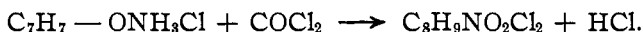


(e) **Phosgene and  $\alpha$ -Benzyl Hydroxylammonium Chloride.**—Phosgene gas was passed over 1.77 g. of  $\alpha$ -benzyl hydroxylammonium chloride which was gradually heated to 180° in the air bath for four hours. Most of the original solid was converted into a liquid. Little charring occurred. The excess phosgene used and the hydrogen chloride liberated during the reaction were passed into a barium hydroxide solution. A precipitate of barium carbonate was formed which was collected and weighed. The chlorine in the solution was precipitated as silver chloride and weighed. The reaction mixture was extracted with ether. A slightly brown solid weighing 0.1008 g. remained undissolved. Upon evaporation of the ether, a yellow oil was obtained which weighed 2.16 g. When an attempt was made to distil this oil under diminished pressure, a small amount of a clear liquid, boiling at 97.5–100° at 49 mm. passed over into the receiver. Much decomposition occurred above 100°. The distillate contained chlorine and was analyzed for nitrogen.

0.2221 g. gave 13.6 cc. N<sub>2</sub> at 28.5° and 740 mm.

Calc. for C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>Cl<sub>2</sub>: N, 6.31. Found: N, 6.57.

The equation which best represents the results obtained is



CINCINNATI, OHIO.

---

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

## HYDROXAMIC ACIDS RELATED TO $\alpha$ -HYDROXY ACIDS AND TO ACRYLIC ACID, AND A STUDY OF THEIR REARRANGEMENTS.

BY LAUDER WILLIAM JONES AND LEONORA NEUFFER.<sup>1</sup>

Received January 5, 1917.

Since Lossen,<sup>2</sup> in 1869, prepared oxalohydroxamic acid by the action of hydroxylamine on oxalic ethyl ester and distinguished a class of compounds having the "structure of amides and the character of acids," many representatives of the hydroxamic acids have been prepared. The principle work on hydroxamic acids containing aromatic groups was done by Lossen<sup>3</sup> and his collaborators, who described the preparation and properties of many of the acids themselves, as well as of their acyl esters and alkyl derivatives.

The chemistry of the hydroxamic acids of the aliphatic series has been developed to some extent by Hoffmann,<sup>4</sup> who prepared acethydroxamic

<sup>1</sup> The material presented here is used by Leonora Neuffer in her dissertation in part fulfillment of the requirements for the Ph.D. degree of the University of Cincinnati.

<sup>2</sup> *Ann.*, **150**, 314 (1869).

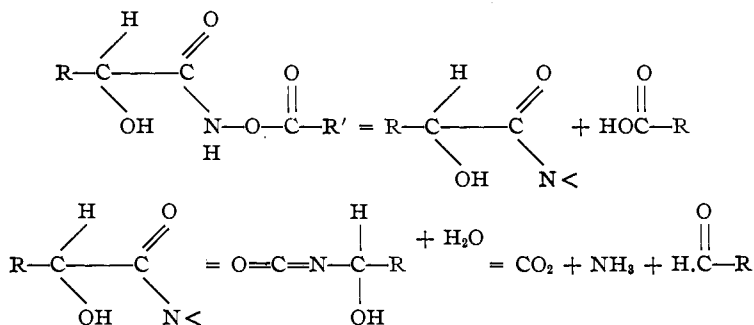
<sup>3</sup> *Ibid.*, **175**, 284 (1875); **178**, 213 (1874); **205**, 273 (1880).

<sup>4</sup> *Ber.*, **22**, 2854 (1889).

acid, by Miolati,<sup>1</sup> and by Bamberger.<sup>2</sup> Jones has described the preparation of hydroxamic acids of the aliphatic series from salts of nitroparaffins,<sup>3</sup> from hydroxylamine salts of organic acids,<sup>4</sup> and from acid esters and free hydroxylamine.<sup>5</sup> The behavior of the hydroxamic acids of the aliphatic series, and of their salts and esters towards hydrolyzing agents and toward heat has been studied by Jones,<sup>6</sup> by Biddle,<sup>7</sup> by Wieland,<sup>8</sup> and by Thiele and Picard.<sup>9</sup> The products obtained were isocyanates, which, in the presence of water, were converted into symmetrical disubstituted ureas, or into the corresponding amines and carbon dioxide. An explanation of these reactions based upon the electronic conception of valence, has been offered, and the relation between hydroxamic acids and the isocyanates pointed out by Jones<sup>10</sup> and by Stieglitz.<sup>11</sup>

The purpose of the present paper is to describe some new hydroxamic acids chiefly of the aliphatic series, namely, those related to propionic,<sup>12</sup> lactic, mandelic, and acrylic acids, and some of their derivatives. A study of the changes suffered by these compounds under the influence of hydrolyzing agents, and of heat, has been made.

Experiments were made to determine whether these  $\alpha$ -hydroxyhydroxamic acids would show a normal rearrangement of the Beckmann type expressed in the following equations:



When the  $\alpha$ -hydroxyhydroxamic acids, or their acyl esters, were heated,

<sup>1</sup> *Ber.*, **25**, 700 (1892).

<sup>2</sup> *Ibid.*, **35**, 45 (1902).

<sup>3</sup> *Am. Chem. J.*, **20**, 1 (1898).

<sup>4</sup> *Ibid.*, **42**, 515 (1909).

<sup>5</sup> *Ibid.*, **20**, 28 (1898).

<sup>6</sup> *Ibid.*, **20**, 1 (1898); **48**, 1 (1912).

<sup>7</sup> *Ann.*, **310**, 15 (1899).

<sup>8</sup> "Die Knallsäure," p. 32 (1909).

<sup>9</sup> *Ann.*, **309**, 189 (1899).

<sup>10</sup> *Am. Chem. J.*, **48**, 26 (1912); **50**, 414 (1913).

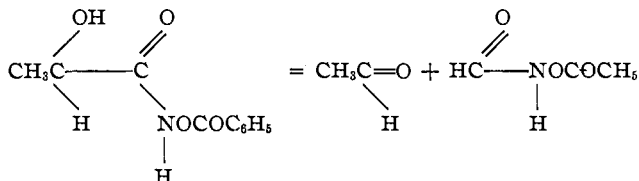
<sup>11</sup> *THIS JOURNAL*, **36**, 272 (1914).

<sup>12</sup> The propionhydroxamic acid obtained showed a melting point different from that mentioned by Miolati (*Ber.*, **25**, 700 (1892)).

an aldehyde was formed. Even when dissolved in water and warmed, an aldehyde could be recognized almost immediately in the case of their benzoyl esters.

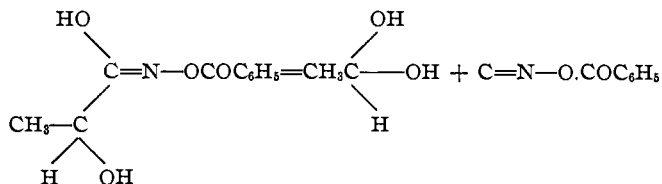
It was to be expected, however, that the presence of hydroxyl in the  $\alpha$  position might lead to reactions similar to those known to occur with  $\alpha$ -hydroxy acids, such as lactic acid, which gives acetaldehyde and formic acid when treated with sulfuric acid. A quantitative experiment with the benzoyl ester of lacthydroxamic acid showed that the actual products observed, when it was heated with water, included not only carbon dioxide, ammonia and acetaldehyde, but, also, considerable *sym.*-dibenzoylurea, and traces of ethyl alcohol (or ethyl benzoate). The formation of the last-named products would be difficult to explain, if the Beckmann rearrangement alone were responsible for the decomposition of the ester.

A dissociation similar to that of lactic acid would require the following equation:

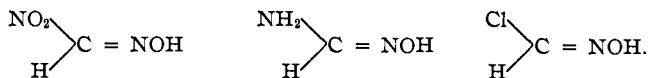


A careful search for the benzoyl ester of formhydroxamic acid, and of formhydroxamic acid, or its decomposition products, hydroxylamine and formic acid, did not lead to the detection of either of these compounds.

The only interpretation which has suggested itself as a possible way of explaining the presence of *sym.*-dibenzoylurea is expressed in the following equation:



A dissociation of the ester in its hydroxamic form would give acetaldehyde and benzoyl fulminate. This reaction would be similar to many others by which fulminates have been synthesized, *viz.*, by the action of silver nitrate and nitric acid upon methylnitrolic acid, upon formamide oxime, upon formylchloride oxime.



The readiness with which the two carbon atoms in lactic acid part com-

pany indicates that the group  $\text{CH}_3\text{CHOH}$  would favor a dissociation of this character.<sup>1</sup>

Benzoyl fulminate, expressed in the equation given above, would rearrange to give benzoylisocyanate.



Hydrolysis of the isocyanate would give benzamide and carbonic acid, and benzamide would react with unchanged benzoylisocyanate to produce *sym.*-dibenzoylurea.

The formation of ethyl alcohol is not accounted for by either of the two sets of equations. Nef's explanation of the dissociation of sodium lactate, applied to this analogous case, offers the only explanation which suggests itself at present.

By the action of optically active alkaloids upon lact- and mandel-hydroxamic acids and upon their acyl esters, attempts were made to prepare optically active hydroxamic acids. The experiments were not successful, but the work will be continued.

#### EXPERIMENTAL PART.

##### I. Propionhydroxamic Acid and Its Derivatives.

(a) **Propionhydroxamic Acid**,  $\text{CH}_3\text{CH}_2\text{CO.NH(OH)}$ .—Fifteen g. of propionic ethyl ester were added to 4.86 g. of free hydroxylamine. The mixture was made homogenous by addition of methyl alcohol, and allowed to stand overnight. After the solvent had been removed *in vacuo*, the resulting oil was allowed to stand for three weeks, when it solidified. Upon recrystallization from acetic ether, 8.7 g. of a white crystalline solid, melting at  $92.5\text{--}93^\circ$ , were obtained. It gave a deep red coloration with ferric chloride.

Propionhydroxamic acid was found to be soluble in alcohol, in hot acetone, and in water, but was insoluble in chloroform, in ligroin; in ether, and in benzene. With copper acetate, it formed a bluish green copper salt, and caused no effervescence with calcium carbonate. When heated above its melting point, it suffered gentle decomposition, and gave a strong odor of isocyanate.

0.2110 g. gave 30 cc.  $\text{N}_2$  at  $23.5^\circ$  and 741.3 mm.

Calc. for  $\text{C}_3\text{H}_7\text{NO}_2$ : N, 15.73. Found: N, 15.68.

(b) **Sodium Salt**.—Two g. of propionhydroxamic acid were dissolved in absolute alcohol and treated with 0.52 g. of sodium in absolute alcohol. When ether was added to the alkaline solution, a white crystalline solid separated at once, which, when recrystallized, weighed 2.2 g. When a water solution of the sodium salt was treated with copper acetate, a stable green copper salt precipitated; with mercuric chloride a pale yellow salt,

<sup>1</sup> Experiments are now in progress to determine whether lacthydroxamic acid, or its esters, when treated with silver nitrate and nitric acid, will yield fulminates.

and with silver nitrate and lead acetate white salts were formed. The sodium salt was slightly hygroscopic.

0.2034 g. gave 0.1294 g.  $\text{Na}_2\text{SO}_4$ .

Calc. for  $\text{C}_3\text{H}_6\text{NO}_2\text{Na}$ : Na, 20.74. Found: Na, 20.61.

(c) **Potassium Salt.**—The alcoholic solution of 2 g. of propionhydroxamic acid was treated with 1.25 g. of potassium hydroxide in alcohol. By the addition of absolute ether, the potassium salt was precipitated as a white crystalline solid. The recrystallized product weighed 2.5 g. Like the sodium salt, it suffered no sudden decomposition when heated.

0.1921 g. gave 0.1306 g.  $\text{K}_2\text{SO}_4$ .

Calc. for  $\text{C}_3\text{H}_6\text{NO}_2\text{K}$ : K, 30.78. Found: K, 30.52.

(d) **Benzoyl Ester of Propionhydroxamic Acid,  $\text{CH}_3\text{CH}_2\text{CO.NH}$  ( $\text{O.CO.C}_6\text{H}_5$ ).**—Five g. of the hydroxamic acid dissolved in water were treated with 3.14 g. of potassium hydroxide dissolved in water, and 7.68 g. of benzoyl chloride were added slowly, while the solution was cooled and vigorously shaken. After several minutes, a white solid separated, which was filtered off, dried, extracted several times with boiling ligroin to remove benzoic acid, and recrystallized from absolute ether by the addition of ligroin. Nine g. of the ester, fine needle-like crystals, were obtained which melted at  $115\text{--}116^\circ$ , and decomposed between  $125^\circ$  and  $130^\circ$  giving an odor of isocyanate. The benzoyl ester of propionhydroxamic acid was soluble in chloroform, in ether, in benzene, and in alcohol, but insoluble in ligroin and in water. It was acid to litmus. When suspended in water it soon gave an intense red coloration with ferric chloride, showing that it was readily hydrolyzed.

0.2295 g. gave 14.9 cc.  $\text{N}_2$  at  $23.5^\circ$  and 740.5 mm.

Calc. for  $\text{C}_{10}\text{H}_{11}\text{NO}_3$ : N, 7.25. Found: N, 7.14.

**Rearrangement of the Benzoyl Ester of Propionhydroxamic Acid.**—Three and eighty-one hundredths g. of the benzoyl ester and 1.02 g. of potassium hydroxide dissolved in water were sealed in a tube and heated on a water bath for about six hours. The tube was opened and its contents distilled into a dilute hydrochloric acid solution. The residue in the flask was found to be potassium benzoate by dissolving it in water, acidifying the solution, and determining the melting point of the precipitate formed. Two and one-tenth g. of benzoic acid were obtained. When the hydrochloric acid solution was evaporated, a white residue was left, which, upon purification, was found to be slightly deliquescent and to melt at  $80\text{--}82^\circ$ . It responded to the isocyanide test for primary amines and corresponded in properties to ethyl ammonium chloride.

This decomposition and rearrangement is wholly analogous to the behavior of hydroxamic acids.

(e) **Sodium Salt of the Benzoyl Ester.**—One g. of the benzoyl ester of propionhydroxamic acid was dissolved in alcohol and treated with 0.12 g.

of sodium dissolved in alcohol. When ether was added slowly to the resulting solution, a white, crystalline solid precipitated at once which was recrystallized from alcohol by addition of ether. When this compound was heated and the temperature reached  $86^{\circ}$ , it decomposed with almost explosive violence, with the evolution of vapors which possessed a strong odor of isocyanate. A similar decomposition was observed by Jones with the potassium salt of the benzoyl ester of phenylacethydroxamic acid,<sup>1</sup> which decomposed spontaneously at ordinary temperature.

0.1084 g. gave 0.0379 g.  $\text{Na}_2\text{SO}_4$ .

Calc. for  $\text{C}_{10}\text{H}_{10}\text{NO}_3\text{Na}$ : Na, 10.71. Found: Na, 11.32.

(f) **Potassium Salt of the Benzoyl Ester.**—By mixing together 1 g. of the benzoyl ester in absolute alcohol and 0.29 g. of potassium hydroxide dissolved in alcohol, and adding ether to the resulting solution, the potassium salt was obtained as a white crystalline precipitate. When heated in a glycerine bath to  $120$ – $124^{\circ}$ , it decomposed with a sudden puff, giving a strong odor of isocyanate.

0.1976 g. gave 0.0751 g.  $\text{K}_2\text{SO}_4$ .

Calc. for  $\text{C}_{10}\text{H}_{10}\text{NO}_3\text{K}$ : K, 16.93. Found: K, 17.15.

(g) **Silver Salt of the Benzoyl Ester.**—Five-tenths g. of the sodium salt of the benzoyl ester of propionhydroxamic acid was dissolved in water and treated with silver nitrate solution until no further precipitation occurred. The silver salt was filtered off and dried in an amber desiccator. It was soluble in hot chloroform, insoluble in benzene, in alcohol and in ether, and was very stable even when exposed to light for a considerable time. When heated above  $150^{\circ}$ , it decomposed, giving an odor of isocyanate.

0.1026 g. gave 0.0371 g. Ag.

Calc. for  $\text{C}_{10}\text{H}_{10}\text{NO}_3\text{Ag}$ : Ag, 35.97. Found: Ag, 36.15.

(h) **Acetyl Ester of Propionhydroxamic Acid,  $\text{CH}_3\text{CH}_2\text{CO.NH}(\text{O.COCH}_3)$ .**—Five-tenths g. of propionhydroxamic acid and 0.57 g. of acetic anhydride were heated on a water bath until the mixture no longer responded to the ferric chloride test for hydroxamic acids. The product was allowed to stand in a vacuum desiccator until a white solid formed. It was crystallized from ether by addition of ligroin, forming glistening plates which melted at  $72.5$ – $73^{\circ}$ . It was soluble in chloroform, in alcohol, in benzene, in ether, and in water. Above  $75^{\circ}$  it decomposed giving a strong isocyanate odor.

0.1133 g. gave 10.95 cc.  $\text{N}_2$  at  $20^{\circ}$  and 746.8 mm.

0.1160 g. gave 0.1949 g.  $\text{CO}_2$ ; 0.07308 g.  $\text{H}_2\text{O}$ .

Calc. for  $\text{C}_8\text{H}_9\text{NO}_3$ : N, 10.68; H, 6.92; C, 45.77.

Found: N, 10.76; H, 6.99; C, 45.82.

(i) **Sodium Salt of the Acetyl Ester.**—One-tenth g. of the acetyl ester

<sup>1</sup> *Am. Chem. J.*, 48, 8 (1912).

was dissolved in alcohol and treated with 0.017 g. of sodium in alcohol. Upon addition of ether, a white crystalline solid was obtained, which was very hygroscopic, and from the water solution of which a fairly stable silver salt was precipitated by addition of silver nitrate solution.

0.1101 g. gave 0.0520 g.  $\text{Na}_2\text{SO}_4$ .  
 Calc. for  $\text{C}_5\text{H}_8\text{NO}_3\text{Na}$ : Na, 15.05. Found: Na, 15.29.

(j) **Potassium Salt of the Acetyl Ester.**—This was prepared by the treatment of 0.14 g. of the acetyl ester in alcohol with 0.06 g. of potassium hydroxide dissolved in alcohol. Absolute ether caused the precipitation of the salt. When recrystallized from alcohol and ether, it formed flaky, shining plates, was not hygroscopic, and, when heated strongly, decomposed giving an odor of isocyanate.

0.1210 g. gave 0.0615 g.  $\text{K}_2\text{SO}_4$ .  
 Calc. for  $\text{C}_5\text{H}_8\text{NO}_3\text{K}$ : K, 23.13. Found: K, 22.92.

## II. Lacthydroxamic Acid and Its Derivatives.

(a) **Lacthydroxamic Acid,  $\text{CH}_3\text{CH}(\text{OH})\text{CO.NH}(\text{OH})$ .**—A mixture was made of 30.4 g. of lactic ethyl ester and 8.4 g. of free hydroxylamine. Sufficient methyl alcohol was added to produce a homogenous solution. Tested at intervals with ferric chloride, it showed a red coloration which increased in intensity rapidly. After two days the solvent was removed by evaporation in a desiccator. The product was a thick, colorless oil which did not solidify after standing several weeks. Eighteen g. of the oil were obtained which gave the following figures on analysis:

0.5827 g. gave 71 cc.  $\text{N}_2$  at  $21^\circ$  and 749.5 mm.  
 Calc. for  $\text{C}_3\text{H}_7\text{NO}_3$ : N, 13.33. Found: N, 13.70.

(b) **Benzoyl Ester of Lacthydroxamic Acid,  $\text{CH}_3\text{CH}(\text{OH})\text{CO.NH}(\text{O.COC}_6\text{H}_5)$ .**—To a solution of 5 g. of lacthydroxamic acid in water and 2.66 g. of potassium hydroxide, 6.68 g. of benzoyl chloride were added slowly while the mixture was cooled and shaken. A white solid separated. When dried, a small amount of benzoic acid was removed from it by repeated extraction with boiling ligroin. The yield was 7.81 g. The benzoyl ester of lacthydroxamic acid melted at  $124.5\text{--}126^\circ$ , was soluble in alcohol, but insoluble in cold water, in ligroin, and in chloroform.

0.3002 g. gave 17.7 cc.  $\text{N}_2$  at  $30^\circ$  and 747.1 mm.  
 Calc. for  $\text{C}_{10}\text{H}_{11}\text{NO}_4$ : N, 6.70. Found: N, 6.34.

**Rearrangement of the Benzoyl Ester of Lacthydroxamic Acid.**—Five g. of the benzoyl ester of lacthydroxamic acid were heated with water for three hours on a boiling water bath. The containing flask was attached to a reflux condenser, from the top of which a glass tube extended into an ice-cooled vessel containing ether. This, in turn, was connected with a vessel containing a calcium hydroxide solution. At the end of the process, dry ammonia gas was passed into the ether solution from which

0.278 g. of aldehyde ammonia, corresponding to 0.2 g. of acetaldehyde, was obtained. From the calcium hydroxide solution, 0.1064 g. of calcium carbonate corresponding to 0.0468 g. of carbon dioxide, was obtained. When the contents of the flask were cooled, a slightly brownish, crystalline solid deposited. This solid was separated into 0.37 g. of benzoic acid and 0.34 g. of the unchanged benzoyl ester. The filtrate possessed a strong odor of benzoic ethyl ester, and when boiled with alkalis, evolved ammonia. It was distilled under diminished pressure. The distillate showed the presence of benzoic ethyl ester, and responded to a test for alcohol. A white solid (1.73 g.) remained in the distilling flask. This substance crystallized in well-developed, shining plates from alcohol, when ether was added. It melted at 196–197°, and corresponded in properties to *sym.*-dibenzoylurea.

0.0769 g. gave 7.2 cc. N<sub>2</sub> at 23° and 751 mm.

Calc. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: N, 10.45. Found: N (1) 10.48; (2) 10.38.

One and five-tenths g. of the solid melting at 196–197° were sealed in a tube with dilute hydrochloric acid, and heated for six hours on a water bath. From the reaction mixture, 1 g. of pure benzoic acid, 0.406 g. of ammonium chloride and 0.15 g. of carbon dioxide were isolated. The ammonium chloride was converted to the chloroplatinate.

Calc. for (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>: Pt, 43.94. Found: Pt, 43.67.

(c) **Potassium Salt of the Benzoyl Ester.**—One g. of benzoyl ester was dissolved in alcohol and treated with an alcoholic solution of 0.27 g. of potassium hydroxide. Ether was added and a fine precipitate of the potassium salt was obtained. It was recrystallized from alcohol and ether and weighed 0.8 g. When heated strongly it decomposed, leaving a charred residue.

0.1511 g. gave 0.0528 g. of K<sub>2</sub>SO<sub>4</sub>.

Calc. for C<sub>10</sub>H<sub>10</sub>NO<sub>4</sub>K: K, 15.83. Found: K, 15.68.

### III. Mandelhydroxamic Acid and Its Derivatives.

(a) **Mandelhydroxamic Acid, C<sub>8</sub>H<sub>9</sub>.CH(OH).CO.NH(OH).**—A mixture of 10 g. of mandelic ethyl ester and 1.82 g. of hydroxylamine was made homogeneous by the addition of a small amount of methyl alcohol. The product gave, with ferric chloride, a red coloration which increased in intensity rapidly. In a day, a large quantity of well-formed white crystals separated from the alcohol solution. When recrystallized from ether and alcohol by addition of ligroin, 7.4 g. were obtained. Mandelhydroxamic acid melted at 143.3°, and decomposed immediately above its melting point to give products which had a strong odor of benzaldehyde.

0.1472 g. gave 11.1 cc. N<sub>2</sub> at 25° and 744 mm.

Calc. for C<sub>8</sub>H<sub>9</sub>NO<sub>3</sub>: N, 8.38. Found: N, 8.28.

(b) **Benzoyl Ester of Mandelhydroxamic Acid, C<sub>8</sub>H<sub>9</sub>.CH(OH).CO.NH.(OCOC<sub>6</sub>H<sub>5</sub>).**—A mixture of 0.5 g. of mandelhydroxamic acid dissolved



in water and 0.16 g. of potassium hydroxide in water was treated with 0.44 g. of benzoyl chloride added slowly while the mixture was cooled and shaken. A white solid separated which, when filtered off immediately, washed with boiling ligroin, and crystallized from a small amount of boiling alcohol, melted at 101–102°. The yield was 0.4 g. When heated alone, or when allowed to stand in contact with water, it gave a strong odor of benzaldehyde.

0.1701 g. gave 8.4 cc.  $N_2$  at 25° and 739.1 mm.

Calc. for  $C_{15}H_{13}NO_4$ : N, 5.17. Found: N, 5.38.

If, however, the ester was allowed to stand for even a short time in contact with the solution from which it was precipitated, the mixture gave a strong odor of benzaldehyde and none of the ester could be isolated. By addition of an acetic acid solution of phenylhydrazine to a part of the water solution, a white precipitate was formed which was recrystallized from alcohol and found to melt at 155–156°. The recorded melting point of benzaldehyde phenylhydrazine is 156°. The remainder of the water solution was distilled under diminished pressure. A white residue remained in the distilling flask. This was found to consist of a mixture of potassium chloride and a substance which dissolved in alcohol and was reprecipitated by ether. The latter was identical with the white solid melting at 196–197° isolated in the hydrolysis of the benzoyl ester of lachydroxamic acid, and identified as *sym.*-dibenzoylurea.

#### IV. Acrylhydroxamic Acid, $CH_2=CH.CO.NH(OH)$ .

Two g. of acrylic ethyl ester and 0.66 g. of hydroxylamine were mixed while cooled with ice. In a short time an oily white solid formed which gave an intense red coloration with ferric chloride. It was recrystallized from alcohol by the addition of ether. Almost the theoretical yield, 1.52 g., of a flaky crystalline solid, melting at 115–116°, was obtained. It was difficultly soluble in acetic ether.

0.1725 g. gave 25.4 cc.  $N_2$  at 27° and 740.5 mm.

Calc. for  $C_3H_5NO_2$ : N, 16.09. Found: N, 15.93.

An investigation of the behavior of hydroxamic acids containing a doubly bound carbon atom toward heat and toward hydrolyzing agents will be made at a later time.

#### Summary.

Some new hydroxamic acids, chiefly members of the aliphatic series, have been prepared by the action of free hydroxylamine on the esters of propionic, lactic, mandelic, and acrylic acids. Their salts, their benzoyl and acetyl esters, and the salts of their acyl esters have been described. Those compounds prepared from esters containing an  $\alpha$ -hydroxyl group showed a behavior toward heat and toward hydrolyzing agents which differed from the behavior of those prepared from the esters of ordinary fatty acids. The former yield aldehydes and symmetrical *di-acyl* ureas,

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.

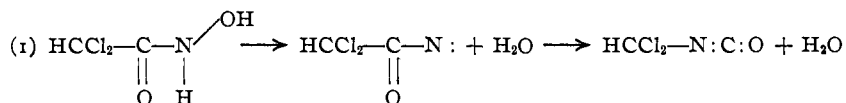
BY LAUDER WILLIAM JONES AND M. CANNON SNEED.<sup>1</sup>

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<sup>2</sup> 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<sup>3</sup> 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:



<sup>1</sup> 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.

<sup>2</sup> *Gazz. chim. ital.*, [1] 34, 428 (1904).

<sup>3</sup> *THIS JOURNAL*, 39, 413 (1917).