Mono-biphenylarsenious sulfide was prepared by the action of hydrogen sulfide on a dilute alcohol solution of the oxide. Ball-like aggregates of microscopic needles separated out. No definite melting point was observed, the substance softening above 108°.

Anal. Calcd. for $C_{12}H_9AsS$: S, 12.3. Found: S, 12.0.

Mono-biphenylarsenic Acid.—To a gram of the arsenious oxide derivative suspended in water containing a little ethyl alcohol was conducted a slow stream of chlorine for an hour. Then an excess of dilute sodium hydroxide solution was added and the mixture saturated with carbon dioxide. It was filtered and hydrochloric acid added. The resulting bulky precipitate was filtered with difficulty by suction and precipitated from alcohol by water.

Anal. Calcd. for $C_{12}H_{11}O_3As$: As, 27.0. Found: As, 27.2.

The new acid separates from alcohol as an amorphous powder partially melting at 180–181° with preliminary softening.

It is planned to continue work with these substances, also to investigate the diphenyl derivatives of antimony and bismuth.

Summary

It has been found that tri-biphenylarsine is obtainable in good yield from the interaction of arsenic chloride, 4-bromodiphenyl and sodium.

Using tri-biphenylarsine as a starting point, some representative tri- and pentavalent arsenic derivatives have been prepared containing one, two and three biphenyl groups.

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[Contribution from the Chemical Laboratory of Princeton University]

CATALYTIC REDUCTION OF O-ALKYL SUBSTITUTED OXIMES[1]

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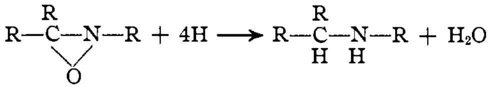
The reduction of N-alkyl substituted oximes was studied about thirty years ago by Dunstan and Goulding,[2] who found that sodium amalgam in absolute alcohol converted them into dialkylamines, according to the equation



$$\mathrm{R{-}\underbrace{\overset{R}{C}{-}N}_{O}{-}R + 4H \longrightarrow R{-}\overset{R}{C}{-}N{-}R + H_2O}$$
$$\mathrm{\qquad\qquad\qquad\qquad H\ \ H}$$

The corresponding reduction of the O-alkyl substituted oximes apparently has not been investigated.

It has long been known, however, that oximes could be reduced to primary amines by the use of a number of different reducing agents.[3] Re-

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[1] Presented at the Columbus meeting of the American Chemical Society, May, 1929.

[2] Dunstan and Goulding, *J. Chem. Soc.*, **79**, 639, 640 (1901).

[3] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Verlag von Veit and Company, Leipzig, **1907**, Vol. I, Part 1, p. 349.

cently Vavon and his co-workers[4] have shown that hydrogen in the presence of a platinum catalyst reduced the hydrochlorides of oximes in dilute alcohol to N-substituted hydroxylamine hydrochlorides.

It was thought, therefore, that by using somewhat similar methods it might be possible to reduce O-alkyl oxime hydrochlorides to O,N-dialkylhydroxylamine hydrochlorides according to the equation

$$\text{R—CR=NOR·HCl} + \text{H}_2 \xrightarrow{\text{Pt}} \text{RHCR—NHOR·HCl}$$

Solutions of the O-alkyl oxime hydrochlorides were prepared in two ways. The first was to dissolve the O-alkyl oxime in a solution of the calculated amount of hydrogen chloride in 65% alcohol. The other method was to add the calculated amount of the carbonyl derivative to a solution of O-alkylhydroxyl-ammonium chloride in 65% alcohol, and to allow the solution to stand long enough to come to equilibrium, usually about an hour. However, it was found that it did not make any difference in the reductions which way the O-alkyl oxime hydrochloride was prepared.

The reductions were carried out by agitating the solution containing the platinum catalyst at room temperature in an Adams Reduction Apparatus.[5] When the solution had absorbed the calculated amount of hydrogen the platinum was removed by filtration and the alcohol and most of the water evaporated. By means of alkali the free bases were obtained from the hydrochlorides, which remained as residues. In this way O-methyl-N-amyl-3-hydroxylamine, $(C_2H_5)_2CH{\cdot}NHOCH_3$, O-methyl-N-*iso*propylhydroxylamine, $(CH_3)_2CH{\cdot}NHOCH_3$, O-methyl-N-heptyl-4-hydroxylamine, $(C_3H_7)_2CH{\cdot}NHOCH_3$, and O-ethyl-N-*iso*propyl-hydroxylamine, $(CH_3)_2CH{\cdot}NHOC_2H_5$ were prepared.

To serve as a means of identification, several derivatives of these compounds were made. The chloroplatinates of all of these substituted hydroxylamines except O-methyl-N-heptyl-4-hydroxylamine, which did not yield a solid chloroplatinate, were prepared. In addition, the phenyl isocyanate addition products, which have the general formula $RRCH{\cdot}NOR{\cdot}CO{\cdot}NHC_6H_5$, of all of them except O-ethyl-N-*iso*propylhydroxylamine were formed. Also, the phenyl mustard oil addition product of O-methyl-N-amyl-3-hydroxylamine, which has the formula $(C_2H_5)_2CH{\cdot}NOCH_3{\cdot}CS{\cdot}NHC_6H_5$, was made.

It was found that the properties of the O-ethyl-N-*iso*propylhydroxylamine that was made in this manner were identical with those ascribed to this compound by Hecker, who made it in another way.[6] O-Methyl-N-amyl-3-hydroxylamine and O-methyl-N-*iso*propylhydroxylamine, which

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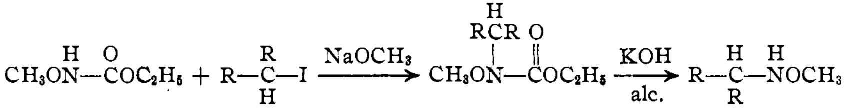
[4] Vavon and Krajcinovic, *Bull. soc. chim.*, [4] **43**, 231 (1928); this paper also contains references to earlier articles on this subject by Vavon and his co-workers.

[5] Manufactured by the Standard Calorimeter Company, East Moline, Ill.

[6] Hecker, *Am. Chem. J.*, **50**, 455 (1913).

previously had not been described, were also prepared, according to the equations



$$CH_3O\overset{H}{N}-\overset{O}{C}OC_2H_5 + R-\underset{H}{\overset{R}{C}}-I \xrightarrow{NaOCH_3} CH_3O\overset{\overset{\overset{H}{RCR}}{|}}{N}-\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow[\text{alc.}]{KOH} R-\underset{R}{\overset{H}{C}}-\overset{H}{N}OCH_3$$

O-methylhydroxyurethan alkyl iodide O-methyl-N-alkylhydroxyurethan O-methyl-N-alkylhydroxylamine

The properties of the hydroxylamines synthesized in this manner were the same as those of the corresponding compounds synthesized by reducing the O-alkyl oximes.

Another reaction always accompanied the formation of the O,N-dialkylhydroxylammonium chlorides when O-alkyl oxime hydrochlorides were reduced. Ammonium chloride, a ketone and an alcohol were always formed. This side reaction was most pronounced in the case of the reduction of methyl and ethyl acetoxime hydrochlorides, when about 75% of the oximes were transformed into these products. Also, O-methylacetaldoxime hydrochloride, when reduced in the same way, gave almost a quantitative yield of ammonium chloride. Presumably the formation of these products depends upon the fact that in the solution there is an equilibrium of the type shown in the equation

$$R—CR{=}NOR\cdot HCl + H_2O \leftrightarrows R—CR{=}O + RONH_2\cdot HCl$$

That this is probable is suggested by the fact that the usual method used to hydrolyze the O-alkyl oximes is to warm them with dilute hydrochloric acid. In this way they yield the carbonyl derivative and O-alkylhydroxylammonium chloride.[7] The reverse reaction of forming O-alkyl oxime hydrochlorides from carbonyl derivatives and O-alkylhydroxylammonium chlorides is indicated by some of the experiments described in this paper. In addition it was found that a solution of O-methylacetoxime hydrochloride in dilute alcohol gave a faint test for acetone. The formation of ammonium chloride, therefore, probably depends upon the reduction of the O-alkylhydroxylammonium chloride. This has been shown to proceed quite readily, according to the equation

$$RONH_2\cdot HCl + H_2 \xrightarrow{Pt} ROH + NH_4Cl$$

The relative amounts of ammonium chloride and O,N-dialkylhydroxylammonium chloride formed evidently might then depend in the main upon three factors: first, the percentage of the products of hydrolysis which are present at equilibrium, second, the relative ease of reduction of the O-alkylhydroxylammonium chloride and the O-alkyl oxime hydrochloride and, third, the readiness with which the system comes to equilibrium when one or more of its products are removed. The first factor mentioned must play a very unimportant role, since it was found that in

[7] Dunstan and Goulding, *J. Chem. Soc.*, 79, 631, 635 (1901).

the case of O-methylacetoxime hydrochloride the percentage of the carbonyl derivative in the solution at equilibrium was very small. It was also established that O-methylhydroxylammonium chloride was reduced more rapidly than any of the oximes investigated. However, it was found that, among themselves, the rate at which the oximes absorbed hydrogen varied considerably, being relatively rapid for O-methyl-diethylketoxime and slow for O-methylacetoxime, O-ethylacetoxime and O-methyl-dipropylketoxime. Another difference in the various oximes which must affect the relative amounts of ammonium chloride and O,N-dialkylhydroxylammonium chloride formed is the third factor previously mentioned, namely, the ease with which the equilibrium is reëstablished after it has been disturbed. The greater general chemical activity of acetaldehyde and acetone than that of the higher ketones is in harmony with this explanation of the relatively larger amounts of ammonium chloride formed in the reduction of the substituted oximes of acetaldehyde and acetone than those of diethyl ketone and dipropyl ketone.[3]

When a solution of O-methylbenzaldoxime in dilute alcohol containing one equivalent of hydrogen chloride was reduced in the same way with one mole of hydrogen, no hydroxylamine was found among the products of reduction but instead the hydrochlorides of benzyl- and dibenzylamine and considerable unchanged O-methylbenzaldoxime were identified. These results may be represented by the following set of equations

$$C_6H_5CH{=}NOCH_3 + HCl + H_2 \xrightarrow{Pt} (C_6H_5CH_2\overset{H}{N}OCH_3{\cdot}HCl) \xrightarrow{H_2} C_6H_5CH_2NH_2{\cdot}HCl + CH_3OH$$

$$C_6H_5CH{=}NOCH_3 + HCl + H_2O \leftrightarrows C_6H_5CH{=}O + CH_3ONH_2{\cdot}HCl$$

$$C_6H_5CH{=}O + C_6H_5CH_2NH_2{\cdot}HCl \leftrightarrows C_6H_5CH{=}NCH_2C_6H_5{\cdot}HCl \xrightarrow{H_2} (C_6H_5CH_2)_2NH{\cdot}HCl$$

$$CH_3ONH_2.HCl + H_2 \xrightarrow{Pt} CH_3OH + NH_4Cl$$

In support of a mechanism of the formation of benzylammonium chloride which involves the intermediate formation of O-methyl-N-benzylhydroxylammonium chloride it may be noted that Vavon suggested, in connection with the reduction of oximes, that the protection afforded by hydrochloric acid against further reduction to an amine of the first formed hydroxylamine becomes less as the basicity of the hydroxylamine becomes smaller.[4] It is very probable that O-methyl-N-benzylhydroxylamine would be a much weaker base than any of the hydroxylamines that we have previously mentioned.

In a somewhat similar manner a solution of O-ethylacetaldoxime in acetic anhydride was reduced to ethyl acetate and ethyl acetamide, according to the equation

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[3] Stewart, *J. Chem. Soc.*, **87**, 185, 410 (1905).

$$CH_3CH{=}NOC_2H_5 + 2(CH_3CO)_2O + 2H_2 \xrightarrow{Pt} CH_3CH_2NH{-}CO{-}CH_3 + CH_3COOC_2H_5 + 2CH_3COOH$$

Experimental Part

Reduction of O-Alkylald- and Ketoxime Hydrochlorides. Method I.—One-fifth of a mole of the carbonyl derivative was added to a solution which had been made by adding the calculated amount of 5 *N* hydrochloric acid to 0.2 of a mole of O-methylhydroxylamine (Eastman Kodak Company) in 150 cc. of alcohol. After this solution had been stirred and had stood for an hour, it was catalytically reduced by shaking it with hydrogen in an Adams reduction apparatus, using a pressure of 1 to 3 atmospheres of hydrogen. About 0.2 g. of a platinum catalyst was used, which was prepared by reducing with hydrogen a platinum oxide catalyst which was made according to the method of Adams and Shriner.[9] When necessary, in order to complete the reduction, more of the same catalyst was added to the solution which was being reduced. After the calculated amount of hydrogen had been absorbed, the platinum was removed by filtration and then the alcohol and nearly all of the water was evaporated on a water-bath.

Investigation of the Products Formed in the Reduction of O-Methyl, Diethyl- and Dipropyl-ketoxime Hydrochlorides.—After the residue left from evaporating the reduced solution had been cooled it was found to consist partly of an oil and partly of a solid. Absolute alcohol was added to a little of the solid portion. That part of the solid which did not dissolve was washed with more alcohol and dried. It was shown to be ammonium chloride by its behavior on being heated, by the fact that its solution in water gave a test for the chloride ion, also that with alkalies a strong odor of ammonia was released and fourth that when benzoyl choride was shaken with an aqueous solution of it to which alkali had been added, a white solid separated, m. p. 128°, which did not lower the melting point of benzamide, m. p. 128°, when the two were mixed.[10]

The rest of the residue from which the alcohol and water had been evaporated was treated with somewhat more than the calculated amount of caustic soda. An oil was extracted from the alkaline solution with ether. The ethereal solution was dried with anhydrous sodium sulfate and then fractionated.

The O-methyl-N-alkylhydroxylamines were colorless oils, which possessed a peculiar terpene-like odor. They were readily soluble in alcohol, ether and ligroin but only slightly soluble in water.

TABLE I

ANALYTICAL AND OTHER DATA

Substituted hydroxylamine	Catalyst, g.	Time of reduction, hours	B. p., °C.	Yield, %	Nitrogen, % Calcd.	Found
$(C_2H_5)_2CH{\cdot}NHOCH_3$	0.2	7	124	48	11.96	11.97
$(C_3H_7)_2CH{\cdot}NHOCH_3$	.6	44	164–166 or 88–89° at 60 mm.	38	9.64	9.68

O-Alkylacetoxime Hydrochloride.—The residue that remained when the reduced solution was evaporated was partly solid and partly an oil. A little of the solid portion was isolated and found to be ammonium chloride. It was possible to isolate in this process a yield of 70 to 80% of ammonium chloride.

In order to isolate the substituted hydroxylamine, the rest of the solid–oil residue mentioned above was made alkaline with concentrated potassium hydroxide and the

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[9] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[10] Schiff and Tassenari, *Ber.*, **10**, 1785 (1877).

free base condensed after water had been removed from it by passing the vapors through solid pieces of potassium hydroxide kept at a temperature of 97°. In order to remove dissolved ammonia air was blown for a short time through the liquid which condensed. It was then redistilled. The substituted hydroxylamines obtained were clear, colorless liquids. O-Methyl-*iso*propylhydroxylamine had a terpene-like odor, but it was not as pronounced as was that of O-methyl-N-amyl-3-hydroxylamine. However, O-ethyl-N-*iso*propylhydroxylamine had an odor more like ethylamine.

TABLE II

ANALYTICAL AND OTHER DATA

Substituted hydroxylamine	Moles of oxime reduced	Catalyst, g.	Time of reduction, hours	B. p., °C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
$(CH_3)_2CHNHOCH$	0.2	0.6	40	76	17	15.72	16.06
$(CH_3)_2CHNHOC_2H_5$	.05	.4	20	78[a]	4	...	...

[a] Hecker, *Am. Chem. J.*, **50**, 455 (1913), gives 78° as the b. p.

O-Methylacetaldoxime Hydrochloride.—The reduction of 0.2 of a mole of O-methylacetaldoxime hydrochloride in the presence of 0.2 g. of platinum catalyst required four hours. Evaporation of the reduced solution left almost pure ammonium chloride, which was identified in the manner previously described.

O-Methylbenzaldoxime in a Solution of Hydrogen Chloride in Dilute Alcohol.—The reduction of 0.1 of a mole of O-methylbenzaldoxime in 0.1 of a mole of hydrogen chloride in dilute alcohol in the presence of two successively added portions of 0.2 g. of the platinum catalyst required forty-five hours. The reduced solution was concentrated on a water-bath until precipitation started. A white solid appeared when it was cooled, which was filtered off and recrystallized from hot butanol; m. p. 263° corr.;[11] yield, 1.2 g. A test for the chloride ion with silver nitrate was positive. It was only slightly soluble in benzene and ether but more readily soluble in water and alcohol. *Anal.* Calcd. for $(C_6H_5CH_2)_2NH\,HCl$: Cl, 15.20. Found: Cl, 15.20. In order to establish the identity of this hydrochloride more completely, its base was isolated by means of alkali, this solution extracted with ether and the ether solution dried with sodium sulfate. An oil was left, when the ether was distilled, which was dissolved in alcohol. Approximately the calculated amount of phenyl isothiocyanate was then added and the solution was warmed for a few minutes. After it had been cooled a white solid was precipitated from it by the addition of petroleum ether; m. p. 145–146°. It possessed all of the properties ascribed by Dixon[12] to α-phenyl-β,β-dibenzylthiourea.

Water was added to the filtrate from which the above-mentioned hydrochloride, m. p. 263°, was removed. An oil separated which was extracted with ether; the ether solution was dried with anhydrous sodium sulfate and then fractionally distilled. After the ether had passed over, all of the oil that remained, aside from a very small amount of a very high-boiling liquid which was unidentified, distilled from 187–194°; yield 2 g. Since this liquid was insoluble in water and dilute acid and since its boiling point was about that of O-methylbenzaldoxime, which boils at 191°,[13] it seemed probable that it was this substituted oxime. In order to hydrolyze it a portion of this liquid was accordingly dissolved in concentrated hydrochloric acid. As it stood at room temperature an oil gradually separated which had the odor of benzaldehyde. After a day this

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[11] Limpricht, *Ann.*, **144**, 314 (1867), gives 256° (probably uncorrected) as the m. p. of dibenzylammonium chloride.

[12] Dixon, *J. Chem. Soc.*, **63**, 539 (1893).

[13] Traube, *Ber.*, **53**, 1486 (1920).

oil was extracted with ether. A solution of *p*-nitrophenylhydrazine hydrochloride in water was shaken for several minutes with this ether solution. Evaporation of the ether left a reddish-brown solid, which was recrystallized from alcohol; m. p. 193°.[14] The aqueous solution from which the benzaldehyde was extracted was evaporated to dryness on a water-bath. A white solid remained which was recrystallized by dissolving it in absolute alcohol and reprecipitating it with dry ether; m. p. 148°.[15] When alkali was added to this hydrochloride the characteristic odor of O-methylhydroxylamine was noted.

The aqueous solution from which the O-methylbenzaldoxime was extracted was made alkaline with caustic soda. An oil separated which was extracted with ether. After the ether solution had been dried with sodium sulfate it was fractionated. An oil which boiled at 184–185° was obtained; yield, 1 g.[16] To a solution of a small amount of this oil in benzene was added the calculated amount of phenyl isocyanate. After this solution had stood overnight a white solid was found, which was recrystallized from alcohol; m. p. 170–171°. α-Phenyl-β-benzylurea made from benzyl isocyanate and aniline according to the method of Letts[17] also melted at 170–171°. In addition, a mixture of these two solids melted at 170–171°, which indicates that the liquid which boiled at 184–185° was benzylamine.

Method II

Preparation of O-Methylketoximes, $R_2C{=}NOCH_3$.—To 0.2 of a mole of O-methylhydroxylamine was added 0.2 of a mole of the ketone. After the solution had stood for four days anhydrous calcium chloride was added to it to absorb water. The unabsorbed oil was decanted, again dried with calcium chloride and fractionated. O-Methylacetoxime boiled at 72–74°;[18] yield, 20%. O-Methyldiethylketoxime distilled at 116–117°; yield, 66%. It was readily soluble in alcohol, ether and ligroin but insoluble in water.

Anal. Calcd. for $C_6H_{13}ON$: N, 12.17. Found: N, 12.36.

Reduction of O-Methylketoxime Hydrochlorides.—The calculated amount of 4 *N* hydrochloric acid necessary to neutralize it was added to the O-methylketoxime and then sufficient alcohol was added in order to unite the two liquid layers which were at first present. The solution was reduced in the manner described previously for the reduction of the O-methyldialkylketoxime hydrochlorides prepared by the other method

Ammonia and O-methyl-N-amyl-3-hydroxylamine, b. p. 124°, with its characteristic terpene-like odor were obtained from the reduction products of O-methyldiethylketoxime hydrochloride in the same way as was described previously.

When the reduction of the O-methylacetoxime hydrochloride was complete the solution gave a distinct qualitative test for methyl alcohol with guaiacol sulfate,[19] and for acetone with sodium nitroprusside.[20] The presence of acetone was also proved

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[14] Rosenthaler, "Der Nachweis organischer Verbindungen," Verlag von Ferdinand Enke, Stuttgart, **1914**, p. 132, gives 192–193° as the m. p. of benzaldehyde-*p*-nitrophenylhydrazone.

[15] Lossen, *Ber.*, **16**, 827 (1883), gives 149° as the m. p. of O-methylhydroxylammonium chloride.

[16] According to "International Critical Tables," McGraw-Hill Book Co., New York, **1926**, Vol. I, p. 211, the b. p. of benzylamine is 184°.

[17] Letts, *Ber.*, **5**, 93 (1872).

[18] Ponzio and Charrier, *Gazz. chim. ital.*, I, **37**, 506 (1907), give 73° as the b. p.

[19] "Deutsches Arzneibuch," Decker's Verlag, Berlin, **1926**, p. LIV.

[20] Gadamer, "Lehrbuch der chemischen Toxicologie," Vanderhoeck and Ruprecht, Göttingen, **1924**, p. 308.

by the formation of its *p*-nitrophenylhydrazone when *p*-nitrophenylhydrazine hydrochloride was added to the solution which had been reduced. It melted at 149° and did not lower the melting point of acetone-*p*-nitrophenylhydrazone; m. p. 149°.[21] When the reduced solution was evaporated, a white solid and a small amount of oil were obtained. The solid portion was proved to be ammonium chloride by tests which have been mentioned previously.

α-Phenyl-β-methoxy-β-amyl-3-thiourea, $C_6H_5NHCS{\cdot}N(OCH_3){\cdot}CH(C_2H_5)_2$.—To a solution of 2.7 g. (0.02 mole) of phenyl isothiocyanate in benzene was added 2.4 g. (0.02 mole) of O-methyl-N-amyl-3-hydroxylamine, which was obtained from the reduction products of O-methyldiethylketoxime hydrochloride. After the solution thus formed had stood at room temperature for a day the benzene was evaporated. A white solid remained which was recrystallized from 50% alcohol; m. p. 57°. It was soluble in alcohol, benzene and ligroin, but insoluble in water.

Anal. Calcd. for $C_{13}H_{20}ON_2S$: N, 11.11. Found: 11.61.

Reduction of O-Methylhydroxylammonium Chloride.—The calculated amount of 4 *N* hydrochloric acid was added to 0.2 of a mole of O-methylhydroxylamine. It was reduced in one hour by hydrogen in the presence of 0.2 g. of the platinum catalyst in the usual manner. The solution which had been reduced gave a strong test for methanol with guaiacol sulfate.[19] Ammonium chloride was left as a residue when the reduced solution was evaporated to dryness. It was identified in the same way as was the ammonium chloride formed in the reduction of the O-alkylacetoxime hydrochlorides which has been previously described.

Partial Hydrolysis of O-Methylacetoxime Hydrochloride.—A solution prepared by mixing equivalent proportions of O-methylhydroxylamine, hydrochloric acid and acetone in dilute alcohol, in the same way as was that prepared for reduction, was allowed to stand for half an hour. At the end of this time it was tested for acetone with sodium nitroprusside.[20] The depth of color produced in this test was compared with the color produced in standard solutions of acetone in dilute alcohol which were treated in the same way. By such comparisons it was found that the solution being tested contained a little acetone but that the amount was less than 5% of that originally added. However, when it was heated rapidly, cooled and then retested, the percentage of acetone was considerably higher for a short time.

Reduction of O-Ethylacetaldoxime in Acetic Anhydride.—A solution of 3.4 g. of O-ethylacetaldoxime in 10 cc. of acetic anhydride was reduced with hydrogen in the usual way in the presence of 0.2 g. of platinum catalyst. Somewhat more than one molecular equivalent of hydrogen was absorbed in fifty minutes. When the reaction bottle was opened at the end of the experiment, the odor of ethyl acetate was quite pronounced. In order to hydrolyze the solution it was refluxed for an hour with a solution of 20 g. of potassium hydroxide in 40 cc. of 50% alcohol and then the volatile portion distilled into dilute hydrochloric acid. This acid solution was evaporated almost to dryness on a water-bath. A concentrated solution of potassium hydroxide was added to the residue and the free base which was released was condensed after it had been passed through solid potassium hydroxide at 97°. When it was redistilled it boiled under 25°. A white solid formed when it was shaken with ethyl oxalate; m. p. 181°. The melting point was not changed when it was mixed with diethyloxamide.[22]

O-Methyl-N-Alkylhydroxylamines from O-Methyl-N-Substituted Hydroxyurethans

Preparation of O-Alkylhydroxyurethan, $RONHCOOC_2H_5$.—O-Methyl- and O-ethyl-hydroxyurethans were prepared by a modification of the method used by Major

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[21] Bamberger and Sternitzki, *Ber.*, **26**, 1306 (1893).

[22] Schiff, *ibid.*, **17**, 1034 (1884), gives 179° as the m. p. of diethyloxamide.

and Fleck[23] to prepare O,N-dialkylhydroxyurethans and small amounts of O-alkylhydroxyurethans. In order to increase the amount of O-alkylhydroxyurethan, only 2.1 moles of dialkyl sulfate and 600 cc. of a 20% solution of potassium hydroxide were used instead of the 4.25 moles of the former and the 1200 cc. of the latter which were used by these investigators. Otherwise the preparation of the O-alkylhydroxyurethans was carried out as it is described by these authors: O-methylhydroxyurethan, yield, 29%, b. p. 186–188°; O-ethylhydroxyurethan, yield, 43%, b. p. 195–196°.

Preparation of O-Methyl-N-alkylhydroxyurethan, $CH_3ONRCOOC_2H_5$.—One molecular equivalent of sodium dissolved in absolute methanol was added to a solution of one molecular equivalent each of O-methylhydroxyurethan and of alkyl iodide. After this mixture had been well shaken and had stood at room temperature for a day a rather large white precipitate had formed. In order to complete the reaction the mixture was refluxed for five hours. At the end of this time most of the methanol was distilled off and water was added to the residue in order to dissolve the white solid. This aqueous solution was then extracted repeatedly with ether. Then, in order to remove unchanged O-methylhydroxyurethan, the ether solution was in turn extracted several times with a dilute solution of sodium hydroxide. The ether solution was dried with anhydrous sodium sulfate, the ether distilled and the oil that remained was fractionated. O-Methyl-N-*iso*propylhydroxyurethan boiled at 164–167° (at 734 mm.); yield, 49% (31 g.). O-Methyl-N-amyl-3-hydroxyurethan boiled at 196°; yield, 16% (3 g.).

Anal. Calcd. for $C_7H_{15}O_3N$: N, 8.70. Found: N, 9.22. Calcd. for $C_9H_{19}O_3N$: N, 7.41. Found: N, 8.09.

Preparation of O-Methyl-N-*iso*propylhydroxylamine, $(CH_3)_2CH{\cdot}NHOCH_3$.—A solution of 0.125 mole of O-methyl-N-*iso*propylhydroxyurethan in 50% alcohol containing 0.475 mole of potassium hydroxide was refluxed for three hours. The volatile portion was then distilled into dilute hydrochloric acid. This acid solution was evaporated to dryness on a water-bath. An oily hydrochloride was left as a residue, from which the free base was obtained by warming it with potassium hydroxide. The vapors which formed were passed through solid potassium hydroxide at a temperature of 97°. Redistillation gave a light liquid with a terpene-like odor; b. p. 75–76°; yield, 60%.

Preparation of O-Methyl-N-amyl-3-hydroxylamine, $(C_2H_5)_2CHNHOCH_3$.—A solution of 2.4 g. (0.013 mole) of O-methyl-N-amyl-3-hydroxyurethan in 50% alcohol containing 3 molecular equivalents of potassium hydroxide was refluxed for four hours. The volatile portion was then distilled into dilute hydrochloric acid. This acid solution was evaporated to dryness on a water-bath. Sufficient cold caustic soda to more than combine with all of the chloride ion was added to this residue. Then the alkaline solution was extracted with ether, the ether solution was dried with sodium sulfate and then fractionally distilled. After the ether had been distilled, an oil remained which boiled at 124° and possessed the characteristic terpene-like odor of O-methyl-N-amyl-3-hydroxylamine; yield, 32%.

Chloroplatinates of O-Alkyl-N-alkylhydroxylamines.—Somewhat more than the calculated amount of hydrogen chloride was passed into a solution of the O-alkyl-N-alkylhydroxylamine in absolute alcohol. To this solution was added the calculated amount of a concentrated solution of chloroplatinic acid in absolute alcohol. When dry ether was added an orange-colored precipitate formed. In order to purify it, it was redissolved in absolute alcohol and reprecipitated with dry ether in the form of orange-yellow colored needles.[24]

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[23] Major and Fleck, THIS JOURNAL, **50**, 1479 (1928).

[24] It was necessary to fractionally precipitate the chloroplatinate formed from the O-methyl-N-*iso*propylhydroxylamine which was obtained when O-methylacetoxime

TABLE III

CHLOROPLATINATES OF THE O-METHYL-N-ALKYLHYDROXYLAMINES WHICH WERE FORMED BY THE HYDROLYSIS OF O-METHYL-N-ALKYLHYDROXYURETHANS

Substituted hydroxylamine	M. p., °C. with dec.	Platinum, %	
		Calcd.	Found
O-Methyl-N-*iso*propyl-	183	33.19	32.93
O-Methyl-N-amyl-3-	161	30.30	30.10

TABLE IV

CHLOROPLATINATES OF THE O-ALKYL-N-ALKYLHYDROXYLAMINES WHICH WERE OBTAINED FROM THE REDUCTION PRODUCTS OF O-ALKYLKETOXIME HYDROCHLORIDES

Substituted hydroxylamine	M. p., °C. with dec.	Platinum, %	
		Calcd.	Found
O-Methyl-N-*iso*propyl-	183[a]	33.19	32.74
O-Ethyl-N-*iso*propyl-	174	31.68	31.65
O-Methyl-N-amyl-3-	161[b]	30.30	30.54

[a] A mixture of the chloroplatinates of the O-methyl-N-*iso*propylhydroxylamine which was obtained from the reduction product of O-methylacetoxime hydrochloride and of that formed in the hydrolysis of O-methyl-N-*iso*propylhydroxyurethan also melted with decomposition at 183°.

[b] A mixture of the chloroplatinate which was obtained from the reduction product of O-methyldiethylketoxime hydrochloride and that formed in the hydrolysis of O-methyl-N-amyl-3-hydroxyurethan also melted with decomposition at 161°.

α-Phenyl-β-methoxy-β-alkylureas, $C_6H_5NHCONROCH_3$.—α-Phenyl-β-methoxy-β-amyl-3-urea was prepared by letting a solution of equimolecular proportions of O-methyl-N-amyl-3-hydroxylamine and phenyl isocyanate in benzene stand for five hours. When the benzene was evaporated, an oil remained as a residue, which solidified after it had stood overnight in a vacuum desiccator. In order to purify it, it was dissolved in freshly distilled petroleum ether, extracted with dilute hydrochloric acid and then the petroleum ether was evaporated. The solid was dried in a vacuum desiccator containing sulfuric acid and solid potassium hydroxide. It was readily soluble in all ordinary organic solvents but insoluble in water.

The other α-phenyl-β-methoxy-β-alkylureas were formed when a solution of equimolecular proportions of the O-methyl-N-alkylhydroxylamine and phenyl isocyanate in petroleum ether had stood for an hour. The white solid precipitated from the petroleum ether was recrystallized from hot ligroin.

The α-phenyl-β-methoxy-β-*iso*propylurea which was made from the O-methyl-N-*iso*propylhydroxylamine that had been obtained from O-methyl-N-isopropylhydroxyurethan melted at 73°.

Anal. Calcd. for $C_{11}H_{16}O_2N_2$: N, 13.46. Found: N, 13.79.

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hydrochloride was reduced. The first portion of the precipitate which formed when ether was added to the solution of the chloroplatinate in alcohol did not melt sharply and analysis revealed that it contained a lower percentage of platinum than that calculated for O-methyl-N-*iso*propylhydroxylamine chloroplatinate. The larger fraction of the chloroplatinate which was precipitated when more ether was added to the filtrate melted sharply and as may be seen from the following table it yielded, within the experimental error the calculated percentage of platinum for the chloroplatinate of O-methyl-N-*iso*propylhydroxylamine. The fraction which first precipitated probably contained a very small amount of ammonium chloride. This was probably formed due to the presence of a small amount of dissolved ammonia in the O-methyl-N-*iso*propylhydroxylamine.

TABLE V

α-PHENYL-β-METHOXY-β-ALKYLUREAS THAT WERE FORMED FROM THE O-METHYL-N-ALKYL-HYDROXYLAMINES WHICH HAD BEEN OBTAINED FROM THE REDUCTION PRODUCT OF O-METHYLKETOXIME HYDROCHLORIDES

Alkyl group	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
*Iso*propyl-	73[a]	13.46	13.43
Amyl-3-	59	11.86	12.11
Heptyl-4-	109	10.41	10.74

[a] A mixture of the α-phenyl-β-methoxy-β-*iso*propylureas that were obtained from the O-methyl-N-*iso*propylhydroxylamine formed from the reduction product of O-methylacetoxime hydrochloride and that which was formed from O-methyl-N-*iso*propyl-hydroxyurethan also melted at 73°.

Summary

1. Several O-alkylketoxime hydrochlorides have been catalytically reduced in dilute alcohol to O-alkyl-N-alkylhydroxylamine hydrochlorides, ammonium chloride and other products. The mechanism of the formation of these compounds has been discussed.
2. The corresponding O-alkyl-N-alkylhydroxylamines have been synthesized by the hydrolysis of O-alkyl-N-alkylhydroxyurethans, which were made by the action of alkyl iodides on O-alkyl-hydroxyurethans in the presence of sodium methylate.
3. A number of derivatives of these substituted hydroxylamines have been prepared.
4. The only nitrogen-containing compound that was isolated when O-methylacetaldoxime hydrochloride was catalytically reduced was ammonium chloride, but when O-ethylacetaldoxime dissolved in acetic anhydride was reduced, ethyl acetate and ethyl acetamide were obtained.
5. When O-methylbenzaldoxime was catalytically reduced in a solution of hydrogen chloride in dilute alcohol, benzyl- and dibenzylammonium chlorides were formed. The mechanism of the formation of these compounds has been discussed.

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