while the latter give first isocyanates, then *di-alkyl-*, or *di-aryl-*ureas and finally carbon dioxide and amines.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

ON DICHLOROACETHYDROXAMIC ACID AND ITS REARRANGEMENT, AND AMINOACETHYDROXAMIC ACID.

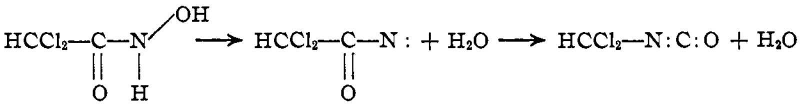
BY LAUDER WILLIAM JONES AND M. CANNON SNEED.[1]

Received January 5, 1917.

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

It has been shown that hydroxamic acids of the aliphatic and of the aromatic series, together with their acyl esters and salts, when subjected to the action of heat, undergo the Beckmann rearrangement. Our concern was not so much to describe new hydroxamic acids, as to obtain a definite knowledge of the changes which take place in halogen substituted hydroxamic acids of the aliphatic series when they are heated at a temperature near or somewhat above their melting points. In order to determine these changes, dichloroacethydroxamic acid was selected, since it seemed best suited to the study of the problem in hand. It was prepared by the action of an alcoholic solution of hydroxylamine upon ethyl dichloroacetate.

It was anticipated that dichloroacethydroxamic acid, when decomposed by heat, would lose a molecule of water and undergo the Beckmann rearrangement to form dichloromethyl isocyanate; and that the latter compound might be hydrolyzed to give dichloromethylamine and carbon dioxide. Furthermore, that dichloromethylamine would dissociate into prussic and hydrochloric acids according to the following equations:

(1)


$$\mathrm{HCCl_2{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{}^{\diagup OH}} \longrightarrow \mathrm{HCCl_2{-}\underset{\underset{O}{\|}}{C}{-}N:} + \mathrm{H_2O} \longrightarrow \mathrm{HCCl_2{-}N{:}C{:}O} + \mathrm{H_2O}$$

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[1] The material presented here is used by Sneed in his dissertation in part fulfillment of the requirements for the Ph.D. degree of the University of Cincinnati.

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

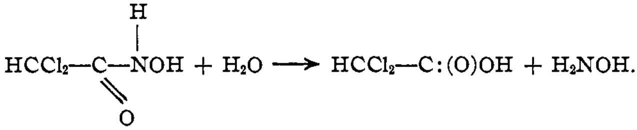
[3] THIS JOURNAL, 39, 413 (1917).

(2) $HCCl_2\text{—}N:C:O + H_2O \longrightarrow HCCl_2\text{—}NH_2 + CO_2$

(3) $HCCl_2\text{—}NH_2 \longrightarrow HCN + 2HCl$

When dichloroacethydroxamic acid was heated at a temperature of about 145°, the products actually isolated were: (1) Carbon dioxide; (2) Prussic acid; (3) hydrochloric acid; (4) formic acid; (5) ammonium chloride; (6) dichloroacetamide; (7) dichloroacetic acid. In addition to these substances, a gas, probably nitrogen, was formed. It is very likely that this gas owed its origin to the decomposition of free hydroxylamine, the formation of which will be accounted for later.

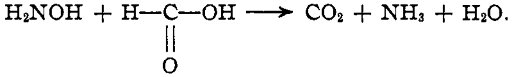
From these experimental results, it is evident that the anticipated reactions actually took place, and that, in addition to them, side reactions also occurred. There are two possible ways in which hydrolysis by water may occur, namely, hydrolysis of the isocyanate to form the products already referred to in the equations given above, and hydrolysis of unchanged dichloroacethydroxamic acid, itself, to yield dichloroacetic acid and hydroxylamine.



$$HCCl_2\text{—}\underset{\displaystyle O}{\overset{}{C}}\text{—}\overset{\displaystyle H}{\overset{|}{N}}OH + H_2O \longrightarrow HCCl_2\text{—}C:(O)OH + H_2NOH.$$

On this basis, 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 to give 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 similar manner, and would yield dichloroacetamide and formic acid. Formic acid would then react with free hydroxylamine to give carbon dioxide, ammonia and water.



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

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 to give chiefly water, nitrogen, and ammonia

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

It was expected that the acyl esters of dichloroacethydroxamic acid and their salts would give interesting results when decomposed by heat, since there is no possibility in this case of water being set free to exert a disturbing influence upon the course of the reaction, so that dichloro-

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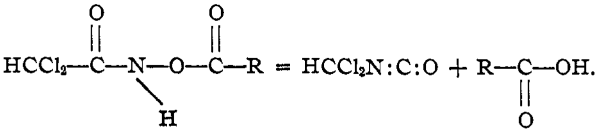
[1] *Ann.*, 287, 347 (1895).

methylisocyanate and an acid, or its salt, would be formed by rearrangement.



$$HCCl_2—\overset{O}{\overset{\|}{C}}—\underset{\diagdown\atop H}{N}—O—\overset{O}{\overset{\|}{C}}—R = HCCl_2N:C:O + R—\underset{O}{\underset{\|}{C}}—OH.$$

For the determination of this point, the benzoyl ester of dichloroacethydroxamic acid was prepared by treating dichloroacethydroxamic acid with benzoic anhydride. Neither the sodium salt nor the potassium salt of this ester could be isolated. The sodium salt was obtained, but it suffered spontaneous decomposition even when placed at once in a desiccator. Similar phenomena were observed by Jones[1] during his study of the potassium salts of the benzoyl ester of phenylacethydroxamic acid.

The benzoyl ester was subjected to heat in an atmosphere of hydrogen. A quantitative yield of benzoic acid was obtained. A liquid distilled which possessed a strong isocyanate odor, and which, on treatment with water, gave carbon dioxide, prussic acid and hydrochloric acid.

$$(1)\quad HCCl_2 — N : C : O + H_2O \longrightarrow CO_2 + HCCl_2 — NH_2.$$

$$(2)\quad HCCl_2 — NH_2 \longrightarrow HNC + 2HCl.$$

In this connection, an attempt was made to prepare dichloromethylisocyanate by the method employed by Schroeter[2] in the preparation of monochloromethylisocyanate. Although the experiment was not entirely satisfactory, a colorless liquid was obtained which boiled between 85° and 90°. It possessed a sharp penetrating odor, but no odor of prussic acid could be detected. Upon the addition of water, however, it gave tests for carbon dioxide, hydrochloric acid and prussic acid. These results are in perfect agreement with the theory expressed by Equations 1 and 2.

By the method used in the preparation of dichloroacethydroxamic acid, aminoacethydroxamic acid was obtained by the action of ethyl aminoacetate on free hydroxylamine.

EXPERIMENTAL PART.

I. Dichloroacethydroxamic Acid, $Cl_2CH.C\overset{\;\;O}{\diagup\!\!\diagup}—NH(OH)$.

1. The Action of Hydroxylamine on Ethyl Dichloroacetate.—To a solution of 30 g. ethyl dichloroacetate in 10 cc. of absolute alcohol cooled to —10°, a concentrated alcoholic solution of hydroxylamine was added drop by drop. At no time was the temperature allowed to rise above —8°. During the addition of the hydroxylamine, the flask was shaken

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

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

continuously 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, "basic" hydroxylammonium chloride, indicates that the temperature has not been kept sufficiently low, or 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 several days. At the end of this time, the action was complete, and the solution was still clear. The alcohol and excess of ester were removed *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 melted at 86° to 87°. It was readily soluble in water, alcohol, ether and ethyl acetate, but practically insoluble in most of the other organic solvents. Its solution in water showed a strong acid reaction towards litmus, and a wine-red coloration on the addition of ferric chloride. The yield was 17.5 g., or 58% of the theory.

0.2045 g. of subst. gave 18.2 cc. N_2 at 26.5° and 742.3 mm. (uncorr.).

Calc. for $C_2H_3O_2NCl_2$: N, 9.73. Found: N, 9.63.

2. Decomposition of Dichloroacethydroxamic Acid by Heat.—Three grams of the acid were heated in a distilling tube connected so that any volatile products formed would first pass through a U-tube immersed in a freezing mixture, and then through a series of three wash bottles each containing a standard solution of barium hydroxide. During the distillation, a constant stream of pure hydrogen flowed through the system. At 110°, 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:

Volatile Products: (*a*) Carbon dioxide which was estimated as barium carbonate; 0.816 g. of barium carbonate equivalent to 0.192 g. of carbon dioxide was obtained. (*b*) The amount of prussic acid, determined by Liebig's method, was 0.027 g. (*c*) The amount of hydrogen chloride determined by Liebig's method was 0.0142 g. (*d*) The liquid, 0.76 g., which condensed in the U-tube was identified as formic acid (0.5 g.), and dichloroacetic acid (0.26 g.). Formic acid was estimated by converting it into the characteristic lead salt.

The Residue: (*e*) After the distillation of the acid, a residue (2.1 g.) remained in the distilling tube. This residue, extracted with ether, left 0.38 g. of ammonium chloride undissolved. The purity of the ammonium chloride was established by an analysis of its platinum salt. (*f*) The ether extract was treated with a solution of sodium carbonate. In this way, a neutral portion consisting of 0.2 g. of dichloroacetamide was obtained upon evaporation of the ether. The amide was purified by precipitating it from an ether solution by ligroin. It melted at 97.5°, and had all the properties of dichloroacetamide prepared from ethyl dichloroacetate and ammonia.

(*g*) The sodium carbonate solution left in (*f*) was acidified and extracted with ether. Upon evaporation of the ether, 1.16 g. of dichloroacetic acid remained. The acid was identified by converting it into its ammonium salt and into the amide. The ammonium salt crystallized in plates which decomposed at 100° without melting. (*h*) On distillation, a separate sample, 1 g. of dichloroacethydroxamic acid gave 27.1 cc. of gas which showed no test for nitrous oxide or for carbon monoxide. If this gas was all nitrogen, the amount which would have been obtained from 3 g. of the hydroxamic acid (81.3 cc.) would have weighed 0.1017 g.

The products which resulted from 3 g. of the hydroxamic acid may be summarized as follows:

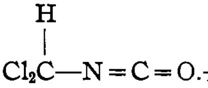
		Gram.			Gram.
(*a*)	Carbon dioxide	0.1920	(*e*)	Ammonium chloride	0.3800
(*b*)	Prussic acid	0.0270	(*f*)	Dichloroacetamide	0.2000
(*c*)	Hydrogen chloride	0.0142	(*g*)	Dichloroacetic acid	1.4200
(*d*)	Formic acid	0.5000	(*h*)	Nitrogen	0.1017
				Total,	2.8349

3. The Benzoyl Ester of Dichloroacethydroxamic Acid, $Cl_2CH.C\overset{O}{/\!\!/}—NH(O\overset{\overset{O}{\|}}{C}—C_6H_5)$.—Three grams of the acid were thoroughly pulverized with 4.8 g. of benzoic anhydride, and the mixture was heated for five minutes between 65° and 70°. The residue was extracted several times with ligroin to remove benzoic acid and unchanged anhydride. The ester was dissolved in ether. The ether solution was filtered and the ester precipitated with ligroin. By careful addition of ligroin so that it did not mix immediately with the ether, sword-like crystals, over an inch long, were obtained. In this way 4.7 g. of the ester were precipitated. The crystals melted at 77° to 78°.

0.3120 g. gave 14.9 cc. N_2 at 19.50 and 751.7 mm. (over 30% KOH solution).
Calc. for $C_9H_7O_2NCl_2$: N, 5.66. Found: N, 5.42.

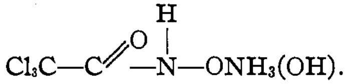
4. Distillation of the Benzoyl Ester of Dichloroacethydroxamic Acid.—One gram of the ester was heated at 150° in an atmosphere of hydrogen. A volatile liquid condensed in a U-tube immersed in a freezing mixture. The evolved gases were passed through dilute hydrochloric acid, and then through a solution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

Since it was assumed (p. 670) that the distillate mentioned above consisted of dichloromethylisocyanate, the following experiments were undertaken to prepare dichloromethylisocyanate:



5. Dichloromethylisocyanate, $Cl_2\overset{H}{C}—N=C=O$.—Five grams of sodium hydrazoate were treated with an equivalent amount of dichloroacetyl chloride dissolved in benzene. No apparent reaction occurred even at the boiling point of benzene. The flask containing the mixture was set away for one month. It was found, then, to contain a solid, consisting largely of a gelatinous mass of sodium chloride, and a benzene solution which was subjected to fractional distillation. An impure product was collected between 85° and 90°. This fraction was a colorless liquid, containing some benzene, which possessed a very sharp penetrating odor. When treated with water, it was decomposed at once with an evolution of carbon dioxide, and the solution gave tests for prussic acid and for hydrochloric acid. Since these products are the products expected, it is probable that dichloromethylisocyanate was present in the impure product described.

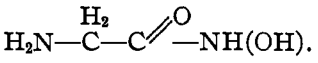
II. Hydroxylammonium Salt of Trichloroacethydroxamic Acid,



$$Cl_3C—C\overset{O}{\swarrow}—\overset{H}{N}—ONH_3(OH).$$

Twenty-nine grams of trichloroacetic ethyl ester were dissolved in 15 cc. of absolute alcohol and the solution cooled to —15°. To the cooled solution, 5 g. of hydroxylamine in alcoholic solution were added, drop by drop. 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 which melted at 72° to 73° with decomposition. The yield was 8 g. A chlorine determination showed that neither of the chlorine atoms had been displaced.

0.4890 g. subst. gave 56 cc. N_2 at 19° and 742.1 mm. (over 30% KOH solution).
Calc. for $C_2H_3O_2.N_2Cl_3$: N, 13.25. Found: N, 13.01.



III. Aminoacethydroxamic Acid, $H_2N—\overset{H_2}{C}—C\overset{O}{\swarrow}—NH(OH)$.

Twenty grams of ethyl glycocollate prepared by the method of E. Fischer were treated, at —10°, 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 began to separate in the course of an hour. The mixture was placed 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 was soluble in water, slightly soluble in alcohol, and insoluble in other organic solvents. Crystallized from a dilute methyl alcoholic solution, it melted at 140° with decomposition. The yield was almost quantitative.

0.1668 g. subst. gave 44.8 cc. of N_2 at 14° and 745 mm. (over 30% KOH solution).
Calc. for $C_2H_6O_2N_2$: N, 31.09. Found: N, 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 products obtained by the rearrangement of dichloroacethydroxamic acid, and of its benzoyl ester when they were subjected to the action of heat.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

A STUDY OF β-BENZYLFORMHYDROXAMIC ACID.

BY LAUDER WILLIAM JONES AND M. CANNON SNEED.[1]

Received January 5, 1917.

Of the type of substituted hydroxylamines to which β-benzylformhydroxamic acid belongs, β-phenylformhydroxamic acid, β-benzylacethydroxamic acid, and β-benzoylbenzhydroxamic acid, are the only representatives known. The first of these compounds was described by Bamberger and Destraz[2] who obtained it by treating β-phenylhydroxylamine with formic acid. They found that β-phenylformhydroxamic acid, upon distillation with phosphorus pentoxide, gave phenylisocyanate. Both β-benzoylbenzylhydroxamic acid and β-acetylbenzylhydroxamic acid were prepared by Beckman.[3]

It has been shown that many β-substituted hydroxylamines and β-disubstituted hydroxylamines, on treatment with mild dehydrating agents, undergo intramolecular oxidation yielding aldehydes and amines (or ammonia). Thus, Walder 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.

It would be expected that β-acyl-β-alkyl(aryl)hydroxylamines containing an oxidizable acyl group, such as formyl, might behave towards mild dehydrating agents in a manner similar to β-dibenzylhydroxylamine, and that they would offer still another possibility for intramolecular

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[1] The material presented here is used by Sneed in his dissertation in part fulfilment of the requirements for the Ph.D. degree of the University of Cincinnati.

[2] *Ber.*, **35**, 1884 (1902).

[3] *Ibid.*, **26**, 2631 (1893).