following their oxidation in the Parr bomb. The gravimetric results are shown in Col. 5. Column 4 marked "Gravimetric check" presents results obtained as follows: immediately at the close of the volumetric analysis the solution was treated with 2 cc. of 1:1 hydrochloric acid and heated to boiling. Twenty-five cc. of hydrogen peroxide (3%) was added to the boiling solution. After the customary period allowed for digestion, the precipitate of barium sulfate was collected and weighed in the usual manner. Not all of the barium chromate is removed by this procedure; enough usually remains to give the precipitate an *extremely faint* yellow tint. However, the results show a fair agreement with those of the direct analysis and in some cases may prove of value as a check.

Summary

The Wildenstein volumetric method of analysis for sulfate has been modified by the use of ferrous thiocyanate as an external indicator and adapted to the analysis of organic compounds following their oxidation in the Parr bomb. Provision has been made for a gravimetric check upon the volumetric procedure.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

O-ALKYL SUBSTITUTED HYDROXYLAMINO ACIDS, ESTERS AND ALCOHOLS[1]

BY LAUDER W. JONES AND RANDOLPH T. MAJOR

RECEIVED SEPTEMBER 14, 1929 PUBLISHED MARCH 6, 1930

N-Hydroxylamino acids of the type, $HONHC_nH_{2n}COOH$, have been prepared,[2] as have also O-hydroxylamino acids of the type, $H_2NOC_nH_{2n}COOH$,[3] but no O-alkyl substituted hydroxylamino acids or esters with the general formula, $RONR'C_nH_{2n}COOR''$, in which R′ and R″ may either be alkyl groups or hydrogen, are described in the chemical literature. As a part of a general study of O-alkyl substituted hydroxylamines, it was thought that it would be of interest to synthesize a few substances of this type and to investigate their properties, especially since they would be derivatives of that very important class of chemical compounds, the amino acids.

When ethyl bromo-acetate was treated with two molecular equivalents of O,N-dimethylhydroxylamine, there was formed ethyl methylmethoxy-

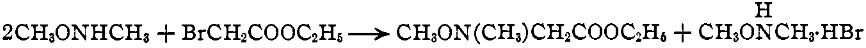
---

[1] Presented in part at the Fall Meeting of the American Chemical Society at Swampscott, Massachusetts, September, 1928.

[2] Traube, *Ber.*, **28**, 2298 (1895); Gomberg, *Ann.*, **300**, 75 (1898); Hantzsch and Wild, *ibid.*, **289**, 309 (1896).

[3] Werner, *Ber.*, **26**, 1567 (1893); Werner and Sonnenfeld, *ibid.*, **27**, 3350 (1894); Werner and Bial, *ibid.*, **28**, 1378 (1895); Werner and Falck, *ibid.*, **29**, 2658 (1896).

amino-acetate and O,N-dimethylhydroxylammonium bromide, according to the equation

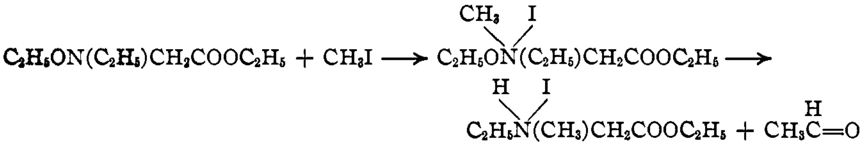


$$2CH_3ONHCH_3 + BrCH_2COOC_2H_5 \longrightarrow CH_3ON(CH_3)CH_2COOC_2H_5 + CH_3O\overset{H}{N}CH_3\cdot HBr$$

Ethyl methylmethoxyamino-acetate was a liquid which rather closely resembled in properties the amino ester to which it is most closely related, ethyl dimethylamino-acetate, $(CH_3)_2NCH_2COOC_2H_5$. That O-alkyl substituted hydroxylamines, in general, have properties often closely resembling those of the alkyl substituted amines to which they are related may readily be seen by comparing their respective properties. This similarity has been pointed out by Jones and Major in connection with a study of the physiological properties of certain O-alkyl substituted hydroxylamines.[4] The boiling points of the derivatives of hydroxylamine are, however, in general somewhat higher than those of corresponding derivatives of ammonia.

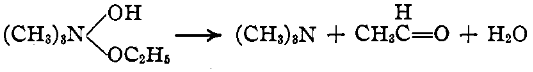
When ethyl bromo-acetate was treated with O,N-diethylhydroxylamine, there was formed ethyl ethylethoxyamino-acetate, $C_2H_5O(C_2H_5)NCH_2COOC_2H_5$. It was thought that methyl iodide would react with this compound to form a methiodide. Instead, however, there were formed acetaldehyde and ethyl methylethylamino-acetate hydroiodide. The hydrochloride of the latter substance was synthesized by adding hydrogen chloride to the ether-soluble oil formed by the interaction of ethyl bromo-acetate and methylethylamine.

It seems probable that the formation of acetaldehyde and ethyl methylethylamino-acetate hydroiodide from methyl iodide and ethyl ethylethoxyamino-acetate involved the intermediate formation of ethyl ethylethoxyamino-acetate methiodide, which was so unstable that it decomposed almost as soon as it formed. This may be represented by the equations



$$C_2H_5ON(C_2H_5)CH_2COOC_2H_5 + CH_3I \longrightarrow C_2H_5O\overset{CH_3\ \ I}{\overset{\diagdown\ \diagup}{N}}(C_2H_5)CH_2COOC_2H_5 \longrightarrow$$
$$C_2H_5\overset{H\ \ I}{\overset{\diagdown\ \diagup}{N}}(CH_3)CH_2COOC_2H_5 + CH_3\overset{H}{C}{=}O$$

Meisenheimer has shown that trimethylethoxyammonium hydroxide decomposes in a somewhat similar manner into trimethylamine, water and acetaldehyde[5]



$$(CH_3)_3N\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix} \longrightarrow (CH_3)_3N + CH_3\overset{H}{C}{=}O + H_2O$$

By the action of O-methylhydroxylamine on ethyl bromo-acetate, there has been obtained O-methylhydroxylammonium bromide and ethyl methoxyamino-acetate, $CH_3ONHCH_2COOC_2H_5$, which may be considered

---

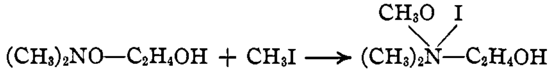
[4] Jones and Major, THIS JOURNAL, **49**, 1540 (1927).

[5] Meisenheimer, *Ann.*, **397**, 294 (1913).

an hydroxylamine analog of the important amino acid sarcosine, CH_3NH-$CH_2COOC_2H_5$. Potassium cyanate with ethyl methoxyamino-acetate hydrochloride formed ethyl N-methoxyhydantoate, $H_2NCON(OCH_3)$-$CH_2COOC_2H_5$. When a solution of this ester in concentrated hydrochloric acid was evaporated to dryness, the corresponding acid, N-methoxyhydantoic acid, was obtained. With phenyl isocyanate and phenyl isothiocyanate the expected derivatives were obtained.

It was thought that the hydroxylammonium analogs of choline and its salts, namely, dimethylmethoxyhydroxyethylammonium hydroxide and its salts, might perhaps be prepared, as shown by the two equations

$$(CH_3)_2NC_2H_4OH + H_2O_2 \longrightarrow (CH_3)_2NOC_2H_4OH + H_2O \qquad (I)$$



$$(CH_3)_2NO{-}C_2H_4OH + CH_3I \longrightarrow (CH_3)_2\overset{CH_3O\ \ I}{N}{-}C_2H_4OH \qquad (II)$$

The amine oxide of dimethylamino-ethanol was obtained by the action of hydrogen peroxide on dimethylamino-ethanol, as shown in Equation I, and several salts of this compound, as well as the picrate of diethylhydroxyethylamine oxide, were made. However, we were not able to isolate dimethylmethoxyhydroxyethylammonium iodide from the products of interaction of dimethylhydroxyethylamine oxide and methyl iodide.

When the attempt was made to repeat the preparation of dimethylmethoxyhydroxyethylammonium iodide according to the method of Jones and Major,[6] it was found that in order to obtain the intermediate compound, O,N-dimethyl-N-hydroxyethylhydroxylamine, $CH_3O(CH_3)NC_2$-H_4OH, which also was described by Jones and Major,[6] it was necessary to add a trace of moisture to the mixture of ethylene oxide and O,N-dimethylhydroxylamine from which the compound was made and that the compound was not obtained under the conditions described by Jones and Major if moisture was not present. It was also found that any more than a trace of moisture caused the reaction to proceed in such a way that no O,N-dimethyl-N-hydroxyethylhydroxylamine but only higher-boiling oils were obtained. Similarly, the presence of a trace of moisture was found to be essential in the preparation of O,N-diethyl-N-hydroxyethylhydroxylamine, according to the method of Jones and Burns.[7] Presumably, the required moisture was accidentally introduced during the earlier experiments with these compounds.

When dimethylmethoxyhydroxyethylammonium hydroxide, $(CH_3)_2$-$(CH_3O)N(OH)C_2H_4OH$, was previously decomposed by us, by heating it, the analyses did not absolutely prove that formaldehyde and dimethylamino-ethanol were obtained.[6] Both of these compounds have now been identified definitely as the products which are formed in the decomposition of this substance.

---

[6] Jones and Major, THIS JOURNAL, **49**, 1533 (1927).

[7] Jones and Burns, *ibid.*, **47**, 2972 (1925).

Experimental Part

Reaction of Ethyl Bromo-acetate with O,N-Dimethylhydroxylamine.—After a solution of 0.1 mole of ethyl bromo-acetate and 0.2 mole of O,N-dimethylhydroxylamine in dry ether had stood at room temperature for two days, a precipitate of white, crystalline needles had formed. These crystals were filtered, dissolved in absolute alcohol and then reprecipitated with dry ether; m. p. 143°. They gave a test for the bromide ion with silver nitrate. In order to identify this compound it was treated with potassium hydroxide and the free base which was thus formed was distilled into dilute hydrochloric acid. The hydrochloric acid solution was evaporated to dryness on a water-bath. The solid which remained melted at 115–116° and a mixture of this substance with O,N-dimethylhydroxylammonium chloride, m. p. 115–116°, also melted at this temperature, indicating that the bromide which melted at 143° was O,N-dimethylhydroxylammonium bromide.

Anal. Subs., 0.2407: AgBr, 0.3192. Calcd. for C_2H_8ONBr: Br, 56.28. Found: Br, 56.40.

Dry hydrogen chloride gas was passed into the ether filtrate from which the above described O,N-dimethylhydroxylammonium bromide was filtered. The white solid which formed was dissolved in water. This solution was made basic with alkali and then repeatedly extracted with ether. The ether solution was dried with anhydrous sodium sulfate, after which the ether was distilled off. A colorless oil remained; b. p. 164–166°; yield of ethyl methylmethoxyamino-acetate, 20%. The oil was rather soluble in water but more so in ether.

Hydrochloride of Ethyl Methylmethoxyamino-acetate, $CH_3O(CH_3)NCH_2COOC_2H_5{\cdot}HCl$.—The hydrochloride of the above described oil, b. p. 164–166°, was a white solid. It was recrystallized by dissolving it in alcohol and reprecipitating it with ether; m. p. 90–91°.

Anal. Subs., 0.2033: AgCl, 0.1602. Calcd. for $C_6H_{14}O_3NCl$: Cl, 19.32. Found: 19.52.

Reaction of O,N-Diethylhydroxylamine with Ethyl Bromo-acetate.—After a solution of 0.02 mole of ethyl bromo-acetate and 0.04 mole of O,N-diethylhydroxylamine in dry ether had stood at room temperature for four days, an oily liquid had precipitated. It was separated by decantation from the ether solution and was washed with ether. It did not solidify when it was allowed to stand for several days in a vacuum desiccator with concentrated sulfuric acid and potassium hydroxide. Accordingly, it was treated with potassium hydroxide and the free base distilled. The base possessed the characteristic odor of O,N-diethylhydroxylamine and boiled at 83°.[8]

Hydrogen chloride caused a heavy pale yellow oil to precipitate from the ether solution from which the above described O,N-diethylhydroxylammonium bromide was separated. It was separated from the ether solution by decantation and washed with ether. Since the oily hydrochloride appeared to be an extremely weak base and was somewhat soluble in ether which contained no hydrogen chloride, the ether solution in addition was extracted with dilute hydrochloric acid and this acid solution added to the oily hydrochloride. After fresh ether had been added to this hydrochloric acid solution in order to dissolve any free base as soon as it formed, the aqueous solution was made basic with solid sodium carbonate and some caustic alkali. The ether layer was separated and the aqueous solution repeatedly extracted with further portions of ether. The combined ether extracts were dried with anhydrous sodium sulfate. After the ether had been removed by distillation, an oil remained which was purified by distillation; b. p. 186–188° with slight decomposition, and 82° at 19 mm. It had a rather

---

[8] Lossen, *Ann.*, **252,** 234 (1889), gives 83° as the b. p. of O,N-diethylhydroxylamine.

pleasant ethereal odor. It formed neither a solid hydrochloride nor chloroplatinate; yield of ethyl ethylethoxyamino-acetate, 43%.

Anal. Subs., 0.3643: N_2, 26.8 cc. (21°, 754 mm.). Calcd. for $C_8H_{17}O_3N$: N, 8.00. Found: N, 8.45.

Ethyl Methylethylamino-acetate, $C_2H_5(CH_3)NCH_2COOC_2H_5$.—To a cooled solution of 0.07 mole of methylethylamine in dry ether was slowly added a solution of 0.07 of a mole of ethyl bromo-acetate in ether. There was a vigorous reaction which was accompanied by considerable heat. A white solid precipitated, m. p. 85–88°, which was apparently methylethylammonium bromide.[9] Ethyl methylethylamino-acetate was recovered from the ether filtrate in the same way that has already been described for the preparation of ethyl methylmethoxyamino-acetate. It was an oily liquid, b. p. 164–165°.

Hydrochloride.—The hydrochloride was precipitated from ether in the usual manner, m. p. 132°.

Anal. Subs., 0.2720: AgCl, 0.2142. Calcd. for $C_7H_{16}O_2NCl$: Cl, 19.53. Found: Cl, 19.50.

Reaction of Methyl Iodide with Ethyl Ethylethoxyamino-acetate.—To 1 g. of ethyl ethylethoxyamino-acetate was added a molecular equivalent of methyl iodide. The mixture was allowed to stand in a sealed container at room temperature for two weeks. During this time a heavy reddish oil formed. the amount of which gradually increased until at the end of two weeks the reaction was apparently complete. When the container was opened the odor of acetaldehyde was quite pronounced. Accordingly the heavy oil was repeatedly extracted with ether in order to remove the acetaldehyde. The ether extract was shaken with an aqueous solution of *p*-nitrophenylhydrazine hydrochloride until there was no further reaction. The ether was then evaporated. A yellow precipitate remained which was recrystallized from 50% alcohol; m. p. 129°. A mixture of this solid with pure acetaldehyde *p*-nitrophenylhydrazone, m. p. 129°, also melted at 129°. There was obtained 0.24 g. of acetaldehyde *p*-nitrophenylhydrazone in this way. This means that 21% of the theoretical amount of acetaldehyde was recovered in this process if it is assumed that all of the ethoxy group present in the ethyl ethylethoxyamino-acetate was converted into acetaldehyde. That some of the acetaldehyde polymerized during the reaction and therefore was not recovered by this process seems very probable. Also, the ether probably did not completely extract the acetaldehyde from the oil.

The pink oil was then dissolved in absolute alcohol and shaken with metallic mercury, in order to remove free iodine. It was then shaken with somewhat more than the calculated amount of silver chloride until its solution no longer gave a test for iodide ion. Dry ether was then added to the alcoholic filtrate from this reaction and a heavy almost colorless oil precipitated. This oil was allowed to stand in a vacuum desiccator with sulfuric acid for some time but did not solidify. It was then redissolved in warm absolute alcohol and fractionally precipitated with dry ether. The first fractions were oils which were not identified. A rather larger solid precipitate then formed as more ether was added. In order to purify it, it was dissolved in alcohol, shaken with animal charcoal, filtered and reprecipitated with ether; m. p. 132°. A mixture of this hydrochloride with pure ethyl methylethylamino-acetate hydrochloride, m. p. 132°, also melted at 132°.

Reaction of O-Methylhydroxylamine with Ethyl Bromo-acetate.—After a solution of 0.1 mole of ethyl bromo-acetate and 0.2 mole of O-methylhydroxylamine in dry ether

---

[9] Wagner, *Z. Krist.*, **43**, 162 (1907), gives 85–88° as the m. p. of methylethylammonium bromide.

had stood at room temperature for five days, the white plate-like crystals which had formed were removed by filtration. They were purified by dissolving in absolute alcohol and precipitating with dry ether; m. p. 164° with decomposition; yield, 63%.

Anal. Subs., 0.2251: AgBr, 0.3325. Calcd. for $CH_3ONH_2 \cdot HBr$: Br, 62.45. Found: Br, 62.86.

Ethyl methoxyamino-acetate, $CH_3ONHCH_2COOC_2H_5$, was recovered from the ether filtrate in the same manner that has already been described for the preparation of ethyl methylmethoxyamino-acetate; b. p. 167–170° (with some decomposition), 112° at 116 mm.; yield, 23%.

Chloroplatinate of Ethyl Methoxyamino-acetate, $(CH_3ONHCH_2COOC_2H_5)_2 \cdot H_2PtCl_6$.—An equivalent of dry hydrogen chloride was passed into a solution of 0.5 g. of ethyl methoxyamino-acetate in absolute alcohol. To this was added the calculated amount of a concentrated solution of chloroplatinic acid in absolute alcohol. The orange colored crystals which precipitated were recrystallized by dissolving in absolute alcohol and reprecipitating with ether; m. p. 141° with decomposition.

Anal. Subs., 0.1998: Pt, 0.0571. Calcd. for $C_{10}H_{24}O_6N_2 \cdot PtCl_6$: Pt, 28.87. Found: Pt, 28.58.

Ethyl N-Methoxyhydantoate, $NH_2—CO—N(OCH_3)CH_2COOC_2H_5$.—A solution of 2 g. of ethyl methoxyamino-acetate in dry ether was saturated with dry hydrogen chloride. The oil which precipitated was separated and washed with ether. A cold saturated solution of the calculated amount of potassium cyanate was slowly added to this hydrochloride while the reaction mixture was kept cold and stirred. Considerable heat developed and a white solid precipitated. It was filtered off, washed with a little water and recrystallized from absolute alcohol; m. p. 112°; yield, 65%. It was somewhat soluble in water, less so in methyl alcohol, still less so in ethyl alcohol and only very slightly soluble in ether.

Anal. Subs., 0.1740: N_2, 24.6 cc. (24°, 741.7 mm.). Calcd. for $C_6H_{12}O_4N_2$: N, 15.91. Found: N, 15.87.

N-Methoxyhydantoic Acid, $NH_2—CO—N(OCH_3)CH_2COOH$.—Slightly more than enough of a 37% solution of hydrogen chloride in water to dissolve it was added to 1 g. of ethyl N-methoxyamino-acetate. After the solution had stood at room temperature overnight, it was placed in a vacuum desiccator containing sulfuric acid and potassium hydroxide. Evaporation of the liquid left a white solid. It was recrystallized from absolute alcohol; decomposition point, 164°; yield, 70%. It was soluble in water and acetone, less so in alcohol, still less so in ether and insoluble in ligroin. It reacted quite acid to litmus and gave no test for the chloride ion with acid silver nitrate. However, when ammoniacal silver nitrate was added to an aqueous solution of the acid, its white silver salt precipitated.

Anal. Subs., 0.1549: N_2, 25.3 cc. (21°, 747.5 mm.). Calcd. for $C_4H_8O_4N_2$: N, 18.92. Found: N, 18.69.

Ethyl N''-Phenyl-N'-methoxyhydantoate, $C_6H_5NHCON(OCH_3)CH_2COOC_2H_5$.—To a solution of 0.5 g. of ethyl methoxyamino-acetate in dry ether was added 0.4 g. of phenyl isocyanate. After this mixture had stood overnight, petroleum ether was added. A precipitate of fine white needles formed which was recrystallized from hot ligroin; m. p. 91°. The crystals were very soluble in benzene, alcohol and ether but insoluble in water.

Anal. Subs., 0.2044: N_2, 20.1 cc. (26°, 749.0 mm.). Calcd. for $C_{12}H_{16}O_4N_2$: N, 11.11. Found: N, 11.08.

Ethyl N''-Phenyl-N'-methoxythiohydantoate, $C_6H_5NHCS—N(OCH_3)CH_2COOC_2H_5$.—To a solution of 2.5 g. of ethyl methoxyamino-acetate in ligroin was added 2.6

g. of phenyl isothiocyanate. Some heat developed and a white precipitate formed. After the mixture had stood overnight, the white solid was filtered off. It was recrystallized from hot carbon tetrachloride; m. p. 110°; yield, 60%. It was readily soluble in benzene.

Anal. Subs., 0.2629: N_2, 24.2 cc. (26°, 762.3 mm.). Calcd. for $C_{12}H_{16}O_3N_2S$: N, 10.45. Found: N, 10.55.

Dimethylhydroxyethylamine Oxide, $(CH_3)_2NOC_2H_4OH$.—To 10 g. of dimethylamino-ethanol an excess of a 3% solution of commercial hydrogen peroxide was added.[10] Considerable heat was generated in the reaction. After the solution had stood for twenty-five hours, platinum black was added in order to decompose the excess of hydrogen peroxide. The mixture was filtered and the excess of water was removed by distillation *in vacuo*. The oil which remained was thoroughly dried in a vacuum desiccator. In order to purify it, this oil was then dissolved in absolute alcohol, filtered and reprecipitated with dry ether. When the oil was further dried in a vacuum desiccator over phosphorus pentoxide, it solidified in the form of white, extremely hygroscopic crystals.

Hydrochloride.—A solution of dimethylhydroxyethylamine oxide in absolute alcohol was saturated with dry hydrogen chloride. An oil precipitated from this solution when ether was added, which solidified after it had stood for a short time. It was recrystallized by dissolving it in absolute alcohol and reprecipitating it with dry ether. It formed white, extremely hygroscopic crystals; m. p. 48–49°.

Anal. Subs., 0.1653: AgCl, 0.1705. Calcd. for $C_4H_{12}O_2NCl$: Cl, 25.06. Found: Cl, 25.45.

Chloroplatinate.—A solution of dimethylhydroxyethylamine oxide in absolute alcohol was saturated with dry hydrogen chloride. The calculated amount of chloroplatinic acid in absolute alcohol was added. An orange colored precipitate formed which was recrystallized from absolute methanol; it decomposed at 191°, with evolution of a gas.

Anal. Subs., 0.2349: Pt, 0.0733. Calcd. for $C_8H_{24}O_4N_2PtCl_6$: Pt, 31.48. Found: Pt, 31.21.

Picrate of Dialkylhydroxyethylamine Oxide.—The calculated amount of a concentrated solution of picric acid in absolute alcohol was added to a solution of the dialkylhydroxyethylamine oxide in absolute alcohol. Petroleum ether precipitated a yellow crystalline solid from this solution.

The picrate of dimethylhydroxyethylamine oxide was recrystallized from hot butanol. It formed long yellow needle-like crystals which were readily soluble in methyl and ethyl alcohols, acetone and water, much less soluble in chloroform, benzene and ether and insoluble in ligroin; m. p. 124°.

Anal. Subs., 0.1793: N_2, 26.0 cc. (17°, 743.1 mm.). Calcd. for $C_{10}H_{14}O_9N_4$: N, 16.77. Found: N, 16.69.

The picrate of diethylhydroxyethylamine oxide was recrystallized from a solution of 75% of benzene and 25% of acetone. It formed yellow plate-like crystals which were soluble in acetone and alcohol, less so in ether and water and insoluble in petroleum ether; m. p. 125–126° with darkening.

Anal. Subs., 0.1773: N_2, 23.30 cc. (13°, 755.0 mm.). Calcd. for $C_{12}H_{18}O_9N_4$: N, 15.47. Found: N, 15.60.

Interaction of Dimethylhydroxyethylamine Oxide and Methyl Iodide.—The calcu-

---

[10] The solution of hydrogen peroxide had been freed from sulfuric acid by shaking it with solid barium carbonate.

lated amount of methyl iodide was added to a solution of dimethylhydroxyethylamine oxide in absolute alcohol. After this solution had stood for four days dry ether was added. A heavy oil precipitated which readily dissolved in water. With silver nitrate it gave a precipitate of silver iodide. It was placed in a vacuum desiccator, but did not solidify. It was then fractionally precipitated from its solution in alcohol by the addition of dry ether. Each fraction was an oil which did not solidify, but which gave a precipitate of silver iodide with silver nitrate. No definite chemical compound was isolated.

Decomposition of Dimethylmethoxyhydroxyethylammonium Hydroxide.—To 0.5 g. of dimethylmethoxyhydroxyethylammonium iodide was added an excess of an aqueous solution of sodium hydroxide. The volatile portion of this solution was distilled into dilute hydrochloric acid. This acid solution was then found to give a positive test for formaldehyde with guaiacol sulfate.[11] The hydrochloric acid solution was evaporated to dryness on a water-bath. An oil was left which was dissolved in dry alcohol. The calculated amount of a solution of chloroplatinic acid in absolute alcohol was added to it. An orange colored precipitate formed, which was recrystallized from hot absolute alcohol; m. p. 178° with decomposition.

Anal. Subs., 0.0106: Pt, 0.0035. Calcd. for $((CH_3)_2NC_2H_4OH)_2 \cdot H_2PtCl_6$: Pt, 33.2. Found: Pt, 33.0.

The chloroplatinate of pure dimethylamino-ethanol was made in an analogous manner. It also melted with decomposition at 178° and exhibited the same properties of color and solubility that were shown by the chloroplatinate of the amine which was obtained in the decomposition of dimethylmethoxyhydroxyethylammonium hydroxide.

Summary

1. Two ethyl alkylalkoxyamino-acetates have been prepared by the action of O,N-dialkylhydroxylamines on ethyl bromo-acetate.

2. By the action of methyl iodide on ethyl ethylethoxyamino-acetate there was formed acetaldehyde and ethyl methylethylamino-acetate hydroiodide. The peculiar course of this reaction has been discussed.

3. Ethyl methoxyamino-acetate has been prepared by the action of O-methylhydroxylamine on ethyl bromo-acetate. Its reactions or those of its hydrochloride with potassium cyanate, phenyl isocyanate and phenyl isothiocyanate have been described.

4. N-Methoxyhydantoic acid has been obtained by hydrolyzing ethyl-N-methoxyhydantoate with hydrochloric acid.

5. Certain similarities in the properties of O-alkyl substituted hydroxylamines and the related amines have been pointed out.

6 Dimethylhydroxyethylamine oxide and several of its salts have been prepared.

7. Formaldehyde and dimethylamino-ethanol have been shown definitely to be formed in the decomposition of dimethylmethoxyhydroxyethylammonium hydroxide.

PRINCETON, NEW JERSEY

---

[11] "Deutsches Arzneibuch," R. v. Deckers Verlag, Berlin, **1926**, p. LIV.