[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

TRIHYDROXY-TRIETHYLAMINE OXIDE AND SUBSTITUTED HYDROXYLAMINES WITH HYDROXY-ETHYL RADICALS[1]

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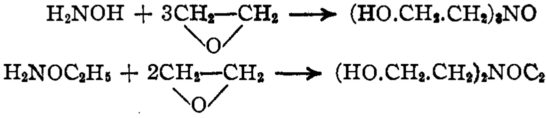
Introduction

In the course of investigations of amine oxides and hydroxylamines, it became necessary to study compounds of these classes which contain hydroxy-ethyl radicals as substituent groups. Only two hydroxylamino alcohols have been described, namely, N-trihydroxy-*tert*-butylhydroxylamine and N-dihydroxy-*tert*-butylhydroxylamine,[2] both prepared by the reduction of the corresponding nitro compound. These derivatives were not suited to our purpose and the methods employed in their preparation were not of general applicability.

It was necessary, therefore, to devise new methods of synthesis for hydroxylamino alcohols. Most of the compounds described in this article were made by the action of ethylene oxide upon hydroxylamine or alkylhydroxylamines at room temperature or below.



$$H_2NOH + 3\underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow (HO.CH_2.CH_2)_3NO$$

$$H_2NOC_2H_5 + 2\underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow (HO.CH_2.CH_2)_2NOC_2H_5$$

Two other hydroxylamino-ethyl alcohols were made in a similar way; N,N-dihydroxy-diethylhydroxylamine $(HO.CH_2.CH_2)_2NOH$, and O,N-diethyl-N-hydroxyethylhydroxylamine $(HOCH_2.CH_2)(C_2H_5)NOC_2H_5$.

At somewhat higher temperatures ethylene oxide reacted with the hydroxy-ethyl radicals of the substituted hydroxylamines themselves to form ethers containing such groups as $HO.CH_2.CH_2.O.CH_2.CH_2$-, or even more complicated chains. The presence of these ethers made it very difficult to obtain solid salts of the simpler hydroxylamines.

These reactions suggest the possibility of preparing many other hydroxylamines with hydroxy-ethyl radicals attached to nitrogen, but our experiments indicate that the problem of preparing O-hydroxy-ethyl derivatives, such as $H_2NOCH_2.CH_2.OH$, will be more difficult. It is interesting to note that ethylene oxide, which reacts so readily with hydroxyl groups, does not attack the hydroxyl group of hydroxylamine. In this respect the behavior of ethylene oxide resembles that of halogen alkyls which convert

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[1] This paper is based upon a thesis submitted by G. Richard Burns to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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[2] Piloty and Reiff, *Ber.*, **30**, 1658, 2058 (1897).

hydroxylamine into N-substituted derivatives, ultimately forming salts of amine oxides, $R_3N(OH)X$.

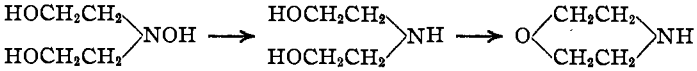
It was expected that ethylene chlorohydrin or ethylene iodohydrin would alkylate salts of hydroxy-urethan to produce esters of the form $C_2H_5O.CO.N(OCH_2.CH_2.OH)H$ which, upon hydrolysis, would yield compounds of the type desired. Jones and his associates[3] prepared many O-substituted and O, N-disubstituted alkylhydroxylamines by this method, but no successful results were obtained when the hydrins were employed as alkylating agents.

A preliminary study of the action of hydroxylamine upon phenylethylene oxide was made; this oxide was found to be much less reactive than ethylene oxide. These experiments will be continued.

Trihydroxy-triethylamine oxide, also prepared by the action of hydrogen peroxide upon trihydroxy-triethylamine, $(HOCH_2CH_2)_3N$, and by the oxidation of the triacetyl ester of this amine with benzoper-acid, was a colorless solid, m. p. 104–105.5°, with a very sweet taste. Its hydrochloride was a liquid; its picrate and its chloroplatinate were solids. The chloroplatinate showed a singular behavior. When it crystallized from the alcoholic solution in which it was prepared, it usually melted at about 99°. Successive recrystallizations caused the melting point to rise about 15° each time until it reached 158.5°, but analysis showed that the platinum content of the salt was not altered so that variations in melting point could not be attributed to a change in composition.

In its readiness to part with oxygen this amine oxide seems to stand between the aliphatic and the aromatic amine oxides.[4] It liberated iodine very slowly from a warm, slightly acid solution of potassium iodide. Zinc dust and water reduced it to trihydroxy-triethylamine, which proved that the three hydroxy-ethyl groups are attached to nitrogen.

N,N-dihydroxy-diethylhydroxylamine, prepared by the action of ethylene oxide on one molecular equivalent of hydroxylamine was a viscous liquid which formed a solid picrate and chloroplatinate. To establish its structure, it was reduced by zinc dust and water to dihydroxy-diethylamine which was converted into morpholine by the action of sulfuric acid.



O,N-diethyl-N-hydroxy-ethylhydroxylamine, b. p. 170°, has been used to prepare a compound similar to novocain in structure in which the substituted amine group is replaced by the similar hydroxylamine group,

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[3] (a) Jones, *Am. Chem. J.*, **20**, 41 (1898). (b) Hecker, *ibid.*, **50**, 444 (1913). (c) Jones and Neuffer, THIS JOURNAL, **36**, 2202 (1914).

[4] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 1004 (1899). Bamberger, *Ber.*, **34**, 12 (1901). Jones and Hartshorn, THIS JOURNAL, **46**, 1840 (1924).

$H_2N.C_6H_4.CO.OCH_2CH_2\text{-}NOC_2H_5(C_2H_5)$. The physiological action of this compound will be tested.

Experimental Part

I. Trihydroxy-triethylamine Oxide, $(HOCH_2CH_2)_3NO$

Preparation of the Amine Oxide from Hydroxylamine and Ethylene Oxide

Eight g. of free hydroxylamine, prepared by the method of Lecher and Hofmann,[5] was covered with an excess of ethylene oxide in a pressure bottle previously cooled to 0°. The bottle, provided with an outlet and calcium chloride tube, was then immersed in water at 0° for two days, the ethylene oxide being renewed if necessary. Then a solid rubber stopper was inserted in the bottle and fastened by a wire, and the mixture was kept at room temperature for two weeks. At the end of this time, a considerable quantity of the crystalline amine oxide had separated. The rest was obtained by allowing the ethylene oxide to evaporate. The crude product melted between 99° and 100°; yield, about 90%. It was obtained pure when a solution of it in boiling absolute ethyl alcohol was cooled, treated with a crystal of the oxide and allowed to stand for a day or two. More of the compound separated from the mother liquor as an oil when dry ether was added. This oil crystallized slowly when allowed to stand with the liquor from which it was precipitated.

Trihydroxy-triethylamine oxide forms large, colorless crystals, m. p. 104–105.5°, which are very soluble in water and in alcohol, slightly soluble in acetone and in chloroform and insoluble in benzene, in ligroin and in ethyl acetate. It is slightly deliquescent, is slightly basic to litmus and has a decidedly sweet taste. It cannot be distilled under reduced pressure. It reduced a hot ammoniacal solution of silver nitrate. Fehling's solution has no action on it. It restored the color to Schiff's reagent.

Anal. Subs., 0.4995: N, 37.4 cc. (22.5° and 753.9 mm. over 40 per cent. KOH). Calcd. for $C_6H_{15}NO_4$: N, 8.48. Found: 8.46.

The benzoyl derivative was an oil. The compounds obtained by heating the oxide with α-naphthylisocyanate could not be solidified. The hydrochloride was a thick liquid.

PICRATE.—Equivalent amounts of trihydroxy-triethylamine oxide and picric acid were dissolved in a little water and the mixture was allowed to stand in a vacuum desiccator for two months. A very deliquescent, crystalline solid was obtained which could be recrystallized by dissolving it in a little absolute ethyl alcohol and precipitating it with 10 volumes of dry ether; m. p., 73–74°. It was insoluble in ether, in chloroform, in benzene and in ligroin.

CHLOROPLATINATE.—The chloroplatinate was prepared by adding a 10% solution of platinic chloride in alcohol to an alcoholic solution of trihydroxy-triethylamine oxide hydrochloride. The salt was precipitated when a little dry ether was added. Considerable difficulty was experienced in getting this salt to crystallize the first time. It could be obtained as a solid when the amine oxide from which it was prepared was pure. It melted at points varying between 99° and 158.5°. In the case of a typical sample precipitated in large, thin leaflets from cold 90% ethyl alcohol by the addition of dry ether, the melting point at first was 99°. Successive recrystallizations of the solid from hot alcohol by the addition of ether gave samples which melted at 115–117°, 133.5–134.0°, 147.5–148.5° and 158.0–158.5°. Two recrystallizations from hot methyl alcohol, in which it is more soluble, usually gave crystals with melting points varying

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[5] Lecher and Hofmann, *Ber.*, **55B**, 912 (1922).

between 141° and 151°. Decomposition took place above the melting point. A sample kept in a vacuum desiccator over sulfuric acid for several weeks showed no loss of weight or change in melting point. These facts, together with the analysis of the chloroplatinates of different melting points, showed that the change in melting point could not be due to hydration of the salt.

Anal. Subs. (I, m. p. 99°), 0.1078 (II, m. p. 146.5°), 0.2341: Pt, (I) 0.0291, (II) 0.0623. Calcd. for $C_{12}H_{32}N_2O_8PtCl_6$: Pt, 26.37. Found: (I) 26.9, (II) 26.6.

The crystals melting at 99° are distinctly different in form from those with higher melting points.

Reduction of the Amine Oxide to Trihydroxy-triethylamine.—One g. of the amine oxide was boiled for 12 hours with zinc dust and water. The solution, filtered and acidified with hydrochloric acid, was evaporated in a vacuum. This gave a thick sirup which, after a month, deposited crystals of trihydroxy-triethylamine hydrochloride. These were collected and crystallized from dil. ethyl alcohol; yield, 0.1 g.; m. p., 176–177°; m. p. of chloroplatinate, 118–119°. These melting points were not changed when samples of these substances were mixed with equal quantities of trihydroxy-triethylamine hydrochloride or of the chloroplatinate, respectively, which had been made from trihydroxy-triethylamine prepared from ammonia and ethylene oxide.

Preparation of the Amine Oxide from Trihydroxy-triethylamine.—This was done by oxidizing the triacetyl derivative of trihydroxy-triethylamine by benzoper-acid in ether solution.

The Preparation of Triacetyl-trihydroxy-triethylamine, $(CH_3CO.O.CH_2CH_2)_3N$.—Trihydroxy-triethylamine was prepared from ammonium hydroxide and ethylene oxide; b. p., 206–207° (15 mm.).[6] A mixture of 9 g. of trihydroxy-triethylamine and an excess of acetyl chloride in 150 cc. of chloroform was boiled for six hours under a reflux condenser. By this time the evolution of hydrogen chloride had practically ceased. The excess of trihydroxy-triethylamine hydrochloride was removed and the chloroform evaporated. This left the hydrochloride of the triacetyl derivative as a thick oil. To obtain the free base, this oil was mixed with an excess of powdered sodium hydroxide and the mixture extracted at once with dry ether. The ether was removed and the mobile oil was distilled; yield, 10 g. or 66%; b. p., 206–207° (27 mm.). The free base was insoluble in water, but very soluble in ether and in alcohol. The hydrochloride was an oil insoluble in ether and soluble in chloroform, in alcohol and in water.

CHLOROPLATINATE.—The chloroplatinate was precipitated from alcoholic solution by dry ether; m. p., 123.5°.

Anal. Subs., 0.2148: Pt, 0.0445. Calcd. for $C_{24}H_{44}N_2O_{12}PtCl_6$: Pt, 20.29. Found: 20.7.

Oxidation of the Acetyl Derivative by Benzoper-acid.—Eight g. of triacetyl-trihydroxy-triethylamine in ether was treated at 0° with an equivalent quantity of benzoper-acid in ether solution.[7] The ether was evaporated at 20° and a slight excess of dil. hydrochloric acid was added. The mixture was allowed to stand two days to hydrolyze the ester. It was extracted twice with ether to remove benzoic acid and some acetic acid and the water was evaporated at 15° under diminished pressure. No traces of trihydroxy-triethylamine hydrochloride remained. The trihydroxy-triethylamine oxide hydrochloride was obtained by this process in almost the calculated yield. It formed a crystalline chloroplatinate readily. Five recrystallizations from hot methyl alcohol gave samples whose melting points varied as follows: 119°, 125.5°, 140.5° and 146.5°.

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[6] Knorr, *Ber.*, **30**, 919 (1897).

[7] Prileshajew, *Chem. Centr.*, **1911**, I, 1279. *Z. physiol. Chem.*, **427**, 493.

Anal. Subs. (m. p. 146.5°), 0.2102: Pt, 0.0552. Calcd. for $C_{12}H_{32}N_2O_1PtCl_6$: Pt, 26.37. Found: 26.3.

Oxidation of the Amine by Hydrogen Peroxide.—A solution of 1 g. of trihydroxy-triethylamine in a large excess of 4% hydrogen peroxide was allowed to stand for three days at room temperature. After the first six hours no more hydrogen peroxide reacted. Platinum black was added in order to decompose the excess of hydrogen peroxide and the solution was evaporated at 20°. When the oil obtained in this way was allowed to stand in a vacuum desiccator for two months, it solidified. The solidified product was recrystallized from ethyl alcohol and 0.3 g. of trihydroxy-triethylamine oxide was obtained; m. p., 104–105.5°. From this the chloroplatinate could be prepared without difficulty; m. p., 123°, 141°, 148°.

Decomposition of Trihydroxy-triethylamine Oxide by a Solution of Sodium Hydroxide

One g. of amine oxide was heated four hours with a solution of sodium hydroxide, acidified and evaporated to dryness at 25°. Thus, 0.1 g. of trihydroxy-triethylamine hydrochloride was isolated by means of its solubility in hot absolute alcohol. The rest of the decomposition product was about 0.8 g. of thick liquid. The chloroplatinate of this was prepared and found to consist mainly of dihydroxy-diethylamine chloroplatinate; m. p., 160–161°.

Analysis of the impure chloroplatinate as precipitated from the thick liquid gave 30.3% of platinum; the calculated percentage for $(HOCH_2CH_2)_2NH$ is 31.47; for $(HOCH_2CH_2)_3N$, 27.56.

This indicated that the sirup contained more of the secondary amine than of the tertiary amine. Any glycolic aldehyde produced would be destroyed by the sodium hydroxide solution.

Decomposition of Trihydroxy-triethylamine Oxide by Hydrochloric Acid.

One g. of the amine oxide was heated for five hours at 100° in a sealed tube with concd. hydrochloric acid. When the excess of acid and water was evaporated a viscous liquid and a crystalline solid appeared. The viscous liquid was found to reduce Fehling solution and ammoniacal silver nitrate and to restore the color to Schiff's reagent. It also contained hydrogen chloride and formed a liquid platinum salt. It probably was an oxidation product of trihydroxy-triethylamine. The crystalline residue, after crystallization from 90% ethyl alcohol, consisted of 0.35 g. of trihydroxy-triethylamine hydrochloride; m. p., 176–177°; yield, 31%. It formed a chloroplatinate; m. p., 118–119°. When these substances were mixed with the corresponding salts prepared by direct synthesis, no changes in the respective melting point were observed. No dihydroxy-diethylamine chloroplatinate or glycolic aldehyde could be found.

II. The Preparation of N,N-Dihydroxy-diethylhydroxylamine, $(HOCH_2CH_2)_2NOH$

Free hydroxylamine and one molecular equivalent of ethylene oxide were kept in a sealed tube at 0° for a week, then at room temperature for a few days and, finally, the excess of hydroxylamine was evaporated under diminished pressure at 25°. The base was a thick liquid which reduced ammoniacal silver nitrate in the cold. It decomposed when it was heated. The hydrochloride was a liquid soluble in water and in alcohol and soluble with difficulty in ether.

PICRATE.—The picrate was obtained from the free base and picric acid in absolute alcohol, followed by addition of dry ether; m. p., 104–106°.

Anal. Subs., 0.2152: N, 29.9 cc. (20.5°, 755 mm., over 40% KOH). **Calcd.** for $C_{10}H_{14}N_4O_{10}$: N, 16.0. Found: 15.9.

The CHLOROPLATINATE was obtained by the addition of dry ether to a solution of the chloride and chloroplatinic acid in absolute alcohol; m. p., 117.5–118.0°.

Anal. Subs., 0.0663: Pt, 0.0196. Calcd. for $C_8H_{24}N_2O_6PtCl_6$: Pt, 29.93. Found: 29.6.

TRIBENZOYL DERIVATIVE.—A thick liquid prepared by the Schotten-Baumann reaction.

Anal. Subs., 3.146: $C_6H_5CO_2H$, 2.703 (by hydrolysis). Calcd. for $C_{25}H_{23}NO_6$: Benzoic acid, 84.5. Found: 85.0.

Conversion to Morpholine.—Two g. of N,N-dihydroxy-diethylhydroxylamine was reduced by means of 10 g. of zinc dust and hydrochloric acid at 0° and the water evaporated at 100° under diminished pressure. Enough concd. sulfuric acid was added to make a concentration of 70% sulfuric acid and the mixture was warmed carefully to 165°. It was then cooled, diluted, made strongly alkaline and distilled with steam into dil. hydrochloric acid. The hydrochloric acid solution was evaporated and the morpholine hydrochloride recrystallized from alcohol; yield, 0.8 g. or 40%. This is about four times the yield obtained by heating dihydroxy-diethylamine with 70% sulfuric acid for eight hours. Apparently the mixture of zinc sulfate, sulfuric acid and, at the lower temperatures, zinc chloride is a better dehydrating agent for this reaction than sulfuric acid alone. The melting points of the morpholine hydrochloride and morpholine chloroplatinate obtained in this way were the same as those of the corresponding salts[8] prepared in the customary way.

Anal. Subs., 0.1700: Pt, 0.0571. Calcd. for $C_8H_{20}N_2O_2PtCl_6$: Pt, 33.41. Found: 33.6.

Reduction of Dihydroxy-diethylhydroxylamine to Dihydroxy-diethylamine, $(HOCH_2CH_2)_2NH$.—The reduction was carried out by means of zinc dust and hydrochloric acid. The zinc was removed as zinc sulfide and the water evaporated. The dihydroxy-diethylamine hydrochloride, a viscous liquid, was separated by dissolving it in absolute alcohol. The chloroplatinate of the amine was prepared and, after two recrystallizations from alcohol, melted at 160–161°, the correct melting point. Very little else was found in the reaction mixture, so the yield was apparently quite good.

Anal. Subs., 0.1688: Pt, 0.0532. Calcd. for $C_8H_{24}N_2O_4PtCl_6$: Pt, 31.47. Found: 31.5.

III. The Preparation of O-Ethyl-N,N-dihydroxy-diethylhydroxylamine, $(HOCH_2CH_2)_2NOC_2H_5$

O-ethylhydroxylamine, prepared by the method of Jones,[3a,3b] and an excess of ethylene oxide were put into a sealed tube and kept at room temperature for two weeks. After the ethylene oxide had been evaporated, the residue consisted of a thick liquid, soluble in absolute ethyl alcohol and in ether. This formed an oily hydrochloride insoluble in ether and soluble in alcohol. As the free base decomposed when it was heated, it could not be distilled. The analysis of the reaction mixture was carried out by means of the chloroplatinates: 3 parts, a solid; 1 part, a viscous liquid; 1 part, a mobile liquid. These were separated by means of their increasing solubility in absolute ethyl alcohol.

The solid recrystallized from absolute alcohol melted at 166–167°. It was the chloroplatinate of the trisubstituted hydroxylamine.

Anal. Subs., 0.1464: Pt, 0.0400. Calcd. for $C_{12}H_{32}N_2O_6PtCl_6$: Pt, 27.56. Found: 27.3.

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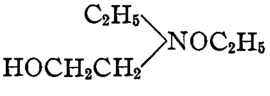
[8] Knorr, *Ann.*, **301**, 1 (1898).

The liquid chloroplatinates appeared to be ether-like derivatives formed by the continued action of ethylene oxide upon the hydroxy-ethyl groups first introduced. The more soluble "mobile" fraction, precipitated from the residual alcoholic solution by the addition of ether, gave a value for platinum required by the chloroplatinate of an ether $(HOCH_2CH_2OCH_2CH_2)_2NOC_2H_5$.

Anal. Subs., 0.1219: Pt, 0.0270. Calcd. for $C_{20}H_{48}N_2O_{11}PtCl_6$: Pt, 22.05. Found: 22.1.

The "viscous" fraction showed a platinum content of 25.6%, about the average of the values for the chloroplatinates obtained from the "solid" and "mobile" fractions. It was undoubtedly a mixture.

IV. The Preparation of O,N-Diethyl-N-hydroxy-ethylhydroxylamine,



$$\begin{matrix} C_2H_5 \searrow & \\ & NOC_2H_5 \\ HOCH_2CH_2 \nearrow & \end{matrix}$$

Six g. of O,N-diethylhydroxylamine obtained by the method of Hecker[3b] was placed in a sealed tube with an excess of ethylene oxide and left at room temperature for two weeks. Distillation of the reaction mixture gave O,N-diethyl-N-hydroxy-ethylhydroxylamine; b. p., 63° (at 10 mm.); 170° (760 mm.); yield, 35%. It is a mobile liquid, soluble in alcohol, in ether and in water.

Anal. Subs., 0.1993: N, 19.2 cc. (27°, 745.3 mm., over 40% KOH). Calcd. for $C_6H_{16}NO_2$: N, 10.5. Found: 10.5.

The hydrochloride was an oil insoluble in ether, soluble in alcohol and in water.

The chloroplatinate was prepared in absolute alcoholic solution and crystallized on the addition of dry ether; m. p., 143–143.5°.

Anal. Subs., 0.0773: Pt, 0.0244. Calcd. for $C_{12}H_{32}N_2O_4PtCl_6$: Pt, 28.86. Found: 29.0.

When the reaction was carried out at 100° for six hours and the mixture was distilled, the following products were obtained: 0.7 g. of O,N-diethyl-N-hydroxy-ethylhydroxylamine, 1.1 g. of a substance boiling at 130–160° (15 mm.) and 2 g. of a residue which did not distil. Further fractionation of the 130–160° portion gave 0.5 g.; b. p., 150–165°. This gave an oily chloroplatinate which contained 24.4% of platinum. It was thought that this fraction might consist of an ether, $(HOCH_2CH_2OCH_2CH_2)(C_2H_5)NOC_2H_5$; calcd. for Pt: 25.54%.

V. The Action of Ethylene Oxide and Ethylene Chlorohydrin upon Hydroxy-urethan

Hydroxy-urethan and ethylene oxide do not react at room temperature. Ethylene oxide bubbled through hydroxy-urethan at 100° did not react. The sodium or potassium salts of hydroxy-urethan are not alkylated by ethylene chlorohydrin or iodohydrin.

Alcoholic potassium hydroxide, added to a solution of hydroxy-urethan in alcohol[3b,9] produced a white solid when part of the alcoholic potassium hydroxide had been added. This proved to be an acid salt of hydroxy-urethan, $C_2H_5O.CO.NHOH.C_2H_5O.CO.NHOK$. The substance puffed when heated.

Anal. Subs., 0.5510: K_2SO_4, 0.1950. Calcd. for $C_6H_{13}O_6N_2K$: K, 16.1. Found: 15.92.

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[9] Ref. 2 a, p. 46.

It was thought that ethylene oxide might react with other hydroxamic acids. However, 7 g. of *m*-nitrobenzo-hydroxamic acid and an excess of ethylene oxide showed no signs of reacting after standing at room temperature for three weeks.

In order to identify glycol and ethylene chlorohydrin when they appeared in reaction mixtures, the following derivatives were prepared.

β-Chloro-ethyl *m*-Dinitrobenzoate.—*m*-Dinitrobenzoyl chloride and ethylene chlorhydrin, when heated together, gave the ester $(NO_2)_2C_6H_3.COOCH_2CH_2Cl$; m. p., 92°. It was very soluble in alcohol and slightly soluble in dry ether.

Anal. Subs., 0.2512: N, 22.2 cc. (21.1°, 751.3 mm., over 40% KOH). Calcd. for $C_9H_7N_2O_6Cl$: N, 10.2. Found: 10.1.

Naphthylisocyanate and Glycol.—Glycol and naphthylisocyanate were heated till the reaction started. When it was complete, the products were boiled with ligroin to remove any isocyanate;[10] the residue was dissolved in alcohol and any dinaphthyl urea removed by filtration. The urethan, $HOCH_2CH_2O.CO.NH.C_{10}H_7$, was precipitated from the alcohol by ether; m. p., 102–103°.

Anal. Subs., 0.5560: N, 29.8 cc. (20°, 747.1 mm. over 40% KOH). Calcd. for $C_{13}H_{13}O_3N$: N, 6.05. Found: 6.05.

Summary

1. Trihydroxy-triethylamine oxide has been prepared from hydroxylamine and ethylene oxide. It has also been prepared by oxidation of trihydroxy-triethylamine. Oxidation of the triacetyl derivative of this amine by benzoper-acid and subsequent hydrolysis of the ester gave a quantitative yield of trihydroxy-triethylamine oxide hydrochloride.

2. When this amine oxide was heated with hydrochloric acid, it decomposed to give trihydroxy-triethylamine and oxidation products of this amine. It was decomposed by heating it with sodium hydroxide solution chiefly into dihydroxy-diethylamine.

3. N,N-dihydroxy-diethylhydroxylamine has been prepared. This was reduced to dihydroxy-diethylamine. As a further proof of its structure this amine was converted into morpholine.

4. O-Ethyl-N,N-dihydroxy-diethylhydroxylamine and O,N-diethyl-N-hydroxy-ethylhydroxylamine have been prepared from the corresponding ethylhydroxylamines.

5. Hydroxy-urethan, $C_2H_5OCO.NHOH$, showed no tendency to react with ethylene oxide. It could not be alkylated by the action of ethylene-chlorohydrin. The potassium salt of hydroxy-urethan dissolved in alcohol reacted with ethylene chlorohydrin to give ethylene oxide as the chief product.

PRINCETON, NEW JERSEY

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[10] Vittenet, *Bull. soc. chim.*, [3] **21**, 957 (1899).