A STUDY OF β-BENZYLFORMHYDROXAMIC ACID AND HYDROXAMIC ACIDS OF SUBSTITUTED ACETIC ACID

A DISSERTATION

Submitted to the Faculty of the Graduate School of the University of Cincinnati in candidacy for the degree of Doctor of Philosophy.

Department of Chemistry

By

M. C. SNEED

Cincinnati, Ohio

April, 1916

A STUDY OF β-BENZYLFORMHYDROXAMIC ACID AND HYDROXAMIC ACIDS OF SUBSTITUTED ACETIC ACID.

PART I

-β-BENZYLFORMHYDOOXAMIC ACID.

Of the type of substituted hydroxylamines to which β-benzylformhydroxamic acid belongs β-~~formylphenylhydroxamic~~ Phenylformhydroxamic acid, β-acetyl-β-benzylhydroxylamine, and β-benzoyl-β-benzylhydroxylamine are the only other representatives known. The first of these compounds was described by Bamberger and Destraz[1] who obtained it by treating β-phenylhydroxylamine with formic acid. They found that ~~N-formylphenylhydroxamic~~ β-Phenylformhydroxamic acid upon distillation with phosphorous pentoxide gave phenylisocyanate. During the reaction there was a considerable charring and only a drop or two of the isocyanate resulted from the operation. They identified the small amount of phenylisocyanate obtained by its odor and by converting it through the action of aniline into diphenylurea. Both β-benzoyl-β-benzylhydroxylamine and β-acetyl-β-benzylhydroxylamine were prepared by Beckmann[2]. Isomeric with β-benzylformhydroxamic acid are the four compounds: α-benzylformhydrox-

[1] Ber., 35, 1884 (1902).
[2] Ibid., 26, 2631 (1893).

21 Jan 29

amic acid,[1] benzylurethane,[2] benzylcarbamic acid,[3] and benzyl ester of formdroximic acid which does not exist; but several hydroximic esters are known which show the interesting phenomenon of existing in two stereoisomeric modifications.[4]

It has been shown that β-substituted hydroxylamines and β-disubstituted hydroxylamines on treatment with mild dehydrating agents undergo intramolecular oxidation yielding aldehydes and amines (or ammonia). Thus, Walder[5] showed that the chief products obtained by treating β-dibenzylhydroxylamine either with acetyl chloride or with a solution of hydrogen chloride in acetic acid (Beckmann's mixture) were benzylamine and benzaldehyde. This transformation probably resulted from a loss of water between carbon and nitrogen in one direction and the addition of water in the reverse direction[6] with the formation of the substituted aldimide, $C_6H_5CH=N-C_7H_7$, as an intermediate product.

In accordance with the electronic conception of valence,[7] there is a possibility, after the loss of water from a β-hydroxylamine, of a change in the carbon-nitrogen linkage of such a nature that the carbon becomes completely oxidized as

[1] Biddle: Ann., 310, 9 (1900); Jones: Am. Chem. J., 20, 1 (1898); Hecker: Ibid., 50, 444 (1913); Beckmann: Ber., 26, 2631 (1893).

[2] Campisi and Amato: Ber., 4, 412 (1871).

[3] Tiemann and Friedländer: Ibid., 14, 1969 (1881).

[4] Pinner: Ibid., 17, 184 (1884); Werner: Ibid., 29, 1146 (1896).

[5] Walder: Ibid., 19, 1627, 3287 (1886)

[6] Jones: An. Chem. J., 50, 422, (1913).

[7] Ibid., 50, 438 (1913).

it is in carbon dioxide, (‡C‡), the nitrogen reduced from the state of oxidation in which it probably exists in hydroxylamine, (‡N=), to that of ammonia (-‡N≡);

$$R{+}\text{-}N^{+}_{-}{\ddagger}C{\ddagger}{=}O \longrightarrow R{+}\text{-}N{=}{\ddagger}C{\ddagger}{=}O$$

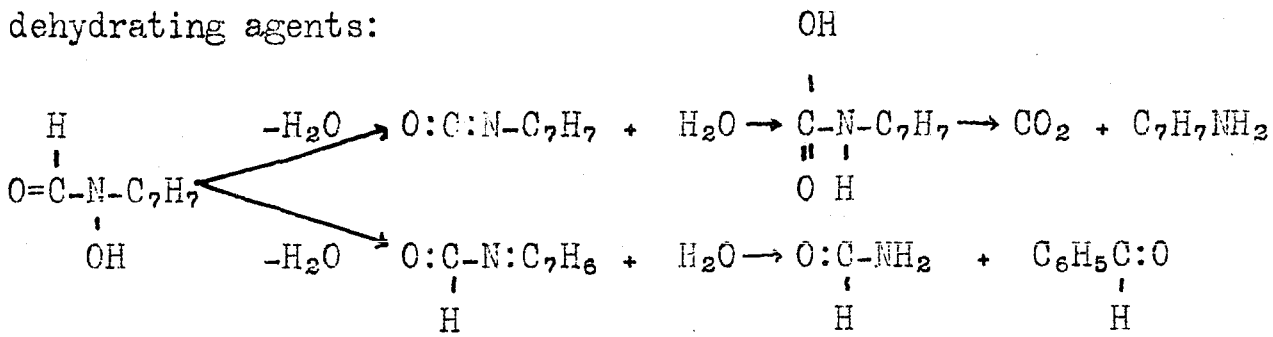
A more striking example[1] of the same process is the transformation brought about by treating formhydroxamic acid with alkalis, namely, to give isocyanates, carbamates, or carbonates and ammonia.

One would expect that β-acyl-β-alkyl(aryl)hydroxylamines containing an oxidizable acyl group would behave towards mild dehydrating agents in a manner similar to β-dibenzylhydroxylamine and that they would offer another possibility for intramolecular oxidation on treatment with strong dehydrating agents, such as phosphorous pentoxide, and might yield isocyanates which give by hydrolysis carbondioxide and amines. In which of the two possible directions, then, will oxidation proceed; will it take place in both directions simultaneously; or will it proceed exclusively in one direction if suitable dehydrating agents are employed? It was for the purpose of answering these questions that the present problem was undertaken.

Of the substituted acylhydroxylamines, β-benzylformhydroxamic acid was found best suited to the study of the problem under consideration. This led to its preparation, which was accomplished by the action of formic ethyl ester on β-benzyl-

[1] Wieland: Die Knallsaure, p. 32 (1909).

hydroxylamine. This compound, $O{:}CH\text{-}N(OH)\text{-}CH_2C_6H_5$, offers two possibilities for intramolecular oxidation when treated with dehydrating agents:



A consideration of these transformations from an electronic point of view will serve to make clear the intramolecular oxidations suggested. By the loss of water from β-benzylformhydroxamic acid, two isomers of the following electromeric formulas would be expected to result depending upon the direction in which the molecule of water is removed:

1. $O{=}C{-}N{-}C_7H_7$

2. $O{=}C{-}N{=}C{-}C_6H_5$ (H, H)

By hydrolysis alone, the first electromer could not give carbon dioxide and benzylamine nor could the second yield formamide and benzaldehyde, but, in each case, the original compound would be regenerated.[1] In order that these substances may result from hydrolysis there must be a transfer of negative electrons from carbon to nitrogen to give electromers of the two forms (1 and 2) previously indicated:

1a. $O{=}C{=}N{-}C_7H_7$

2a. $O{=}C{-}N{=}C{-}C_6H_5$ (H, H)

[1] Or be hydrolysed in the first case to give β-benzylhydroxylamine formic acid and in the other the same products.

These are the only electromers which would yield respectively carbon dioxide and benzylamine on hydrolysis in the one case and formamide and benzaldehyde in the other case.

It has been pointed out that Walder obtained benzylamine and benzaldehyde by treating β-dibenzylhydroxylamine with Beckmann's mixture and that Bamberger and Destraz got phenyl-isocyanate as a product by distilling β-benzylformhydroxamic acid with phosphorous pentoxide. With the hope of obtaining similar results the action of Beckmann's mixture and phosphorous pentoxide was tried separately upon β-benzylformhydroxamic acid.

(a) Two grams of β-benzylformhydroxamic acid was treated with an excess of a solution of dry hydrogen chloride in glacial acetic acid (Beckmann's mixture) and the mixture digested on a water-bath for two hours. At the end of the operation the benzaldehyde which was produced was extracted with ether. The aldehyde was identified by converting it into benzalphenylhydrazone. Of this last product, which melted sharply at 152.5°, 0.3 of a gram was obtained. A portion of the solution which remained after the extraction of benzaldehyde gave an isocyanide reaction for a primary amine which was likely benzylamine. Another portion reduced an ammoniacal solution of silver nitrate, probably due to the presence of formic acid. The remainder of the solution, upon evaporation, gave a residue consisting chiefly

of ammonium chloride. From these results it is evident that oxidation proceeded in both possible directions which have have been previously indicated.

(2) Five grams of the acid thououghly mixed with an excess of phosphorous pentoxide were subjected to distillation. By heating gently the mixture on a water-bath the components reacted violently with considerable charring, and giving, at the same time, two or three drops of a liquid smelling strongly of an isocyanate. This liquid upon treatment with aniline gave a crystalline product of phenylbenzylurea melting at 167° to 168°.

The β-benzylformhydroxamic acid used in the experiments which we have just described was obtained by carrying out the following reactions: (1) β-dibenzylhydroxylamine[1] by the action of benzyl chloride on hydroxylammonium chloride in the presence of sodium carbonate; (2) N-benzylisobenzaldoxime[2] by oxidizing β-dibenzylhydroxylamine with potassium ferricyanide; (3) β-benzylhydroxylamine[3] by hydrolysing N-benzylisobenzaldoxime with hydrochloric acid; (4) β-benzylformhydroxamic acid by treating β-benzylhydroxylamine with formic ethyl ester. In the experimental part, which follows, an account will be of our modifications of the first three processes and also a description of the method employed for obtaining β-benzylformhydroxamic acid.

[1] Behrend and Leuchs: Ann., 257, 216 (1890).

[2] Ibid.,

[3] Ibid., 257, 224; Beckmann: Ber., 22, 438 (1889).

EXPERIMENTAL PART

β-dibenzylhydroxylamine.

To a solution of 14g. of hydroxylammonium chloride and 50g. of benzyl chloride in 200cc. of 70% alcohol 60g. of crystallized sodium carbonate were added. The mixture was then boiled for two hours in a flask provided with a reflux-condenser. The product was filtered and to the filtrate was added an excess of ice water to precipitate the β-dibenzylhydroxylamine. After the addition of water the flask was placed in a freezing-mixture where it was allowed to remain until complete precipitation had taken place. Upon filtration 26g. of pure white needle-like crystals of β-dibenzylhydroxylamine were obtained which melted at 123°.

N-benzylisobenzaldoxime.

Eighteen grams of β-dibenzylhydroxylamine were placed in a one liter separatory-funnel and to it were added 30cc. of ehter, and concentrated solutions of 13.5g. of potassium hydroxide and 72g. of potassium ferricyanide. The mixture was shaken vigorously until the oxidation of the β-benzylhydroxylamine was complete. The process of oxidation required only ten minutes. The aldoxime was obtained by making three extractions with ether. Upon evaporation of the ether a residue of 17g. of N-benzylisobenzaldoxime resulted. The pure substance, which was obtained by precipitating it from an ehter solution with ligroin, melted at 81°.

β-benzylhydroxylamine.

Hydrolysis of N-benzylisobenzaldoxime.- The preparation of β-benzylhydroxylamine has been described by Beckmann[1] and also by Behrend and Leuchs; but they do not state their yields. By modifying their methods we have been able to obtain better results than by following their directions.

Seventeen grams of the aldoxime was treated with 34cc. of concentrated hydrochloric acid and steam passed through the mixture until all the benzaldehyde had distilled over. The resulting product, free from the aldehyde, was then heated over a low flame until the greater portion of hydrochloric acid had been driven off. To the cooled residue a cold saturated solution of sodium carbonate was added until the solution reacted neutral to litmus. A small amount of solid remained which was separated by filtration. To the filtrate, after it had been cooled to zero, was added enough sodium carbonate to make the solution distinctly alkaline. After an hour the β-benzylhydroxylamine had precipitated in an absolutely pure state from the filtrate. The solid residue which was obtained from the first filtration was extracted with ligroin from which a small amount of the desired substance was recovered. In this way 6 grams of the pure compound, which melted at 57°, was obtained.

β-benzylformhydroxamic Acid.

Action of formic ehtyl ester on β-benzylhydroxylamine.- A solution of 4 grams of β-benzylhydroxylamine in 8 grams of formic ethyl ester was kept at room temperature, in a stoppered flask, for 14 days. At the end of this time, a

test portion of the mixture showed no reduction of copper acetate but gave a copper salt. The contents of the flask were transferred to an evaporating dish. The solution was evaporated in a vacuum desiccator until a thick paste remained. This paste was placed over solid potassium hydroxide in a desiccator and kept in a cool place to facilitate crystallization. At the end of three days most of the contents had crystallized. The substance was separated from impurities by dissolving it in ether and precipitating it with ligroin. Only enough ligroin was added to give a slight turbidity. On evaporation of the ether crystals of β-benzylformhydroxamic acid separated as long white needles. The yield was three grams or 67 per cent of the theory.

An analysis gave the following values for nitrogen, carbon, and hydrogen:

0.2211 gram substance gave 19.2cc. N_2 at 25.5° and 743.5 mm. (uncorr.)

	Calculated for $C_8H_9O_2N$	Found
N	9.27	9.45

0.2028 gram gave 0.4720 gram CO_2 and 0.1126 gram H_2O.

	Calculated for $C_8H_9O_2N$	Found
C	63.54	63.48
H	6.00	6.16

β-benzylformhydroxamic acid is easily soluble in ether and alcohol and slightly soluble in water. It melted at 49° to 50°

and shows little if any decomposition at its boiling point. With a hot alcoholic solution of the acid a concentrated solution of copper acetate gave a copper salt which precipitated as gray greenish blue crystals. The salt was purified by recrystallization from hot 60 to 70 per cent alcohol. It decomposed without melting.

An analysis of substance gave for copper the following value:

0.3394 gram substance gave 0.0593 gram copper.

Calculated for $C_{16}H_{16}O_4N_2Cu$	Found
17.48	17.47

Action of Beckmann's Mixture on β-benzylformhydroxamic Acid

Two grams of β-benzylformhydroxamic acid was digested for two hours, on a water-bath, with an excess of a solution of dry hydrogen chloride in glacial acetic acid (Beckmann's mixture). The benzaldehyde which was pdoduced during the operation was extracted with ether. The aldehyde was identified by converting it through the action of phenylhydrazine into benzalphenylhydrazone. There was only 0.3g. of the hydrazone obtained. The substance was pure as shown by the fact that it melted sharply at 152.5 degrees. The solution which remained after the separation of benzaldehyde was divided into two portions, after it was shown to reduce an ammoniacal silver nitrate solution.

One portion gave isocyanide reaction for a primary amine upon treatment with chloroform and alcoholic potash; the other, on evaporation, gave a residue consisting chiefly of ammonium chloride.

Action of Phosphorous Pentoxide upon β-benzylformhydroxamic Acid.

Five grams of β-benzylformhydroxamic acid thoroughly mixed with an excess of phosphorous pentoxide was subjected to distillation. On heating the mixture gently, by means of a water-bath, the components reacted violently. Practically the entire contents of the flask became a black tarry mass. The water-bath was replaced by a metal-bath in order to secure a higher temperature, so that any liquid present would be caused to distill over. In this way two or three drops of a liquid, which smelled strongly of an isocyanate, was obtained. By treating the distillate with aniline a crystalline product of phenylbenzylurea melting at 167° to 168° resulted.

Summary

(1) β-benzylformhydroxamic acid was obtained by the action of β-benzylhydroxylamine on formic ethyl ester.

(2) β-benzylformhydroxamic gave a characteristic copper salt.

(3) β-benzylformhydroxamic acid upon treatment with Beckmann's mixture suffered intramolecular oxidation in two directions giving carbon dioxide and benzylamine in the one case and formamide and benzaldehyde in the other.

(4) β-benzylformhydroxamic acid upon treatment with phosphorous pentoxide suffered intramolecular oxidation giving benzylisocyanate.

PART II

HYDROXAMIC ACIDS OF SUBSTITUTED ACETIC ACID.

It is rather singular that until very recently no halogen substituted hydroxamic acids of the aliphatic series have been prepared. The first representative of these compounds was described in 1904 by Francesconi[1] who by the action of hydroxylammonium chloride on chloroacetamide obtained chloroacethydroxamic acid. Later the same substance was prepared by Jones[2] on treating a cold alcoholic solution of chloroacetic ethyl ester with free hydroxylamine dissolved in absolute alcohol. In this laboratory both bromo- and iodoacethydroxamic acids have been made by Jones and Werner[3].

It has been shown that hydroxamic acids of both the aliphatic and aromatic series together with their acyl esters and salts undergo Beckmann rearrangement giving interesting decomposition products when subjected to the action of heat. Our concern was not so much to describe new hydroxamic acids as to obtain a definite knowledge of the changes which halogen substituted hydroxamic acids of the aliphatic series would undergo if heated at or somewhat above their melting points. In order to determine these changes, dichloroacet-

[1] Gazz. chim. ital., (I) 34, 428 (1904).

[2]

[3]

[4] Pieschel: Ann., 175, 305 (1877); Ibid., p. 324

[5] Losen: Ibid., 186, 2 (1887); Ibid., p. 21; Ibid., p. 27; Ibid., p. 44.

hydroxamic acid was prepared since it seemed best suited to the study of the problem in hand. The preparation was accomplished by the action of an alcoholic solution of hydroxylamine on dichloroacetic ethyl ester. It was found necessary to carry out the reaction at minus ten degrees to prevent decomposition and to increase the yield of the acid. The decomposition is evidently due to the replacement of the chlorine atoms giving hydroxylammonium chloride and other products the nature of which has not been determined. Dichloroacethydroxamic acid is readily soluble in water, alcohol, ether, and acetic ethyl ester but practically insoluble in most of the other organic solvents. Its solution in water gives a strong acid reaction towards litmus, and a wine red coloration on the addition of ferric chloride. It crystallizes in the form of needles which melt at 86^{0} to 87^{0}.

It is a well established fact that hydroxamic acids and also many of their derivatives undergo rearrangement of the Beckmann type. The early researches of Lossen and his collaborators[1] furnish many striking instances of such rearrangement among the aromatic hydroxamic acids. He found that the mono-, di- and triacylated derivatives of hydroxamic acids upon being subjected to the action of heat gave isocyanates or their decomposition products. These changes

[1] Loc. cit.

are evidently of the Beckmann type as shown by Lossen's results as follows:

(1) Monohydroxamic acids gave on distillation products according to the equation:

$$R\text{-}C(:O)NH(OH) \longrightarrow R\text{-}N{:}C{:}O + H_2O \longrightarrow R\text{-}NH_2 + CO_2$$

(2) Dihydroxamic acids gave an isocyanate, an acid, an anilide and carbon dioxide:

a. $R\text{-}C(:O)NH(OCOR') \longrightarrow R\text{-}N{:}C{:}O + HO\text{-}C(:O)R' +$

b. $R\text{-}C(:O)NH(OCOR') \longrightarrow RNH\text{-}C(:O)R' + CO_2$

(3) Trihydroxamic acids. The three isomers, benzanisbenzhydroxylamine, dibenzanishydroxylamine and anisdibenzhydroxylamine on distillation gave the same substances although the proportion of these products were quite different:

a. $N(C_8H_7O_2)(C_7H_5O)(C_7H_5O) \longrightarrow CH_3OC_6H_4N{:}C{:}O + (C_6H_5CO)_2O$

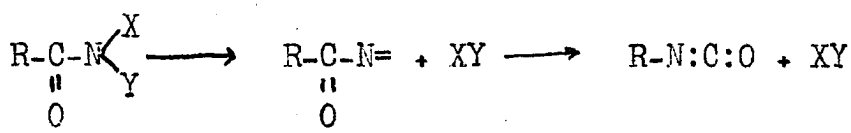
b. $N(C_8H_7O_2)(C_7H_5O)(C_7H_5O) \longrightarrow C_6H_5N{:}C{:}O + C_6H_5CO\text{-}O\text{-}COC_6H_4CC$

A few years later Thiele and Pickard[1] showed in their study of potassium salts of dihydroxamic acids that it was necessary to assume as the first stage in the decomposition, by heat, of the salts of these acids that an isocyanate is formed together with the potassium salt of the acid ~~related~~ related to the acyl group substituted for the hydrogen in the oxime group. It is evident that by hydrolysis the isocyanate would yield amines which in the presence of the unchanged isocyanate

[1] Ann., 309, 189(1899).

would give disubstituted ureas. Their assumption was based on the fact that when alcohol was used instead of water urethanes were obtained in place of disubstituted ureas.

Theories have been advanced by both Stieglitz[1] and Jones[2] to interpret the mechanism of the Beckmann rearrangement. Stieglitz maintains the position that such a rearrangement results from a molecular dissociation followed by a change in valence of nitrogen from three to one and a subsequent readjustment of groups due to the influence of univalent nitrogen:



It may be said in favor of Stieglitz's interpretation that Beckmann rearrangement occurs in each case where it is possible to foresee from the constitutional formula the probability of a dissociation in the manner indicated by the foregoing equation. On the other hand when such conditions are not apparent, rearrangement does not occur.

Reference has been made to the fact that the esters of hydroximic acid exist in two stereoisomeric modifications. The two isomeric forms of ethylbenzhydroximic acid were obtained by Lossen.[3] It was observed by Alfred Werner[4] that the syn-modi-

[1] Am. Chem. J., 18, 751 (1896); Ibid., 29, 49 (1903); Stieglitz and Earl: Ibid., 30, 399, 412 (1903); Stieglitz and Slossen; Ber., 28, 3236 (1896); Ibid., 34, 1613 (1902)

[2] Am. Chem. J., 48, 1 (1912); Ibid., 50, 440 (1913).

[3] Ann., 252, 211 (1889).

[4] Ber., 29, 1146 (1896).

fication upon treatment with phosphorous pentachloride and a subsequent treatment with water suffered Beckmann rearrangement giving the ethyl ester of phenylcarbamic acid, while the other isomer gave a complex ester of phosphoric acid. He assumed that the following reactions took place:

1. $C_6H_5-\underset{\underset{HO-N}{\|}}{C}-O-C_2H_5 \longrightarrow C_6H_5-\underset{\underset{Cl-N}{\|}}{C}-O-C_2H_5 \longrightarrow Cl-\underset{\underset{C_6H_5-N}{\|}}{C}-O-C_2H_5$

$Cl-\underset{\underset{C_6H_5-N}{\|}}{C}-O-C_2H_5 + H_2O \longrightarrow HCl + HO-\underset{\underset{C_6H_5-N}{\|}}{C}-O-C_2H_5$

2. $3\ C_6H_5-\underset{\underset{N-OH}{\|}}{C}-O-C_2H_5 + PCl_5 \longrightarrow 3\ HCl + (C_6H_5-\underset{\underset{NO-}{\|}}{C}-O-C_2H_5)_3PCl_2$

$(C_6H_5-\underset{\underset{NO-}{\|}}{C}-O-C_2H_5)_3PCl_2 + H_2O \longrightarrow (C_6H_5-\underset{\underset{NO-}{\|}}{C}-O-C_2H_5)_3PO + 2\ HCl$

Werner's interpretation of the behavior of the two isomers towards phosphorous pentachloride gives evidence to show that both forms do not suffer Beckmann rearrangement. But the hypothesis of Stieglitz[1], that the presence of univalent nitrogen together with some reagent HX (as hydrogen chloride), is the determining factor for such a rearrangement leads one to assume that both forms might undergo Beckmann rearrangement, a condition not in accord with Werner's experiment. In terms of the corpuscular atomic hypothesis Jones[2] was first to suggest an explanation of this difference in behavior of the isomers.

[1] Loc. Cit.

[2] Am. Chem. J., 50, 414 (1913).

On the basis of the theories of Stieglitz[1] and Jones[2] it was anticipated that dichloroacethydroxamic acid, on decomposition by heat, would lose a molecule of water and undergo rearrangement to form dichloromethyl isocyanate, and that the latter compound would be hydrolysed to give dichloromethylamine and carbon dioxide, and furthermore dichloromethylamine would break down into prussic and hydrochloric acids according to the following equations:

(1) $HCCl_2-\underset{\underset{O}{\|}}{C}-\overset{OH}{\overset{|}{N}}\longrightarrow HCCl_2-\underset{\underset{O}{\|}}{C}-N: \longrightarrow HCCl_2-N:C:O + H_2O$

(2) $HCCl_2-N:C:O + H_2O \longrightarrow HCCl_2-NH_2 + CO_2$

(3) $HCCl_2-NH_2 \longrightarrow HNC + 2HCl$

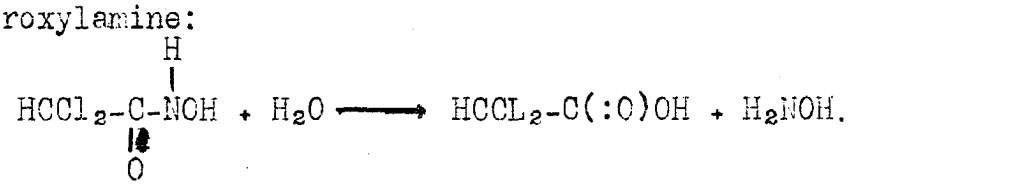
In the actual experiment the acid was decomposed, at a temperature of 145 degrees, in an atmosphere of hydrogen. A U-tube, immersed in a freezing mixture, was connected with the distilling-tube in order to condense any volatile liquid. The evolved gases were led through three wash-bottles each containing a solution of barium hydroxide. The products which were isolated were as follows: (1) Hydrochloric acid; (2) Prussic acid; (3) Carbon dioxide; (4)

[1] Loc. cit.

[2] Loc. cit

Formic acid; (5) Ammonium chloride; (6) Dichloroacetamide; (7) Dichloroacetic acid. Together with the substances enumerated were also obtained 81.3cc. of a gas which was probably nitrogen. Very likely this gas owed its origin to the decomposition of free hydroxylamine the formation of which will be accounted for later.

From these experimental results it is evident that the anticipated reactions actually took place and that in addition to them side reactions also occured. There are but two plausable possibilities of hydrolysis by the water which was liberated according to the first reaction, namely, hydrolysis of the isocyanate to give the products already referred to and hydrolysis of unchanged dichloroacethydroxamic acid itself to yield dichloroacetic acid and hydroxylamine:



On the basis of this interpretation it was easy to account, in a quantitative way, for all the products identified.

It was pointed out by Nef[1] that prussic acid acts on acetic acid giving acetic anhydride and formamide which , at a higher temperature , react to form acetamide and formic acid. It is likely that under the conditions of the experiment dichloroacetic acid would behave in a manner similar

[1] Ann., 287, 347(1895)

to acetic acid and would form dichloroacetamide and formic acid.

The formic acid produced would react with free hydroxylamine to give carbon dioxide, ammonia, and water:

$$H_2NOH + H\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH \longrightarrow CO_2 + NH_3 + H_2O.$$

And ammonium chloride would be formed from ammonia and hydrogen chloride. Furthermore, at the temperature of the experiment any hydroxylamine which had not reacted with formic acid would decompose chiefly into water, nitrogen, and ammonia:

$$3H_2NOH \longrightarrow 3H_2O + N_2 + NH_3$$

It was thought likely that the acyl esters of dichloroacethydroxamic acid and their salts would give interesting results when decomposed by heat. In this case there is little possibility of water being set free which would have a disturbing influence upon the course of the reaction, so that in each instance dichloromethylisocyanate and an acid or its salt would be expected;

$$HCCl_2\text{-}\underset{\underset{H}{\diagdown}}{\overset{\overset{O}{\|}}{C}}\text{-}N\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}R \longrightarrow HCCl_2N{:}C{:}O + R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH$$

For the determination of this point the benzoyl ester of dichloroacethydroxamic acid was prepared by treating dichloroacethydroxamic acid with benzoic anhydride. Neither the sodium or potassium salt of this ester could be isolated in the pure state. A small amount of the sodium salt was obtained but suffered spontaneous decompositon even

when placed at once in a desiccator. Similar phenomena were observed by Jones[1] during his study of the salts of the benzoyl ester of phenylacethydroxamic acid.

The benzoyl ester was subjected to heat in an atmosphere of hydrogen in a manner similar to that employed in the decomposition of dichloroacethydroxamic acid itself. A quantitative yield of benzoic acid was obtained. A liquid condensed in the U-tube which possessed a strong isocyanate odor and which on treatment with water gave carbon dioxide, prussic acid, and hydrochloric acid;

(1) $HCCl_2\text{-}N{:}C{:}O \longrightarrow CO_2 + HCCl_2\text{-}NH_2$

(2) $HCCl_2\text{-}NH_2 \longrightarrow HNC + 2HCl$

In this connection an attempt was made to prepare dichloromethylisocyanate by the method employed by Schroeter[2] and to study its properties. Although the experiment was not entirely satisfactory, it was not repeated. Five grams of sodium hydrazoate was treated with an equivalent amount of dichloroacetyl chloride dissolved in benzene. The components of the mixture did not react readily even at the boiling point of benzene. The flask containing the substances was set aside for a month, at the end of which time its contents were examined. It was found to contain a solid portion consisting largely of a gelatinous mass of sodium chloride and a liquid portion. The liquid was subjected to fractional distillation. An impure product

[1] Am. Chem. J., 48, 8 (1912).

[2] Ber., 42, 3356 (1909).

was collected which boiled between 85° and 90°. This fraction was a colorless liquid possessing a sharp penetrating odor; but not a trace of prussic acid could be detected. It gave, however, after the addition of water, distinct tests for carbon dioxide, hydrochloric acid, and prussic acid. These results are in perfect agreement with the theory expressed by equations (1) and (2).

In the case of the preparation of dichloroacthydroxamic acid it was found, as previously stated, that at a temperature of minus ten degrees a better yield of the acid was obtained. Using this information, an attempt was made to prepare trichloroacethydroxamic acid which we had not been able to make. Accordingly, an alcoholic solution of trichloroacetic ethyl ester was cooled to minus fifteen degrees and to it was added drop by drop a calculated amount of hydroxylamine dissolved in alcohol. Instead of getting the compound sought, the hydroxylammonium salt of trichloroacethydroxamic acid, $CCl_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}\underset{\underset{OH}{|}}{NH_3}$, was obtained. At present this is the only hydroxylammonium salt of a hydroxamic acid described.

By the method used for the preparation of dichloroacethydroxamic acid, glycocoll hydroxamic acid was obtained by the action of glycocoll ethyl ester on free hydroxylamine. The acid decomposed at 140° giving a tarry residue as the chief product. A small amount of a volatile product was given off which when passed into water gave an isocyanide reaction, which showed the presence of a primary amine, possibly methyl amine.

EXPERIMENTAL PART

Dichloroacethydroxamic Acid

The action of hydroxylamine on dichloroacetic ethyl ester.- To a solution of 3o grams of dichloroacetic ethyl ester in 10cc. of absolute alcohol cooled to minus ten degrees by means of a freezing mixture, a concentrated alcoholic solution of hydroxylamine was added drop by drop. At no time was the temperature allowed to rise above minus eight degrees. During the addition of the hydroxylamine the flask was shaken continously to prevent local heating. These precautions were found to be necessary in order to avoid decomposition due to the replacement of the chlorine atoms. No precipitate should form during the entire operation. The separation of a white solid indicates that the temperature has not been kept sufficiently low, or that ~~that~~ the hydroxylamine has been added too rapidly. After the two substances were mixed they were kept at a temperature of a freezing mixture for two hours and then the flask was transferred to an ice box where it was allowed to remain for a week. At the end of this time the action was complete and the solution was clear. The alcohol and excess ester was then evaporated in vacuo. A white crystalline solid remained admixed with a small amount of unchanged ester. The product was then collected, dried and dissolved in acetic ethyl ester. From this solution ligroin precipitated dichloroacethydroxamic acid as fine

needles which belonged to the regular system and melted at 86° to 87°. The yield was 17.5 grams or 58% of the theory.

An analysis gave the following value for nitrogen:

0.2045 gram of substance gave 18.2cc of nitrogen at 26.5° 742.3mm. (uncorr.).

	Calculated for $C_2H_3O_2NCl_2$	Found
N	9.73	9.63

DECOMPOSITION OF DICHLOROACETHYDROXAMIC ACID BY HEAT

Three grams of the acid were heated in a distilling-tube so connected that any volatile products formed would first have to pass through a U-tube, immersed in a freezing mixture, and then, if gaseous, through a series of three wash-bottles each containing a solution of barium hydroxide. During the distillation a constant stream of pure hydrogen was caused to flow through the system. At 110° a vigorous decomposition of the acid took place. The temperature was raised to 145°, at which point it was maintained for ten minutes. The products isolated and their amounts were as follows:

(1) Carbon dioxide which was estimated as barium carbonate.

0.816g. of barium carbonate equivalent to 0.192g. of carbon dioxide was obtained.

(2) Amount of prussic acid determined by Liebig's method was 0.027g.

(3) Amount of HCl determined by Liebig's method was 0.0142g.

In the experiment 200cc. of 0.385 normal barium hydroxide

solution was used. After the reaction was complete the hydroxide solution had been reduced to 0.300 normal.

Amount of $Ba(OH)_2$ used	6.136 grams
,, ,, ,, not neutralized	5.139 ,,
,, ,, ,, neutralized	0.997 ,,
,, ,, ,, ,, by carbon dioxide	0.748 ,,
,, ,, ,, ,, ,, prussic acid	0.086 ,,
,, ,, ,, ,, ,, hydrochloric acid	0.0343 ,,
Total amount of barium hydroxide neutralixed	0.883 ,,

(4) There condensed in the U-tube 0.76g. of formic acid which was identified by converting it into its characteristic lead salt.

(5)After the distillation of the acid there remained in the distilling-tube a residue of 1.8g. This residue was extracted with ether leaving 0.38g. of ammonium chloride undissolved. It was identified by making an analysis of its platinum salt.

Weight of $(NH_4)_2PtCl_6$	0.1538 gram
,, ,, platinum	0.0648 ,,

Calculated percent of Pt	Found
43.96	43.72

(6) The ether extract was treated with a solution of sodium carbonate. In this way a neutral portion of 0.2g. of dichloroacetamide was obtained upon evaporation of the ether. The amide was purified by precipitating it from an ether solution

with ligroin. It melted at 97.5° and had all the properties of dichloroacetamide prepared from dichloroacetic ethyl ester and ammonia.

(7) The solution left from (6) was acidified and extracted with ether. From the abstraction 1.14g. of dichloroacetic acid resulted after the evaporation of the ether. The acid was identified both by comverting it into its ammonium salt and its amide. The ammonium salt crystallized in plates which decomposed at 100° without melting.

The products resulting from the distillation of three grams of dichloroacethydroxamic acid may be summarized as follows:

1. Prussic acid	0.0270	gr.
2. Hydrochloric acid	0.0142	,,
3. Carbon dioxide	0.192	,,
4. Ammonium chloride	0.38	,,
5. Formic acid	0.776	,,
6. Dichloroacetamide	0.20	,,
7. Dichloroacetic acid	1.18	,,
Total	2.7692	,,

One gram of dichloroacethydroxamic acid gave on distillation 27.1cc. of gas which did not give a test for either nitrous oxide or carbon monoxide. If the gas was all nitrogen, the the amount from three grams would have weighed 0.1017g. This would give a total of 2.8709g. of products from 3g. of the acid.

The Benzoyl Ester of Dichloroacethydroxamic Acid

Action of dichloroacethydroxamic acid on benzoic anhydride.- Three grams of the acid was thoroughly pulverized with 4.8g. of benzoic anhydride and the mixture heated for five minutes at 65° to 70°. The residue was extracted several times with ligroin to remove the benzoic acid. The ester which remained was dissolved in ether. The ether solution was filtered and the ester precipitated with ligroin. By carefully adding the ligroin so that it did not mix with the ether and letting the flask remain undisturbed sword-like crystals over an inch long were obtained. In this way 4.7g. of the ester was precipitated. The crystals belong to the irregular system and melt at 77° to 78°.

An analysis gave the following value for nitrogen:

0.3120 gram gave 14.9cc. of nitrogen at 19.5° and 751.7mm.

	Calculated for $C_9H_7O_2NCl_2$	Found
N	5.66	5.42

Hydrolysis of Benzoyl Ester of Dichloroacethydroxamic Acid with Hydrochloric Acid

Five grams of the ester was treated with hydrochloric acid and the mixture heated in a sealed tube for one hour at 100°. The resulting product was extracted with ether. From this extraction 2g. of benzoic acid and a small amount of dichloroacetic acid was obtained. The water solution on evaporation gave a

residue of 0.08g. of hydroxylammonium chloride which was identified by converting it into benzophenoxime which melted at 140° to 141°.

Distillation of the Benzoyl Ester of Dichloroacethydroxamic Acid

One gram of the ester was heated at 150° in an atmosphere of hydrogen. A volatile liquid was condensed in a U-tube immersed in a freezing mixture. The evolved gases were passed through hydrochloric acid and then through a solution of barium hydroxide. The hydrochloric acid remained unaffected. A precipitate of 0.09g. of barium carbonate was obtained. In the U-tube were condensed a few drops of a liquid possessing a sharp isocyanate odor. The liquid when treated with water gave carbon dioxide, hydrochloric acid and prussic acid. The residue, which was colored slightly brownish, consisted almost entirely of benzoic acid.

Hydroxylammonium Salt of Trichloroacethydroxamic Acid

The action of hydroxylamine on trichloroacetic ethyl ester.- Twenty-nine grams of trichloroacetic ethyl ester was dissolved in 15cc. of absolute alcohol and the solution cooled to -15°. To the cooled solution were added drop by drop 8g. of hydroxylamine in alcoholic solution. At no time was the temperature

permitted to rise above -15° and during the addition of the hydroxylamine the flask was shaken vigorously to prevent local heating. After the solution had remained at the given temperature for about twenty minutes crystals began to form and continued to do so until the entire contents of the flask seemed solid. The crystals were separated from the small amount of liquid, dried and dissolved in acetic ethyl ester. From this solution the salt was precipitated as needles belonging to the irregular system. They melted at 72° to 73° with decomposition. The yield was 8 grams. A chlorine determination showed that neither of the chlorine atoms had been displaced.

An analysis gave the following value for nitrogen:

0.4890 gram substance gave 56cc. N at 19° and 742.1mm. (uncorr.).

	Calculated for $C_2H_5O_2N_2Cl_3$	Found
N	13.25	13.01

Glycocoll Hydroxamic Acid

Action of hydroxylamine on gylcocoll ethyl ester.- Twenty grams of glycocoll ethyl ester prepared by the method of E. Fischer[1] were treated, at minus ten degrees, with an alcoholic solution of hydroxylamine. The hydroxylamine was added slowly and the flask shaken vigorously after each addition. A clear solution resulted from which a white solid

[1] Ber., 34, 436(1901).

began to separate in the course of an hour. The mixture was left in an ice-box for 12 hours. At the end of this time the reaction was complete. The contents of the flask were collected and dried. The acid is soluble in water, slightly soluble in alcohol and insoluble in other organic solvents. It crystallized from a dilute alcohol solution as parallelopipeds melting at 140° with decomposition. The yield was quantitative.

An analysis gave the following value for nitrogen:

0.1668 gram gave 44.8cc. of nitrogen at 14° and 745mm. (uncorr.).

Calculated for $C_2H_6O_2N_2$	Found
31.09	31.16

Summary

The foregoing pages are a record of the method of preparation of dichloroacethydroxamic acid; of the benzoyl ester of dichloroacethydroxamic acid; of the hydroxylammonium salt of trichloroacethydroxamic acid; of glycocoll hydroxamic acid; and an investigation of the decomposition products of dichloroacethydroxamic acid, of its benzoyl ester and glycocoll hydroxamic acid when they were subjected to the action of heat.