

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## A STUDY OF THE ACTION OF DIAZONIUM SALTS, NITROUS ACID AND HYPOCHLOROUS ACID ON CERTAIN O-ALKYLHYDROXYLAMINES<sup>1</sup>

BY ALBERT B. BOESE, JR., LAUDER W. JONES AND RANDOLPH T. MAJOR

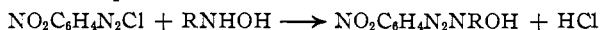
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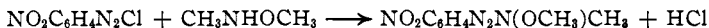
### Introduction

In connection with the work that has been done in this laboratory on O-substituted alkylhydroxylamines, it was thought desirable to determine the behavior of O-alkylhydroxylamines and especially of O,N-dialkylhydroxylamines toward the diazonium salts, nitrous acid and hypochlorous acid, since primarily the secondary amines, compounds analogous in structure, react in very characteristic and interesting ways with these reagents.

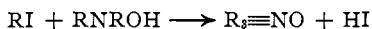
**Action of Diazonium Salts on O-Alkylhydroxylamines.**—The action of diazonium salts on N-alkylsubstituted hydroxylamines has been studied by Bamberger,<sup>2</sup> who obtained compounds of the type,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{NROH}$ , according to the equation



By the action of methyl iodide on *p*-nitrophenylazohydroxymethylamine a compound was formed to which he gave the structure  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_3)\text{CH}_3$ . It seemed probable that the same compound could also be prepared from *p*-nitrophenyldiazonium chloride and O,N-dimethylhydroxylamine.



The reaction between *p*-nitrophenyldiazonium chloride and O,N-dimethylhydroxylamine gave a stable yellow crystalline compound but it was not identical with the compound made by Bamberger. It is known, however, that N,N-disubstituted hydroxylamines, when they are treated with an alkyl iodide, give amine oxides.<sup>3</sup>



It seems possible then that the compound described by Bamberger does not have the structure  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_3)\text{CH}_3$ , but rather that of an amine oxide,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{NO}(\text{CH}_3)_2$ . An attempt was made to prepare this compound by the action of *p*-nitrophenyldiazonium chloride on N,N-dimethylhydroxylamine, which might react in the amine oxide form in acid solution. However, considerable decomposition took place with the formation of tars which could not be identified.

In addition to *p*-nitrophenylazomethoxymethylamine, the following

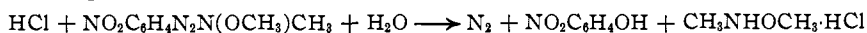
<sup>1</sup> Presented at the Atlanta meeting of the American Chemical Society, April, 1930.

<sup>2</sup> Bamberger, *Ber.*, 30, 2285 (1897).

<sup>3</sup> Dunstan and Goulding, *J. Chem. Soc.*, 75, 1004 (1899).

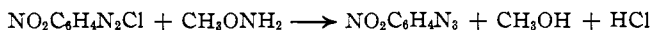
compounds have been prepared in a similar manner: *p*-nitrophenylazobenzoyloxybenzylamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OC}_7\text{H}_7)\text{C}_7\text{H}_7$ , *p*-nitrophenylazothoxyethylamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OC}_2\text{H}_5)\text{C}_2\text{H}_5$  and *p*-nitrophenylazomethoxyisopropylamine,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_3)\text{C}_3\text{H}_7$ .

*p*-Nitrophenylazomethoxymethylamine was hydrolyzed in concentrated hydrochloric acid. It gave O,N-dimethylhydroxylammonium chloride, *p*-nitrophenol and nitrogen.

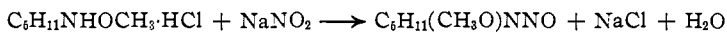


When it was hydrolyzed in the same manner, *p*-nitrophenylazomethoxyisopropylamine gave O-methyl-N-isopropylhydroxylammonium chloride, *p*-nitrophenol and nitrogen.

The reaction between *p*-nitrophenyldiazonium chloride and O-mono-substituted hydroxylamines has been studied only in the case of O-benzylhydroxylamine. It was found by Bamberger that the expected *p*-nitrophenylazobenzoyloxyamine was not formed, but that the products of the reaction were benzyl alcohol and *p*-nitrophenylazide.<sup>2</sup> It was thought desirable to study the reaction between *p*-nitrophenyldiazonium chloride and an O-alkylhydroxylamine. *p*-Nitrophenyldiazonium chloride and O-methylhydroxylamine were found to react in an entirely analogous manner. Methyl alcohol and *p*-nitrophenylazide were identified as the products of the reaction



**Action of Nitrous Acid on O-Alkylhydroxylamines.**—The action of nitrous acid on O,N-disubstituted hydroxylamines has apparently been studied in only one case. Behrend and Lindner prepared O,N-dibenzylnitrosohydroxylamine by the action of nitrous acid on O,N-dibenzylhydroxylamine.<sup>4</sup> O-methyl-N-amylnitrosohydroxylamine was prepared in a similar manner by adding a solution of the calculated amount of sodium nitrite to a solution of O-methyl-N-amyl-3-hydroxylammonium chloride



O,N-diethylnitrosohydroxylamine,  $\text{C}_2\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{NNO}$ , and O,N-dimethylnitrosohydroxylamine,  $\text{CH}_3(\text{CH}_3\text{O})\text{NNO}$ , were prepared in the same manner.

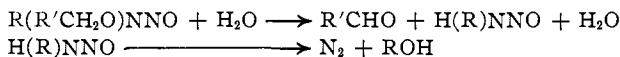
When it was hydrolyzed in concentrated hydrochloric acid, O-methyl-N-amyl-3-nitrosohydroxylamine gave nitrogen, diethylcarbinol and formaldehyde



When it was hydrolyzed under the same conditions, O,N-diethylnitrosohydroxylamine gave ethyl alcohol, acetaldehyde and nitrogen. O,N-dimethylnitrosohydroxylamine gave methyl alcohol, formaldehyde and nitrogen. It appears that the mechanism of the hydrolysis consists in

<sup>4</sup> Behrend and Lindner, *Ann.*, 275, 136 (1893).

the splitting off of the alkoxy group to form the aldehyde, leaving an intermediate primary nitroso amine which decomposes giving the alcohol and nitrogen

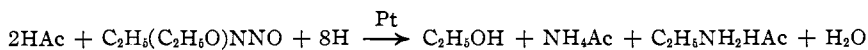


In order to identify diethylcarbinol, its 3,5-dinitrobenzoate was made. The properties of this ester were identical with those of the ester made by the action of 3-5-dinitrobenzoyl chloride on the alcohol formed during the hydrolysis of O-methyl-N-amy1-3-nitrosohydroxylamine.

**Reduction of O,N-Dialkylnitrosohydroxylamines.**—It is well known that the reduction of dialkylnitrosoamines gives unsymmetrical hydrazines.<sup>5</sup> It was thought possible that O,N-dialkylnitrosohydroxylamines might be reduced to compounds of the type R(RO)NNH<sub>2</sub>

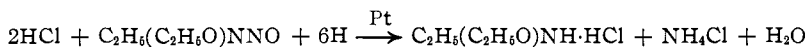


The reduction was carried out by agitating the solution to be reduced, with a platinum catalyst, at room temperature in an Adams reduction apparatus.<sup>6</sup> The attempt was first made to reduce O,N-diethylnitrosohydroxylamine catalytically with platinum black in alcohol as a solvent. Very little hydrogen was absorbed before the reduction stopped completely. However, traces of ammonia and O,N-diethylhydroxylamine were found to have been formed. Possibly the reaction products acted as a poison to the catalyst. In order to remove the free amines as they were formed, the reduction was carried out in glacial acetic acid. In this medium four moles of hydrogen were absorbed and O,N-diethylnitrosohydroxylamine was reduced to ammonium acetate, ethyl alcohol and ethylammonium acetate



Similarly O,N-dimethylnitrosohydroxylamine was reduced to methyl alcohol, methylammonium acetate and ammonium acetate; O-methyl-N-amy1-3-nitrosohydroxylamine was reduced to methyl alcohol, amy1-3-ammonium acetate and ammonium acetate.

O,N-Diethylnitrosohydroxylamine was also reduced in a solution of two equivalents of anhydrous hydrogen chloride in absolute alcohol. In this medium three moles of hydrogen were absorbed and the products of the reduction were O,N-diethylhydroxylammonium chloride and ammonium chloride.

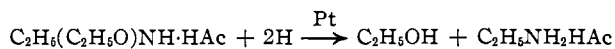


When O,N-diethylhydroxylamine was catalytically reduced in glacial

<sup>5</sup> Renouf, *Ber.*, 13, 2171 (1880).

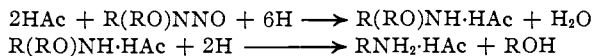
<sup>6</sup> Adams and Voorhees, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 11.

acetic acid, one mole of hydrogen was absorbed. The products of the reduction were ethyl alcohol and ethyl ammonium acetate.

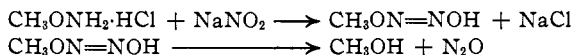


However, in a solution of anhydrous hydrogen chloride in absolute alcohol no reduction took place.

From these results it appears that the reduction in glacial acetic acid proceeded in two steps: first the nitroso group was reduced and split off to form ammonia, leaving the substituted hydroxylamine, which was then reduced to an amine and alcohol according to the equations

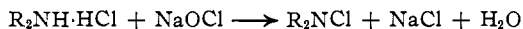


The action of nitrous acid on *O*-substituted hydroxylamines has until the present apparently not been studied. It has now been found that nitrous acid reacts with *O*-methylhydroxylamine to give nitrous oxide and methyl alcohol. Assuming the intermediate formation of a mono-methyl ester of hyponitrous acid, which decomposes completely into nitrous oxide and methyl alcohol, the mechanism of the reaction is probably as follows

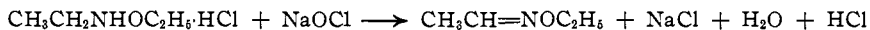


In support of this mechanism might be cited the well-known reaction between hydroxylamine itself and nitrous acid, in which the first product formed is the unstable hyponitrous acid which decomposes to give water and nitrous oxide.<sup>7</sup>

**Action of Hypochlorous Acid on *O*-Alkylhydroxylamines.**—The chloroamines have been investigated by Berg,<sup>8</sup> who obtained dialkyl chloroamines by the action of sodium hypochlorite on the hydrochlorides of the secondary alkyl amines.



By a similar reaction it was thought that it might be possible to prepare chloro derivatives of the *O,N*-dialkylhydroxylamines of the type  $\text{R}(\text{RO})\text{NCl}$ . However, when a solution of sodium hypochlorite was added to a solution of *O,N*-diethylhydroxylammonium chloride, no chloroamine was obtained. Instead *O*-ethyl-acetaldoxime was identified as a product of the reaction

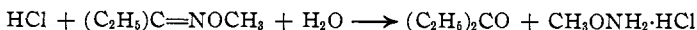


In a like manner the action of sodium hypochlorite on *O*-methyl-*N*-amyl-3-hydroxylammonium chloride gave *O*-methyl-diethylketoxime,  $(\text{C}_2\text{H}_5)_2\text{C}=\text{NOCH}_3$ . In order to identify *O*-methyl-diethylketoxime, pure *O*-

<sup>7</sup> Wislicenus, *Ber.*, 26, 772 (1893).

<sup>8</sup> Berg, *Ann. chim.*, (7) 3, 320 (1894).

methyl-diethylketoxime was hydrolyzed in dilute hydrochloric acid. The products were diethyl ketone and O-methylhydroxylammonium chloride



When O-methyl-diethylketoxime, obtained by the action of sodium hypochlorite on O-methyl-N-amyl-3-hydroxylamine, was hydrolyzed in a similar manner, the products were also diethyl ketone and O-methylhydroxylammonium chloride.

In order to identify the diethyl ketone, the *p*-nitrophenylhydrazone of pure diethyl ketone was made. It was found that the properties of this compound were the same as those of the compound made by the action of *p*-nitrophenylhydrazine on the ketone formed during the hydrolysis of O-methyl-diethylketoxime, which in turn had been made by the action of sodium hypochlorite on O-methyl-N-amyl-3-hydroxylammonium chloride.

### Experimental Part

**Preparation of *p*-Nitrophenylazoalkoxyalkylamines.**—To a cold solution containing one-tenth mole of *p*-nitrophenyldiazonium chloride and 50 g. of sodium acetate in 100 cc. of water was added with stirring one-tenth mole of O,N-dialkylhydroxylamine.<sup>9</sup> The precipitate which soon formed was collected on a filter, washed with cold water and recrystallized from 50% alcohol.

TABLE I  
ANALYTICAL AND OTHER DATA

<i>p</i> -Nitrophenylazoalkoxyalkylamine	M. p., °C.	Yield, %	Nitrogen, %	
			Calcd.	Found
$\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_3)\text{CH}_3$	66	60	26.66	26.72
$\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OC}_2\text{H}_5)\text{C}_2\text{H}_5$	38	40	23.53	23.52
$\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_3)\text{C}_3\text{H}_7$	67	75	23.53	23.60
$\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OC}_7\text{H}_{15})\text{C}_7\text{H}_{17}$	100	50	15.47	15.62

**Hydrolysis of *p*-Nitrophenylazoalkoxyalkylamines.**—*p*-Nitrophenylazomethoxymethylamine and *p*-nitrophenylazomethoxyisopropylamine were hydrolyzed in an apparatus which consisted of a small flask with a three-holed rubber stopper through which passed a dropping funnel, an entrance tube leading from a carbon dioxide generator and an outlet tube leading to an azotometer. A weighed quantity of *p*-nitrophenylazoalkoxyalkylamine was placed in the flask. After the air in the flask had been swept out with carbon dioxide, the azotometer was filled and concentrated hydrochloric acid was added through the dropping funnel. The hydrolysis started immediately. The flask was kept at a temperature of about 70° until no more nitrogen was evolved.

When the reaction mixture was cooled, a white crystalline solid of m. p. 113–114° separated. The compound was identified as *p*-nitrophenol. A mixture of this compound and pure *p*-nitrophenol melted at 113°. <sup>10</sup> *p*-Nitrophenol was formed during the hydrolysis of both *p*-nitrophenylazomethoxymethylamine and *p*-nitrophenylazomethoxyisopropylamine. After the *p*-nitrophenol had been separated, the filtrates

<sup>9</sup> Major and Fleck, THIS JOURNAL, 50, 2024 (1928); Jones and Major, *ibid.*, 52, 675 (1930).

<sup>10</sup> "International Critical Tables," Vol. I, p. 199, McGraw-Hill Book Co., New York, gives 113° as the melting point of *p*-nitrophenol.

were slowly evaporated to dryness on a water-bath. In both cases a white crystalline solid remained. The residue remaining from the solution in which *p*-nitrophenylazomethoxymethylamine had been hydrolyzed was dissolved in absolute alcohol and to this solution was added absolute ether. A white crystalline substance, m. p. 115–116°, precipitated which was identified as *O*-methylhydroxylammonium chloride. A mixture of this substance and pure *O*-methylhydroxylammonium chloride also melted at 115–116°. <sup>11</sup> The residue which remained from the solution in which *p*-nitrophenylazomethoxyisopropylamine had been hydrolyzed was covered with a layer of dry benzene and to this was added powdered potassium hydroxide. The benzene layer was removed, dried and to it were added a few drops of phenyl isocyanate. When the benzene was evaporated there remained a white solid, m. p. 73°. When the compound was mixed with pure  $\alpha$ -phenyl- $\beta$ -methoxy- $\beta$ -isopropylurea, the melting point remained unchanged. <sup>12</sup>

TABLE II  
ANALYTICAL DATA

<i>p</i> -Nitrophenylazo-alkoxyalkylamine	Used, g.	Nitrogen evolved during hydrolysis	
		Calcd., cc.	Amount found, corrected to N. T. P., cc.
$\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_3)\text{CH}_3$	0.2416	25.75	25.91
$\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{OCH}_2)\text{C}_3\text{H}_7$	0.3128	28.71	28.50

Action of *p*-Nitrophenyldiazonium Chloride on *O*-Methylhydroxylamine.—To a cold solution of one-tenth mole of *p*-nitrophenyldiazonium chloride and 25 g. of sodium acetate in 150 cc. of water was slowly added with stirring a solution of one-tenth mole of *O*-methylhydroxylammonium chloride in 20 cc. of water. A yellow precipitate formed. This was separated, washed with cold water and recrystallized from 95% alcohol. It occurred as brown yellow needles, m. p. 71°. The compound was *p*-nitrophenylazide. <sup>13</sup>

*Anal.* Calcd. for  $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ : N, 34.14. Found: N, 33.96.

A portion of the filtrate was distilled. Methyl alcohol was detected in the distillate by the test described in the "Deutsches Arzneibuch." <sup>14</sup>

Preparation of *O,N*-Dialkylnitrosohydroxylamines.—To a cold solution of one-tenth mole of *O,N*-dialkylhydroxylammonium chloride in 50 cc. of water was added slowly a solution of one-tenth mole of sodium nitrite in 30 cc. of water. The reaction mixture was extracted with ether. The ether solution was dried over anhydrous sodium sulfate, the ether distilled off and the remaining yellow oil distilled under re-

TABLE III  
ANALYTICAL AND OTHER DATA

<i>O,N</i> -Dialkylnitroso- hydroxylamine	B. p., °C.	Yield, %	Nitrogen, %	
			Calcd.	Found
$\text{CH}_3(\text{CH}_3\text{O})\text{NNO}$	59–60 at 30 mm.	50	31.11	31.01
$\text{C}_2\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{NNO}$	56–57 at 15 mm.	80	23.73	23.86
$\text{C}_6\text{H}_{11}(\text{CH}_3\text{O})\text{NNO}$	83–84 at 15 mm.	75	19.18	19.04

<sup>11</sup> Jones, *Am. Chem. J.*, 20, 43 (1909), gives 115–116° as the melting point of *O,N*-dimethylhydroxylammonium chloride.

<sup>12</sup> Jones and Major, *THIS JOURNAL*, 52, 679 (1930), give 73° as the melting point of  $\alpha$ -phenyl- $\beta$ -methoxy- $\beta$ -isopropylurea.

<sup>13</sup> Bamberger, *Ber.*, 30, 2291 (1897), gives 71° as the melting point of *p*-nitrophenylazide.

<sup>14</sup> "Deutsches Arzneibuch," Deckers Verlag, Berlin, 1926, p. liv.

duced pressure. The O,N-dialkylnitrosohydroxylamines that were obtained were stable yellow oils. When they were heated above 200° they decomposed with explosive violence. They gave the characteristic Liebermann nitroso reaction.

**Hydrolysis of O,N-Dialkylnitrosohydroxylamines.**—The hydrolysis was carried out in the apparatus previously described. A known weight of O,N-dialkylnitrosohydroxylamine contained in a very thin walled glass bulb was placed in the flask and the air swept out by a stream of carbon dioxide. When all the air had been displaced, 25 cc. of concentrated hydrochloric acid was added through the separatory funnel. By shaking the flask, the bulb containing the compound to be hydrolyzed was broken. The compound was hydrolyzed rapidly when the flask was gently heated. Carbon dioxide was passed through the system until no more nitrogen was evolved. The hydrolysis was also carried out in the same manner in an apparatus which only differed from that described in that between the outlet tube and the azotometer was placed a hot tube containing copper oxide and a reduced copper spiral to remove any hydrocarbons or oxides of nitrogen which might have been present. Since the results were the same in both cases, the possibility that any other gases than nitrogen were formed during the hydrolysis was eliminated.

TABLE IV  
ANALYTICAL DATA

O,N-Dialkylnitrosohydroxylamine	Percentage nitrogen evolved during hydrolysis		
	Calcd.	Found	Found when gas was passed over hot Cu and CuO
CH <sub>3</sub> (CH <sub>3</sub> O)NNO	31.11	31.01	31.28
C <sub>2</sub> H <sub>5</sub> (C <sub>2</sub> H <sub>5</sub> )NNO	23.73	23.45	23.60
C <sub>6</sub> H <sub>11</sub> (CH <sub>3</sub> O)NNO	19.18	19.29	19.11

**Preparation of the Ester of Diethylcarbinol and 3,5-Dinitrobenzoic Acid.**—To 15 g. of 3,5-dinitrobenzoyl chloride was added 5 g. of diethylcarbinol. The mixture was heated in a closed tube for twenty minutes at 75–85°. The contents of the tube were cooled, filtered and washed with cold 60% methyl alcohol. The product was recrystallized from 60% methyl alcohol as colorless needles, m. p. 97°; yield, 60%.

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>6</sub>N<sub>2</sub>: N, 9.93. Found: N, 10.28.

**Investigation of the Products Other Than Nitrogen Obtained When the O,N-Dialkylnitrosohydroxylamines Were Hydrolyzed.**—About one gram of O,N-dialkylnitrosohydroxylamine was hydrolyzed in concentrated hydrochloric acid in a small flask with a reflux condenser. At the top of the condenser was placed a delivery tube leading into a solution of *p*-nitrophenylhydrazine hydrochloride. The *p*-nitrophenylhydrazone of the aldehyde formed during the hydrolysis precipitated. This was filtered and recrystallized from 95% alcohol. Formaldehyde was formed when O,N-dimethylnitrosohydroxylamine and O-methyl-N-amyl-3-nitrosohydroxylamine were hydrolyzed. Its *p*-nitrophenylhydrazone was made in the manner described and melted at 181°. When it was mixed with pure formaldehyde-*p*-nitrophenylhydrazone the melting point remained unchanged.<sup>15</sup> When the hydrolysis was complete, a small part of the solution in which O,N-dimethylnitrosohydroxylamine had been hydrolyzed was distilled. Methyl alcohol was detected in the distillate by the formation of methyl 3,5-dinitrobenzoate made according to the method of Mulliken.<sup>16</sup> It melted at 112°. When

<sup>15</sup> Bamberger, *Ber.*, 32, 1807 (1899), gives 181° as the melting point of formaldehyde-*p*-nitrophenylhydrazone.

<sup>16</sup> Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 168.

this compound was mixed with pure methyl 3,5-dinitrobenzoate the melting point remained unchanged.<sup>17</sup> In a similar manner ethyl alcohol was identified as a product of the hydrolysis of O,N-diethylnitrosohydroxylamine. Its 3,5-dinitrobenzoate melted at 91°. The melting point remained unchanged when this compound was mixed with pure ethyl 3,5-dinitrobenzoate.<sup>18</sup> The solution in which O-methyl-N-amylyl-3-nitrosohydroxylamine had been hydrolyzed was made alkaline with potassium hydroxide and a portion of it distilled. Diethylcarbinol was identified in the distillate by means of its 3,5-dinitrobenzoate, m. p. 97°. No depression of the melting point was observed when this compound was mixed with the ester made from diethylcarbinol and 3,5-dinitrobenzoyl chloride.

**Action of Nitrous Acid on O-Methylhydroxylamine.**—To 0.2 mole of O-methylhydroxylammonium chloride in 50 cc. of water contained in a 200-cc. flask fitted with a delivery tube and a dropping funnel was added 0.2 mole of sodium nitrite in 50 cc. of water. Reaction took place and a gas was evolved. After the air in the flask had been displaced by the gas, it was collected over water. The gas was shown to be nitrous oxide and was distinguished from oxygen by the fact that although it supported combustion vigorously, no brown fumes of nitrogen dioxide were formed when nitric oxide was mixed with it, as would have been the case if oxygen had been present. A portion of the reaction mixture was distilled. Methyl alcohol was detected in the distillate according to the test in the "Deutsches Arzneibuch."<sup>14</sup>

**Determination of Nitrous Oxide Evolved.**—A known weight of O-methylhydroxylammonium chloride was placed in a flask fitted with a dropping funnel and a tube leading to the top of a graduated buret containing mercury and connected with a leveling bulb. Through the dropping funnel was added an equivalent quantity of a solution of sodium nitrite. The volume of the gas was measured by the change in the mercury level after correcting for the volume of sodium nitrite solution added.

In order to make sure that no other gases such as hydrocarbons were formed during the reaction, the nitrous oxide was measured as nitrogen. It was reduced to nitrogen by passing the gas through a hot tube containing copper oxide and a reduced copper spiral, and then collected in an azotometer.

TABLE V  
ANALYTICAL DATA

	Used, g.	Calcd., cc.	Found, cc.
Gas measured as nitrous oxide	0.0808	21.7	21.9
Gas measured as nitrogen	0.0894	23.8	23.5

**Catalytic Reduction of O,N-Dialkylnitrosohydroxylamines.**—A small quantity (0.2 mole) of O,N-dialkylnitrosohydroxylamine was dissolved in 20 cc. of glacial acetic acid and was catalytically reduced by shaking it with hydrogen under a pressure of 1-3 atmospheres, in an Adams reduction apparatus, in the presence of about 0.2 g. of a platinum catalyst. The catalyst was made according to the method of Adams and Shriner.<sup>19</sup> When necessary, in order to complete the reduction, more of the same catalyst was added to the solution which was being reduced. After the required amount of hydrogen had been absorbed, the catalyst was removed by filtration. The equivalent of four moles of hydrogen was absorbed.

<sup>17</sup> Hesse, *Ber.*, **28**, 596 (1895), gives 112° as the melting point of methyl 3,5-dinitrobenzoate.

<sup>18</sup> Kurbatow, *Ann.*, **202**, 223 (1880), gives 91° as the melting point of ethyl 3,5-dinitrobenzoate.

<sup>19</sup> Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923).



TABLE VI  
 REDUCTION DATA

O,N-Dialkylnitrosohydroxylamine	Catalyst, g.	Time of reduction, hours
$\text{CH}_3(\text{CH}_2\text{O})\text{NNO}$	0.4	6
$\text{C}_2\text{H}_5(\text{C}_2\text{H}_5\text{O})\text{NNO}$	0.3	8
$\text{C}_3\text{H}_7(\text{CH}_3\text{O})\text{NNO}$	0.5	7

Investigation of the Products Formed by the Reduction of O,N-Dialkylnitrosohydroxylamines in Glacial Acetic Acid.—After the reduction had been completed, the catalyst was removed and a small portion of the filtrate distilled. The distillates from the solutions in which O,N-dimethylnitrosohydroxylamine and O-methyl-N-amyl-3-hydroxylamine had been reduced were found to contain methyl alcohol, which was identified in the manner previously described. The distillate from the solution in which O,N-diethylnitrosohydroxylamine had been reduced was found to contain ethyl alcohol, which was also identified in the previously described manner. The remaining acetic acid solutions were made alkaline with potassium hydroxide and the liberated amines were distilled into cold dilute hydrochloric acid. The acid solutions were evaporated to dryness on a water-bath. The residues were treated with absolute alcohol, in which a portion was soluble. The insoluble portion was in each case shown to be ammonium chloride. When benzoyl chloride was added to an aqueous solution of it, to which alkali had been added, a white solid separated, m. p.  $128^\circ$ , which did not lower the melting point of benzamide when the two were mixed.<sup>20</sup> Absolute ether was added to the alcoholic solutions from which the ammonium chloride had been separated. A white compound precipitated. The compound obtained by the reduction of O,N-diethylnitrosohydroxylamine was identified as ethylammonium chloride. When it was treated with alkali and the liberated amine distilled into a solution of diethyl oxalate, a white compound separated, m. p.  $179^\circ$ , which did not change the melting point of diethyl oxamide when mixed with it.<sup>21</sup> The analogous compound obtained by the reduction of O,N-dimethylnitrosohydroxylamine was identified as methylammonium chloride. When it was treated with alkali and the liberated amine distilled into a solution of ethyl oxalate, a white compound separated, m. p.  $216^\circ$ , which did not change the melting point of dimethyl oxamide when mixed with it.<sup>22</sup> The analogous compound that resulted when O-methyl-N-amyl-3-nitrosohydroxylamine was reduced was identified as diethyl carbinammonium chloride, m. p.  $216^\circ$ .<sup>23</sup>

*Anal.* Calcd. for  $\text{C}_6\text{H}_{13}\text{N}\cdot\text{HCl}$ : Cl, 28.72. Found: Cl, 28.85.

Reduction of O,N-Dialkylnitrosohydroxylamines in a Solution of Anhydrous Hydrogen Chloride in Alcohol.—A solution of 0.02 mole of O,N-dialkylnitrosohydroxylamine in 30 cc. of absolute alcohol containing 0.04 mole of anhydrous hydrogen chloride was reduced in the previously described manner, using about 0.4 g. of a platinum catalyst which was prepared by reducing with hydrogen a platinum oxide catalyst which had been made according to the method of Adams and Shriner. It was usually necessary, in order to complete the reduction, to add more of the same catalyst to the solution

<sup>20</sup> Schiff and Tassinari, *Ber.*, 10, 1785 (1877), give  $128^\circ$  as the melting point of benzamide.

<sup>21</sup> Schiff, *ibid.*, 17, 1034 (1884), gives  $179^\circ$  as the melting point of diethyl oxamide.

<sup>22</sup> Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. II, p. 131, gives  $216^\circ$  as the melting point of dimethyloxamide.

<sup>23</sup> Noyes, *Am. Chem. J.*, 15, 540 (1904), gives  $216\text{--}217^\circ$  as the melting point of diethyl carbinammonium chloride.

which was being reduced. *O,N*-Dimethylnitrosohydroxylamine required twelve hours and *O,N*-diethylnitrosohydroxylamine required ten hours to absorb the equivalent of three moles of hydrogen.

**Investigation of the Products Obtained by the Reduction of *O,N*-Dialkylnitrosohydroxylamines in a Solution of Anhydrous Hydrogen Chloride in Alcohol.**—After the reduction was complete, the catalyst was removed and the alcoholic solutions evaporated to dryness on a water-bath. The solution in which *O,N*-dimethylnitrosohydroxylamine had been reduced left a white residue. It consisted of two substances, one of which was insoluble in absolute alcohol. This insoluble portion was identified as ammonium chloride in the manner previously described. The portion soluble in alcohol was precipitated by the addition of absolute ether. The compound was identified as *O,N*-dimethylhydroxylammonium chloride, m. p. 115°. A mixture of this compound and pure *O,N*-dimethylhydroxylammonium chloride also melted at 115°.<sup>24</sup> On evaporation of the solution in which *O,N*-diethylnitrosohydroxylamine had been reduced, there remained a residue which consisted partly of a solid and partly of an oil. A little of the solid was separated and identified as ammonium chloride. The oil was separated from the solid, dissolved in absolute alcohol and reprecipitated by the addition of absolute ether. It was removed from the mixture and dried in a vacuum desiccator containing sulfuric acid and solid potassium hydroxide. To the oil was added a layer of dry benzene and then solid potassium hydroxide. The mixture was stirred and the benzene layer removed and dried. To it were added a few drops of phenyl isocyanate. When the benzene was evaporated, there remained a white solid which after recrystallization from benzene melted at 63° and did not change the melting point of  $\alpha$ -phenyl- $\beta,\beta$ -ethylethoxyurea when mixed with it.<sup>25</sup>

**Reduction of *O,N*-Diethylhydroxylamine in Glacial Acetic Acid.**—A solution of 0.02 mole of *O,N*-diethylhydroxylamine in 30 cc. of glacial acetic acid was catalytically reduced in the previously described manner. About 0.2 g. of platinum catalyst was used. The catalyst was removed and the products of the reduction were identified as ethyl alcohol and ethylamine by the methods already described.

**Action of Hypochlorous Acid on *O,N*-Diethylhydroxylamine.**—To a cold solution of one-tenth mole of *O,N*-diethylhydroxylammonium chloride in 20 cc. of water was added slowly with stirring, cooling after each addition, 50 cc. of a solution of sodium hypochlorite prepared by passing chlorine into a cold solution of 20% sodium hydroxide until the solution turned yellow. A light yellow oil separated. The oil was washed first with water, then with dilute hydrochloric acid, dried over anhydrous sodium sulfate and distilled. The greater part of the oil distilled at 71° was colorless and had the odor of *O*-ethylacetaldoxime. When the oil was hydrolyzed in 10% hydrochloric acid, the products were ammonium chloride and acetaldehyde, which were identified by the methods previously described.<sup>26</sup>

*Anal.* Calcd. for  $C_4H_9NO$ : N, 16.09. Found: N, 15.93.

**Preparation of Diethyl Ketone *p*-Nitrophenylhydrazone.**—To 0.05 mole of diethyl ketone and 50 cc. of water was slowly added with stirring 0.05 mole of *p*-nitrophenylhydrazine hydrochloride in 30 cc. of water. The solution was diluted to 200 cc. with

<sup>24</sup> Jones, *Am. Chem. J.*, 20, 43 (1909), gives 115–116° as the melting point of *O,N*-dimethylhydroxylammonium chloride.

<sup>25</sup> Jones and Major, *THIS JOURNAL*, 49, 1539 (1927), give 63° as the melting point of  $\alpha$ -phenyl- $\beta,\beta$ -ethylethoxyurea.

<sup>26</sup> Dunstan and Goulding, *J. Chem. Soc.*, 79, 631 (1901), give 71.5° as the boiling point of *O*-ethylacetaldoxime and show that when the compound is hydrolyzed in hydrochloric acid, the products are acetaldehyde and ammonium chloride.

water. A yellow flocculent precipitate formed. This was separated, washed with water and recrystallized from 50% alcohol. It occurred as orange-yellow needles, m. p. 144°; yield, 90%.

*Anal.* Calcd. for  $C_{11}H_{14}O_2N_2$ : N, 19.09. Found: N, 19.03.

**Hydrolysis of O-Methyldiethylketoxime.**—One gram of O-methyldiethylketoxime prepared by the method of Jones and Major,<sup>27</sup> and 15 cc. of 10% hydrochloric acid were heated for two hours on a water-bath in a small flask with a reflux condenser. After the hydrolysis was complete, the acid solution had a strong odor of diethyl ketone. The diethyl ketone was identified by making a portion of the solution alkaline and distilling it into a solution of *p*-nitrophenylhydrazine hydrochloride. The *p*-nitrophenylhydrazone made in this way melted at 144° and did not change the melting point of diethyl ketone *p*-nitrophenylhydrazone when mixed with it. The remainder of the solution was evaporated to dryness on a water-bath. A white crystalline substance remained. This was dissolved in absolute alcohol and reprecipitated by the addition of absolute ether. It melted at 150° and when mixed with pure O-methylhydroxylammonium chloride, the melting point remained unchanged.<sup>28</sup>

**Action of Hypochlorous Acid on O-Methyl-N-amyl-3-hydroxylamine.**—To a cold solution of one-tenth mole of O-methyl-N-amyl-3-hydroxylammonium chloride in 20 cc. of water was added 50 cc. of a solution of sodium hypochlorite prepared in the manner already described. A yellow oil separated. The oil was washed with very dilute hydrochloric acid, dried over anhydrous sodium sulfate and distilled. A large portion of the oil distilled at 116°. When the oil was hydrolyzed in 10% hydrochloric acid, the products were O-methylhydroxylammonium chloride and diethyl ketone, which were identified in the previously described manner.<sup>29</sup>

### Summary

1. Several *p*-nitrophenylazoalkoxyalkylamines have been prepared by the action of *p*-nitrophenyldiazonium chloride on O,N-dialkylhydroxylamines; *p*-nitrophenol and O,N-dialkylhydroxylamine were formed when these compounds were hydrolyzed.

2. The reaction between *p*-nitrophenyldiazonium chloride and O-methylhydroxylamine was found to give *p*-nitrophenylazide and methyl alcohol.

3. Several O,N-dialkylnitrosohydroxylamines have been prepared by the action of nitrous acid on O,N-dialkylhydroxylamines. Nitrogen an aldehyde and an alcohol were formed when O,N-dialkylnitrosohydroxylamines were hydrolyzed in hydrochloric acid. The mechanism of the hydrolysis has been discussed.

4. The O,N-dialkylnitrosohydroxylamines have been catalytically reduced in glacial acetic acid and in an alcoholic solution of anhydrous hydrogen chloride. In the first medium the products were ammonium acetate and an alcohol. In the second medium the reduction products were ammonium chloride and O,N-dialkylhydroxylammonium chloride. The course of the reductions has been discussed.

<sup>27</sup> Jones and Major, *THIS JOURNAL*, **52**, 675 (1930).

<sup>28</sup> Lossen, *Ber.*, **16**, 827 (1883), gives 150° as the melting point of O-methylhydroxylammonium chloride.

<sup>29</sup> Jones and Major<sup>27</sup> give 116–117° as the boiling point of O-methyldiethylketoxime.

5. Nitrous acid and O-methylhydroxylamine were found to react to give nitrous oxide and methyl alcohol. The mechanism of the reaction has been discussed.

6. The action of hypochlorous acid on O,N-dialkylhydroxylamines has been found to give either an O-alkyl-ald- or ketoxime depending on the structure of the substituted hydroxylamine.

7. Diethyl ketone *p*-nitrophenylhydrazone and the ester of diethyl-carbinol with 3,5-dinitrobenzoic acid have been prepared in order to identify the products of hydrolysis of O-methyldiethylketoxime and O-methyl-N-amyl-3-nitrosohydroxylamine, respectively.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## ALLYLIC REARRANGEMENT IN THE REACTION BETWEEN CINNAMYL CHLORIDE AND MAGNESIUM

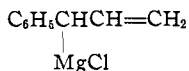
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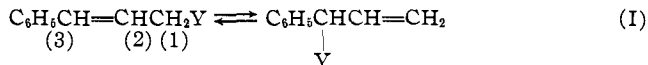
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### Introduction

If ozone is a reliable reagent for the determination of the constitution of unsaturated compounds, then there is no doubt concerning the structure of cinnamyl bromide and chloride,  $C_6H_5CH=CHCH_2Cl$ .<sup>1</sup> In its reaction with magnesium and ether, cinnamyl chloride might be expected to give cinnamylmagnesium chloride,  $C_6H_5CH=CHCH_2MgCl$ . However, the products obtained from the so-called cinnamylmagnesium chloride appear to be derived from an  $RMgCl$  compound having the formula



This transformation is another illustration of the following general interchange



modifications of which have been variously designated as an allylic rearrangement, three-carbon anionotropic system, mobile anion tautomerism, "synionie," etc.<sup>2</sup> The mechanism or mechanisms proposed for the rearrangement of systems like that indicated in Reaction I are various, and at present there is no general agreement. Actually, the transforma-

<sup>1</sup> Burton and Ingold, *J. Chem. Soc.*, 904 (1928). See also, Verley, *Bull. soc. chim.*, 43, 854 (1928), and Doevre, *ibid.*, 45, 140 (1929).

<sup>2</sup> Some recent references are Hurd and Cohen, *THIS JOURNAL*, 53, 1917 (1931); Prévost, *Bull. soc. chim.*, 49, 261 (1931); Prévost and Daujat, *ibid.*, 47, 588 (1930); Kirmann, *ibid.*, 47, 834 (1930); Meisenheimer and Link, *Ann.*, 479, 211 (1930); Burton, *J. Chem. Soc.*, 455 (1929); Burton and Ingold, *ibid.*, 904 (1928).