound referred to in the preceding paragraph in a form pure enough for analysis has been discovered, although cuprous chloride is left as a residue after heating it above 88.5°.

Analyses. Calc. for $C_6H_{14}N_2$: C, 63.15; H, 12.28; N, 24.56. Found: C, 63.18, 63.88, 63.02; H, 12.03, 12.45, 12.46; N, 24.67.

Reduction of 2,2'-Azobispropane.—Two cc. of azo derivative in a small reduction apparatus absorbs the calculated amount of hydrogen in less than an hour under the influence of colloidal platinum as catalyst. Reduction with sodium amalgam or with sodium and alcohol yields the same product, the symmetrical di-*isopropyl*-hydrazine.

Hydrolysis of 2,2'-Azobispropane.—The azo derivative does not change to an appreciable extent when it is boiled for 4 hours with a 4% solution of hydrochloric acid. When it is heated for 4 hours with a 10% acid so that the condensate refluxes, a considerable decrease in the volume of the supernatant layer of azo compound is produced and 1 hour of similar treatment with a 50:50 mixture (18%) of hydrochloric acid readily effects hydrolysis of the azo compound to *isopropyl*-hydrazine and acetone. As is to be expected, the odor of the hydrazone that is assumed as an intermediate product in this hydrolysis cannot be detected on neutralization of the mixture after partial hydrolysis, since the hydrazone instantly hydrolyzes in an acid solution.

To identify the products of hydrolysis, a 5cc. sample of the azo derivative was hydrolyzed by means of a 10% hydrochloric acid solution and the acetone obtained identified by forming from it dibenzal-acetone melting at 111°, and by means of the sodium nitroprusside color reaction, and by means of the iodoform test. On concentration of the acid solution in a vacuum to a thick sirup, the hydrochloride of *isopropyl*-hydrazine crystallizes and can be identified by means of its dibenzoyl and phenyl-thiosemicarbazide derivatives described elsewhere in this paper.

Conversion of 2,2'-Azobispropane to Acetone-*isopropyl*-hydrazone, $(CH_3)_2CH-NH-N=C(CH_3)_2$.—When the azo compound is allowed to stand for 1 week or longer in contact with solid alkali, or when it is heated with solid potassium or sodium hydroxide for 3 hours in a closed tube at 180°, it is partially transformed to the hydrazone. The yield, however, is small, even on heating it for 3 hours at 180°. The hydrazone formed was identified by means of its boiling point (120–130° for the small amount obtained), the changed index of refraction, and by its characteristic pungent odor.

***Isopropyl*-hydrazine, $(CH_3)_2CH-NH-NH_2$.**—This new hydrazine may be pre-

¹³ Hantsch and Lifschütz, *Ber.*, **45**, 3016 (1912).

pared by 4 different methods: (1) hydrolysis of the azo derivative, (2) hydrolysis of acetone-*isopropyl*-hydrazone, (3) direct reduction of a mixture of equimolecular amounts of acetone, hydrazine hydrate and hydrochloric acid, and (4) hydrolysis of *isopropyl*-semicarbazide, described by Neighbors and Bailey.⁶ The essential part of the first method has been described. The second method is similar to the first except that hydrolysis of the hydrazone proceeds even in neutral aqueous solution.

The third method is the most practical one for the preparation of primary *iso*-*propyl*-hydrazine. Equimolecular amounts of hydrazine hydrate, acetone and hydrochloric acid are mixed and diluted to a total volume of about 300 cc. (when 1 mol. of hydrazine hydrate is used). Chloroplatinic acid, gum arabic, and "seeding colloid" are added in the same proportion and amount as in case of the preparation of symmetrical di-*isopropyl*-hydrazine. The catalytic reduction is carried out in exactly the same manner as in the case of the symmetrical hydrazine.

Purification of Acetone.—In the course of the work with catalytic reduction, it was found that acetone as drawn from stock is rarely pure enough to be used. The most satisfactory method of purification for work of this nature is the method of Shipsey and Werner.¹¹ Acetone and sodium iodide are heated under a reflux condenser for an hour or more, giving a very concentrated solution which, when cooled to -10° or lower, yields a precipitate of large reddish crystals which are rapidly drained on a large Büchner funnel. No filter paper is used in the funnel, as the crystals are so large that there is no danger of loss. The crystals are decomposed on a water-bath and pure acetone distills. The residual iodide is ready for use in purifying another lot of acetone. In case the sodium iodide becomes sirupy and unfit for use, it is recovered by drying and gradually igniting it until the organic matter is destroyed or carbonized.

After the theoretical amount of hydrogen has been absorbed in the preparation of primary hydrazine, the apparatus is disconnected and the colloid, if not already flaky, precipitated by means of acetone or by a mixture of alcohol, ethyl acetate, and ether. The concentration in a vacuum is carried out in the same manner for all three methods of preparing primary *isopropyl*-hydrazine. Instead of evaporating all of the water, as in the case of preparation of the symmetrical hydrazine, the concentration is carried only to the point where a thick sirup results. Since the hydrochloride of the primary hydrazine melts at 114° , the steam-bath is hot enough to keep the crude product melted. As the sirup cools, it turns to a solid mass of crystals which are then purified by recrystallization from a very small amount of alcohol. The salt is extremely soluble in water or alcohol, and slightly soluble in the other common organic solvents, except ether or petroleum ether, in which it is insoluble.

The *iso*-*propyl*-hydrazine hydrochloride formed on hydrolysis of the azo derivative is very hygroscopic, while the hydrochloride obtained by the other two methods is only slightly hygroscopic. Probably the hygroscopic salt is the acid salt, while the other one, which melts at 114° and is easily purified, is the neutral salt. The latter was analyzed.

Analysis. Calc. $C_3H_{10}N_2.HCl$: N, 25.34. Found: 25.39.

The free base is liberated by means of very conc. alkali solution and dried with potassium hydroxide, and finally with aluminum amalgam as in the case of the symmetrical hydrazine. The base is very easily decomposed. Even when freshly distilled and kept under nitrogen it constantly gives off tiny bubbles of gas.

Kischner¹⁵ reports the same behavior for the corresponding heptyl and octyl hydrazines. No satisfactory analyses were obtained for the free primary hydrazine, and its physical constants were not determined, as the evolution of the gas would have

¹¹ Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1898).

¹⁵ Kischner, *J. prakt. Chem.*, [2] **64**, 125 (1901).

made such work useless. In other respects the primary hydrazine is similar to the symmetrical secondary one. It is a very powerful reducing agent, reducing Fehling's solution, silver nitrate, and even potassium chromate in the cold. The boiling point of the base is 106–107° at 750 mm. The base is only slightly soluble in ether, but is miscible with alcohol, water, ethyl acetate or benzene; yield, 80–90%.

Dibenzoyl-isopropyl-hydrazine.—In benzoylating this hydrazine, the dibenzoyl derivative is always formed even though only 1 mol. of benzoyl chloride is used. It is purified by crystallization from hot alcohol to which water is added until the first permanent cloudiness appears. Thus recrystallized, the small colorless needles melt at 161.5° and are soluble in all common solvents except water, ether, and petroleum ether.

Analyses. Calc. for $C_{17}H_{18}O_2N_2$: N, 9.93. Found: 9.85, 10.09

Phenyl-thiosemicarbazide of Isopropyl-hydrazine, $(CH_3)_2CH-NH-NHCSNH-C_6H_5$.—A few seconds after a mol. of phenyl mustard oil is added to an ether solution of one mol. of isopropyl-hydrazine, this derivative is precipitated as fine silky needles. When these are dissolved in hot alcohol and water is added, as in the case of the dibenzoyl derivative, the product is obtained pure. It melts at 141.5° and is very soluble in hot alcohol, acetone, chloroform or ethyl acetate, and insoluble in water, ether or petroleum ether.

Analyses. Calc. for $C_{10}H_{16}N_3S$: N, 20.09. Found: 19.86, 20.23.

Acetone-isopropyl-hydrazone, $(CH_3)_2CH-NH-N=C(CH_3)_2$.—When a few drops of acetone are added to 1 cc. of primary isopropyl-hydrazine, no reaction is noticed, but a slight menthol-like odor may be detected. The same phenomenon is noted when acetone and the primary hydrazine are mixed under other conditions, but in all cases the yield is too small to permit isolation of the hydrazone unless, as we shall see later, the reagents are thoroughly dried. Satisfactory yields were first obtained by using anhydrous zinc chloride as a dehydrating agent according to the method used by Reddelien⁹ in the preparation of Schiff's bases. When one mol of base is mixed with 1.5 mols. of pure acetone, the stinging menthol-like odor is always evident, and when a small piece of zinc chloride is added a violent reaction takes place, instantly followed by precipitation of a white zinc salt. To prevent volatilization of the acetone, the mixture is cooled until the reaction moderates. The mixture is then distilled without separation of the liquid from the gelatinous zinc salts. The distillate is diluted with several volumes of dry ether and dried over anhydrous sodium sulfate for 15 to 20 hours.

On fractionation of the dry mixture, the ether and acetone pass over below 65° and the remainder of the mixture distills between 132° and 134° at 750 mm. The residue in the flask is a deep red liquid that contains zinc salts and probably oxidation products of the hydrazone.

A study of the hydrazone showed that it is extremely easily hydrolyzed even by water. With this fact as a guide, another attempt was made to prepare the hydrazone without the use of zinc chloride. Two cc. of carefully dried primary hydrazine was treated with 5 cc. of pure acetone and 10 cc. of absolute alcohol. The odor of the hydrazone became very strong almost immediately, although no noticeable heat was evolved. From this mixture a distillate of more than 2.5 cc. was obtained which boiled between 130° and 134°. Inasmuch as the primary hydrazine is never quite pure (as explained previously) and since a product boiling over a range of 4° is obviously not quite pure the exact yield cannot be calculated from the above results, but it is evident that this is undoubtedly the best method of preparing acetone-isopropyl-hydrazone.

The product obtained by either of the methods, after refractionation, is a colorless mobile liquid of a stinging, menthol-like odor. All attempts to obtain derivatives failed,

since the product isolated in each case was the corresponding derivative of primary isopropyl-hydrazine; $d_4^{26.6}$, 0.8225; n_D^{22} , 1.4360.

Analyses. Calc. for $C_6H_{14}N_2$: C, 63.15; H, 12.28; N, 24.56. Found: C, 62.69, 63.00; H, 12.47, 12.55; N, 24.98, 24.34. Mol. wt. (by lowering of f. p. of benzene). Calc.: 114. Found: 105, 108, 104.

Reduction of Acetone-isopropyl-hydrazone.—Catalytic reduction of the hydrazone by the same method and with the same small apparatus used for the azo derivative yielded the same product, symmetrical di-isopropyl-hydrazine. While reduction by this method is readily effected, the hydrazone, in contrast to the azo derivative, appears to be much more difficultly reduced by means of sodium and alcohol. Whether this behavior may be considered as generally true remains to be determined through further study of this and other azo and hydrazone compounds. From a study of the data now available it appears that this may perhaps be a means of distinguishing between azo and hydrazone derivatives of symmetrical secondary hydrazines.

Oxidation of Acetone-isopropyl-hydrazone.—Strong oxidizing agents decompose the compound entirely with the liberation of the total amount of nitrogen, while weak oxidizing agents, including air, produce only a partial decomposition with simultaneous formation of a deep red color.

Mononitroso Derivative of Symmetrical Di-isopropyl-hydrazine, $(CH_3)_2CH-NH-N(NO)-CH(CH_3)_2$.—Two methods were developed for preparing the mononitroso-hydrazine from symmetrical di-isopropyl-hydrazine. While the yield by the first method is somewhat better, the product obtained by the second is purer.

A concentrated aqueous solution of the hydrochloride of symmetrical di-isopropyl-hydrazine is treated with 1.5 mols. of sodium nitrite, also in concentrated aqueous solution. The mixture is then thoroughly cooled while it is agitated vigorously by a mechanical stirrer; and a small amount of alcohol added. One mol. of glacial acetic acid is next added, drop by drop, from a dropping funnel in the course of an hour. After separating the supernatant layer of yellow oil the aqueous layer is extracted once with ether, the ether extract and the separated oil are mixed, and the acetic acid is neutralized by means of a concentrated solution of sodium carbonate. The nitroso derivative, in the meantime, gives off a steady stream of gas. Cooling slows down this gradual decomposition while, if the solution is allowed to heat up to 40° , the decomposition becomes violent with the sudden decomposition of the whole yield of nitroso compound. To prevent this accident, the ether solution is treated overnight in an ice box, with anhydrous sodium sulfate. The decomposition and gas evolution cease in the course of 5 to 6 hours and the mixture may be distilled in a vacuum, preferably after standing over sodium sulfate for 2 or 3 days. When the ether has all been removed, the distillation is continued at 6 to 8 mm. pressure. Almost all of the residual liquid distills at $65-66^\circ$ under a pressure of 6 to 8 mm. as a yellow oil of peculiar odor.

In the second method of preparing the nitroso derivative, a paste of sodium nitrite, water, and the hydrochloride of the base is made of such a consistency that it can readily be poured. This mixture of equimolecular amounts of the nitrite and hydrochloride is then heated in a water-bath kept at 60° to 70° . If the temperature goes above 70° the reaction is liable to proceed too rapidly and cause discoloration of the product. At the end of an hour, the flask is removed from the bath and the paste thoroughly extracted with ether, after pouring off the layer of yellow oil that forms during the reaction. The mixture of oil and ether extract is then treated as in the case of the first method except that obviously the neutralization is not necessary. The yield by the first method reaches 70%, but that by the second is seldom over 65%. In view of the greater purity of the product the second method is to be preferred to the first in most cases.

The pure nitroso derivative has a deep straw color, a peculiar sweetish odor, and is unstable at room temperature. Attempts to distil the pure product at atmospheric

pressure show that the liquid decomposes rapidly at 160–162°, the apparent boiling point. The product is fairly soluble in water, slightly soluble in benzene and in petroleum ether, and readily soluble in alcohol, ethyl acetate or ether. The derivative gives the Liebermann reaction in the cold. When a drop of ferric chloride is added to an aqueous solution of a few drops of the nitroso compound a blue-violet color is produced; in case of an alcoholic solution the color is green, while in chloroform or benzene solution a red color is produced. In all of these cases the color is not permanent; d_4^{22} , 0.9440; n_D^{23} , 1.4420.

Analyses. Calc. for $C_6H_{15}ON_3$: C, 49.65; H, 10.35; N, 28.96. Found: C, 49.65, 49.39; H, 10.43, 10.22; N, 28.66, 28.20.

Sodium Salt of the Nitroso Derivative.—When the nitroso derivative is treated with a very concentrated solution of sodium hydroxide in alcohol, or with sodium ethoxide, the whole mass turns to a close meshwork of very fine needles in the course of 10 to 24 hours. The mass of needles is collected with the aid of suction, washed with dry ether, and dried for 2 to 3 hours in a warm vacuum desiccator before it is analyzed for sodium. Since the salt could not be purified by recrystallization, different lots were not of uniform purity. The sodium was determined as the sulfate.

Analyses. Calc. for $C_6H_{14}ON_3Na$: Na, 13.77; N, 25.15. Found: Na, 13.99, 14.54; N, 25.17.

All attempts failed to reduce the nitroso group to an amine either by common reducing agents or by catalytic reduction, since the product obtained invariably consisted of ammonia, symmetrical hydrazine, and unchanged nitroso derivative together with small amounts of unidentified products. The results seem to indicate that the reduction of the nitroso group is so difficult that when this step is once taken the reduction proceeds only with cleavage from the rest of the molecule, thus producing ammonia and the original hydrazo compound.

Conductivity Determinations.—Conductivity determinations according to the method of Bredig¹⁶ were made on the symmetrical hydrazine, and were attempted with the primary hydrazine. The latter showed that, even in a 1:1 solution, it is appreciably hydrolyzed, as indicated by the rapid drop in the resistance of the cell. At a dilution of 0.0156 *N* the hydrolysis is practically complete.

In the case of symmetrical di-*isopropyl*-hydrazine the results were more satisfactory. Through the use of the value Λ_γ for the hydrochloride as calculated according to Bredig, the value for $100 \frac{\gamma}{(1-\gamma)v}$ of the base is found to be 0.00020, while the corresponding value for hydrazine itself, according to Bredig, is 0.00027, that for ammonia is 0.0023 and that for *isopropyl*-amine 0.053. In view of the fact that the hydrochloride is appreciably hydrolyzed even at a dilution of 0.0039 *N*, and since, in spite of the use of dry nitrogen for stirring and as an inert gas above the solution, the base probably was not quite free from azo derivative, no claim of great accuracy is made for the results. They do show unmistakably, however, that the symmetrical hydrazine has very nearly the same strength as a base that hydrazine has.

Summary

1. Symmetrical di-*isopropyl*-hydrazine has been carefully purified and its physical constants redetermined. Extension of the method used in its preparation will probably make readily available a large number of symmetrical secondary hydrazines.

2. 2,2'-Azobispropane has been prepared and its structure definitely

¹⁶ Bredig, *Z. physik. Chem.*, **13**, 308 (1894).

established. The method employed may probably be employed in the preparation of other azoparaffins.

3. Acetone-*isopropyl*-hydrazone, the first aliphatic hydrazone of this type (containing only simple hydrocarbon radicals) has been prepared and its properties determined. The preparation of both isomers constitutes the first case in which both the azo and the hydrazone derivatives of a symmetrical di-alkyl hydrazine have been isolated. In case our method of preparing aliphatic hydrazones is of general application, a convenient method of making the hitherto unknown mixed hydrazo and azo paraffins is opened up.

4. The mononitroso derivative of symmetrical di-*isopropyl*-hydrazine has been isolated and a sodium salt prepared—as far as we know, the first salt obtained from a nitroso derivative of a symmetrical secondary hydrazine.

5. *Isopropyl*-hydrazine, heretofore unknown, has been prepared by (a) hydrolysis of 2,2'-azobispropane with strong mineral acids; (b) hydrolysis of acetone-*isopropyl*-hydrazone with weak acids; (c) catalytic reduction of a mixture of equimolecular amounts of hydrazine hydrate, acetone and hydrochloric acid. The latter very simple method of preparing mono-alkyl hydrazines should prove of preparative value in hydrazine chemistry.

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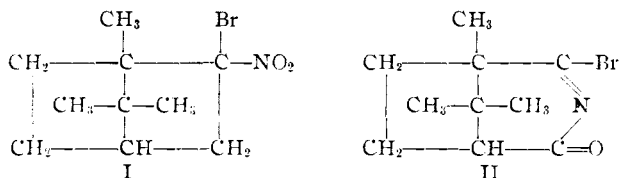
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

INVESTIGATION OF BROMONITROCAMPANE¹

By P. M. GINNINGS WITH W. A. NOYES

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About 20 years ago Forster² discovered that when potassium hypobromite is allowed to act on camphoroxime, a bromonitro compound is obtained which he named bromonitrocampane and to which he assigned the structure I.



He and his collaborators established fairly conclusively the main points

¹ Abstract of a thesis submitted by P. M. Ginnings in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Forster, *J. Chem. Soc.*, **71**, 199 (1897); **71**, 1030 (1897); **75**, 1141 (1899); **77**, 251 (1900); **79**, 108 (1901); **79**, 264 (1901); **79**, 644 (1901); Ref. 4; **79**, 987 (1901); **79**, 1003 (1901); **81**, 865 (1902); **83**, 78 (1903); *Proc.*, **28**, 313 (1912).