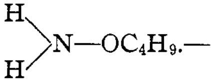
Ten grams of α-secondarybutyl hydroxyurethane were sealed in a tube with 20 g. of potassium hydroxide dissolved in water and heated at 90–100°, for 28 hrs. The contents of the tube were treated as described above and 2.4 g. of a white, crystalline solid, melting at 54.7–55° and not in the least deliquescent, were obtained. The chloroplatinate was precipitated as beautiful, well defined, deep yellow crystals.

Calc. for $[C_4H_9ONH_3]_2PtCl_6$: Pt, 33.19; found: Pt, 32.89.

(*b*) *α-Secondarybutyl Hydroxylamine*,  $\frac{H}{H}\!>\!N{-}OC_4H_9$.—One and eight-tenths grams of the chloride and 5 g. of potassium hydroxide were gently heated in a distilling flask. A clear, colorless liquid with a strongly ammoniacal odor, boiling at 85.5°, was obtained.

Calc. for $C_4H_{11}ON$: N, 15.72; found: N, 15.78.

The preparation of α-ethyl β-secondarybutyl and α-secondarybutyl β-ethyl hydroxylamines completes a set of three isomers of the type R_1R_2HNO.

The following table summarizes the properties of the compounds described:

	Esters of hydroxyurethane. B. p.	Alkyl hydroxylamines. B. p.	Alkyl hydroxyl ammonium chloride. M. p.
β-Ethyl β-sec.-butyl...	....	155–158° (Bewad)	56–57° (Bewad)
α-Ethyl β-sec.-butyl...	105–106.4° [55 mm.]	88.4–89°	94°
α-Sec.-butyl β-ethyl...	86.5–87 [30 mm.]	93.5–94°	[deliquescent]
α-Sec.-butyl..........	116–116.6° [27 mm.]	85.5°	54.7–55°

Summary.

(1) The preparation and properties of secondarybutyl, and mixed ethyl secondarybutyl hydroxyurethanes are described in this paper. These compounds are high boiling, oily liquids with a characteristic odor. They reduce neither ammoniacal silver nitrate nor Fehling's solution. They are readily hydrolyzed by potassium hydroxide solution below 100°.

(2) The preparation and the properties of secondarybutyl, and mixed ethyl secondarybutyl hydroxylamines, their chlorides and chloroplatinates are described. The free hydroxylamines are liquids which have a characteristic ammoniacal odor, all boil between 85 and 90° at ordinary pressure, and are reducing agents toward ammoniacal silver nitrate in the cold, and toward Fehling's solution when heated.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

SOME NEW HYDROXYURETHANES AND CHROMOISOMERIC SILVER SALTS OF THEIR ACYL DERIVATIVES.

BY LAUDER WILLIAM JONES AND RALPH OESPER.

Received July 31, 1914.

In a recent article[1] we described some experiments which had in view

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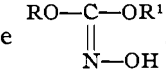
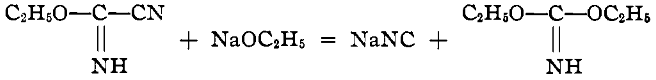
[1] THIS JOURNAL, 36, 726 (1914).

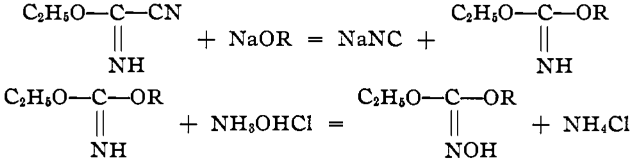
the preparation of mixed oximidocarbonic esters, *i. e.*, compounds of the type  $\mathrm{RO{-}\underset{\underset{\displaystyle N{-}OH}{\|}}{C}{-}OR^1}$. It seemed possible to obtain these compounds by several different methods, but, so far, none of them has proved satisfactory. We have found that the reactions expected either did not occur, or that unstable products were formed which we were not able to isolate, or that isomers of the desired materials were produced. Although we have not been able to work out a general method of preparing mixed oximidocarbonic esters,[1] we have obtained some very interesting results, and an account of these, together with a description of our experiences with the various reactions, form the subject matter of this paper.

Our first experiments were directed toward the preparation of the imidocarbonic esters, since these compounds can be converted into the corresponding oximido esters[1] by treatment with hydroxylammonium chloride. By the action of sodium ethylate on cyanimidocarbonic ethyl ester Nef[2] obtained imidocarbonic ethyl ester:



$$\mathrm{C_2H_5O{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}CN + NaOC_2H_5 = NaNC + C_2H_5O{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}OC_2H_5}$$

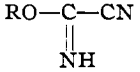
By using other alcoholates in place of sodium ethylate, the mixed imidocarbonic esters might be obtained, from which the oximido esters could be formed:



$$\mathrm{C_2H_5O{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}CN + NaOR = NaNC + C_2H_5O{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}OR}$$

$$\mathrm{C_2H_5O{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}OR + NH_3OHCl = C_2H_5O{-}\underset{\underset{\displaystyle NOH}{\|}}{C}{-}OR + NH_4Cl}$$

Preliminary experiments indicate that these reactions take place readily when aliphatic alcoholates (including sodium benzylate) are allowed to react with the cyanimidocarbonic ester, but sodium phenolate, and α- and β-naphtholate reacted very slowly, if at all, and then gave rise to thick black oils from which it was not possible to extract any of the desired imidocarbonic esters. A further study of the influence of the acid character of the aromatic alcohols will be made later.

Experiments were also carried out in which attempts were made to extend a method used by Nef[3] for the preparation of cyanimidocarbonic ethyl ester to the other compounds of the type  $\mathrm{RO{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}CN}$ By the

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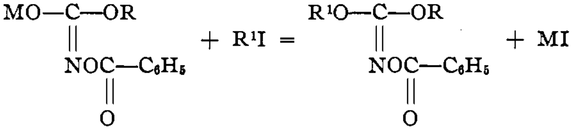
[1] Houben and Schmidt, *Ber.*, 46, 2458 (1913); Jones and Oesper, THIS JOURNAL, 36, 729 (1914).

[2] Nef. *Ann.*, **287**, 286 (1895); *Ber.*, 46, 2458 (1913).

[3] Nef, *Loc. cit.*, p. 293.

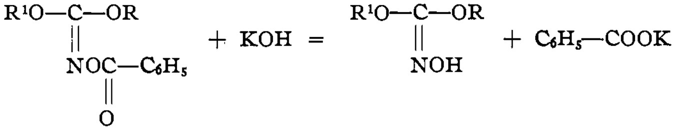
action of potassium cyanide upon an alcoholic solution of bromocyanogen, he obtained cyanimidocarbonic ethyl ester, but when isoamyl alcohol or phenol was substituted for the ethyl alcohol, in the hope of obtaining the corresponding isoamyl or phenyl ester, the chief product of the reaction was a black tar, and the alcohol or the phenol apparently had taken no part in the reaction. When an aqueous solution of the cyanide was slowly added to an ether solution of the bromocyanogen and the alcohol at temperatures not exceeding —5°, a greenish yellow oil was formed which changed to a black semi-solid mass as soon as the temperature rose to 10°. Although these experiments were repeated under the most varied conditions, using dilute or concentrated solutions of the cyanide, or even adding powdered cyanide to a moist ether solution of the other materials, a definite product was not obtained, and further efforts to prepare these compounds in this way were abandoned.

It seemed probable that the mixed oximidocarbonic esters might be prepared by the following method: The salts of the acyl derivatives of carbalkoxyhydroximic acids, when treated with alkyl halides, might be expected to give acylated oximidocarbonic esters.



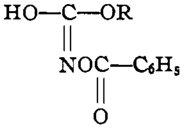
$$\begin{array}{c}\mathrm{MO{-}C{-}OR}\\ \|\\ \mathrm{NOC{-}C_6H_5}\\ \|\\ \mathrm{O}\end{array} + \mathrm{R^1I} = \begin{array}{c}\mathrm{R^1O{-}C{-}OR}\\ \|\\ \mathrm{NOC{-}C_6H_5}\\ \|\\ \mathrm{O}\end{array} + \mathrm{MI}$$

On careful hydrolysis with alkalies, the acyl radical might be eliminated.



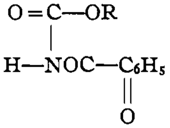
$$\begin{array}{c}\mathrm{R^1O{-}C{-}OR}\\ \|\\ \mathrm{NOC{-}C_6H_5}\\ \|\\ \mathrm{O}\end{array} + \mathrm{KOH} = \begin{array}{c}\mathrm{R^1O{-}C{-}OR}\\ \|\\ \mathrm{NOH}\end{array} + \mathrm{C_6H_5{-}COOK}$$

However, the acylated derivatives of the carbalkyloxyhydroxamic acids may exist in two possible forms:



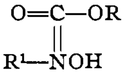
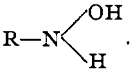
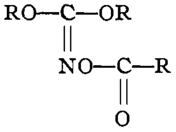
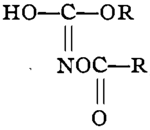
$$\begin{array}{c}\mathrm{HO{-}C{-}OR}\\ \|\\ \mathrm{NOC{-}C_6H_5}\\ \|\\ \mathrm{O}\end{array}$$

(I)

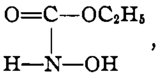


$$\begin{array}{c}\mathrm{O{=}C{-}OR}\\ |\\ \mathrm{H{-}NOC{-}C_6H_5}\\ \|\\ \mathrm{O}\end{array}$$

(II)

If the *silver salts* correspond to Formula I, then the reaction outlined above might lead to the desired compounds, but if they react according to type (II), isomeric derivatives,  $\begin{array}{c}\mathrm{O{=}C{-}OR}\\ \|\\ \mathrm{R^1{-}NOH}\end{array}$, would be obtained. When such possibilities exist, the silver salt usually gives compounds in which the alkyl group is bound chiefly to oxygen, while the sodium salt leads to the corresponding nitrogen derivative. In the cases investigated so far, *viz.*, those in which either the ethyl group or the isoamyl group was introduced, we have found that the silver salts gave rise to *nitrogen esters*, since the resulting compounds, when hydrolyzed with hydrochloric acid, yielded β-substituted hydroxylamines,  $R{-}N{<}^{OH}_{H}$. This proved that the alkyl group was bound to nitrogen. Under the same treatment, the isomeric oxygen derivatives would have yielded hydroxylamine itself. Furthermore, compounds of the form  $\begin{array}{c} RO{-}C{-}OR \\ \| \\ NO{-}C{-}R \\ \| \\ O \end{array}$ have been prepared, and were found to be crystalline solids, while the nitrogen alkyl derivatives obtained by us were oils, which did not solidify, even when cooled to —20°. It is possible that moist silver oxide may form silver salts with the metal bound to oxygen, just as Tafel and Enoch[1] have assumed to be the case for amides, or that some of the other compounds of the type  $\begin{array}{c} HO{-}C{-}OR \\ \| \\ NOC{-}R \\ \| \\ O \end{array}$, may give the desired mixed oximido esters. Then again it may be that the oxygen esters actually were formed first, and that the conditions of our experiments have not been chosen properly to prevent their rearrangement to N-esters, in much the same way that imido esters have been found to rearrange to give alkyl amides.[2]

As a matter of fact, we have found that some of these silver salts may be obtained in two forms, white and yellow, which, under proper conditions, may be converted into one another. It is possible that these may be the *oxygen* and *nitrogen* silver salts, *i. e.*, they may correspond to Formula I and II, respectively. In this case, by choosing the proper conditions, it should be possible to form the desired mixed oximidocarbonic esters. These silver salts will be described at length somewhat later.

Carbethoxyhydroxamic acid (hydroxyurethane),  $\begin{array}{l} O{=}C{-}OC_2H_5 \\ \quad | \\ H{-}N{-}OH \end{array}$, was first prepared by Hantzsch.[3] Jones[4] modified the method of preparation, and also studied some of its alkyl and acyl derivatives. This modified method has now been applied in the preparation of several of the homologs

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[1] Tafel and Enoch, *Ber.*, **23**, 104 (1890); Meyer and Jacobson, *Lehrbuch*, Vol. 1, p. 615.

[2] Comstock and Wheeler, *Am. Chem. J.*, **13**, 522 (1891); Wheeler, *Ibid.*, **21**, 1865 (1899); **23**, 140 (1901).

[3] Hantzsch, *Ber.*, **27**, 1254 (1894).

[4] Jones, *Am. Chem. J.*, **20**, 39 (1898).

of carbethoxyhydroxamic acid, and also the benzyl derivative, H(HO)-N—CO.OC_7H_7, the first solid compound of this type.

The benzoyl esters of these compounds were readily obtained by treating the aqueous solution of the hydroxamic acid with benzoyl chloride in the presence of potassium carbonate. The silver salts of these esters were precipitated when an aqueous solution of silver nitrate was added to an alcoholic solution of the benzoyl ester, to which an equivalent quantity of ammonium hydroxide had been added.

When treated in this way, all of the compounds investigated produce bright yellow silver salts; but while the yellow color of the methyl, ethyl and propyl compounds was permanent, the yellow precipitates produced in the case of the higher members of the series (*viz.*, isobutyl, isoamyl, benzyl) immediately became colorless. The precipitates separated as curds, and if one of the lumps was broken, the interior was found to be of the original yellow color. Whether the change was due to contact with the alcohol or the water, or whether the phenomenon was a photochemical one has not yet been definitely determined. The *white* salts are much more sensitive to the light than the yellow ones, and blacken readily, even if preserved in an amber desiccator.

Interestingly enough, these salts, both the *yellow and the white*, were slightly soluble in ether, and readily dissolved by chloroform or benzene. When alcohol was added to these solutions, *bright yellow needles* were precipitated, regardless of the original color of the salt. The yellow salts thus produced were perfectly stable, scarcely affected by light, and showed no tendency to change to the white forms at room temperature (see, however, the silver salt of the isoamyl derivative). At higher temperatures, however, the conversion was rapid, and the resulting *white* modifications were also stable; that is, at room temperature, even in contact with the yellow variety they did not revert to the yellow modifications. No decomposition occurred during this change; there was no apparent change in the crystalline form, and both modifications had the same ultimate composition, which was that of the simple silver salts, without any solvent of crystallization. Therefore, the two forms must represent either polymers or tautomers.

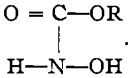
In the dry state, the yellow silver salt of the benzoyl ester of carbisoamyloxyhydroxamic acid changed to the white modification rapidly at about 75°, and it seemed possible that the molecular weight in boiling benzene (b. p. 80.5°) might differ from the value determined by the freezing point method in the same solvent. If the same values were obtained, it would argue for a tautomeric change, while if the values were multiples of each other, polymerization would be indicated. The values actually obtained, however, were not conclusive. By both methods of determining the molecular weight, association of two or more molecules was indicated;

and furthermore, the molecular weight of these complexes increased as the concentration of the solutions increased. No change in color was apparent when the solution was raised to the boiling point, and the change which occurs when the dry salt was heated probably does not take place in solution, or proceeds in such a way that equilibrium is reached between the yellow and the white modifications.

All of the *white* salts investigated so far dissolved in chloroform or in benzene to form *yellow* solutions from which alcohol precipitated the *yellow* salts. As mentioned above, when prepared in alcoholic solution, the yellow salts of the compounds with the larger alkyl radicals, became white on the surface where they are in contact with the solvent. Furthermore, if the yellow salts precipitated from chloroform or benzene solutions were dried and then suspended in alcohol, they gradually lost their yellow color and passed over into the *white* form. Therefore, it appears that low temperature and the presence of chloroform, benzene (and ether) favor the yellow form, while alcohol, water and higher temperatures stabilize the white salts. No solvent has been found in which the white salts do not change to the yellow form, so it does not seem possible to determine their molecular weight at present.

All the chemical evidence indicates that the yellow salts have the silver bound to nitrogen, but as these reactions were carried out in the presence of ether, which favors the yellow form, it may be that, if alcohol (which favors the white form) is used as the medium, alkyl halides may react to give compounds in which the alkyl group will be bound to oxygen. Such results, of course, would indicate that the white and yellow salts are tautomeric. These experiments will be carried out. Likewise, attempts will be made to prepare the carbalkyloxyhydroxamic acids containing large aromatic radicals in order to study the effect of such groups on the relative stability of the white and yellow forms.

Experimental Part.

Derivatives of Carbalkyloxyhydroxamic Acids,  $\begin{array}{l}O=C-OR\\ \quad\ |\\ H-N-OH\end{array}$.—The only one of these compounds which has been described is the ethyl derivative prepared by Hantzsch and later by Jones.[1] It seemed desirable to prepare some of the homologs of this compound as they are the materials from which it seemed possible, as outlined above, to obtain the oximidocarbonic esters. The method used by Jones[1] for preparing carbethoxyhydroxamic acid was used to prepare the corresponding methyl, propyl, isobutyl, isoamyl and benzyl derivatives. The procedure was as follows: One equivalent of hydroxylammonium chloride was pulverized and thoroughly mixed with two equivalents of powdered potassium carbonate.

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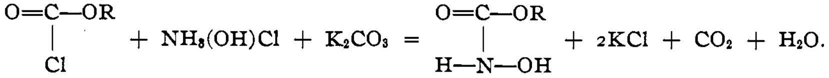
[1] Jones, *Loc. cit.*

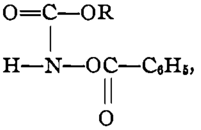
The mixture was covered with moist ether and one equivalent of the chlorocarbonic ester was added in small portions, while the flask was cooled by running water. After all the chlorocarbonate was added, the flask was connected with a reflux condenser, and the reaction mixture allowed to stand until the evolution of carbon dioxide had ceased (10 to 12 hours).



$$\begin{array}{l} O{=}C{-}OR \\ \quad | \\ \quad Cl \end{array} + NH_3(OH)Cl + K_2CO_3 = \begin{array}{l} O{=}C{-}OR \\ \quad | \\ H{-}N{-}OH \end{array} + 2KCl + CO_2 + H_2O.$$

After removing the potassium chloride by filtration, the ether was washed with a small quantity of water, and dried over fused sodium sulfate. The ether was then removed by distillation, and the remaining oil was placed in a desiccator which was exhausted for several hours to remove the last traces of ether. In this way, colorless or slightly yellow oils possessing characteristic odors were obtained. The benzyl derivative was a crystalline solid. When treated with ferric chloride, solutions of these compounds give a deep blue or purple color reaction. They immediately reduced ammoniacal silver nitrate.

As mentioned above, the benzoyl esters of these compounds,

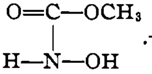


$$\begin{array}{l} O{=}C{-}OR \\ \quad | \\ H{-}N{-}OC{-}C_6H_5, \\ \qquad\quad \| \\ \qquad\quad O \end{array}$$

were formed when their aqueous solutions were treated with benzoyl chloride in the presence of potassium carbonate. These esters may be purified by extracting their ether solutions with sodium hydroxide. If carbon dioxide was passed through the alkaline solution, the benzoyl esters were precipitated. However, these compounds were very easily hydrolyzed by dilute alkalies, even in the cold, and some of the product was invariably lost in this way.

I. Derivatives of Carbmethoxyhydroxamic Acid.

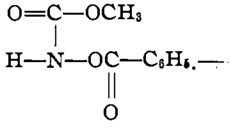
Carbmethoxyhydroxamic Acid,



$$\begin{array}{l} O{=}C{-}OCH_3 \\ \quad | \\ H{-}N{-}OH \end{array}$$

.—Twenty-five grams of chlorocarbonic methyl ester, 18.4 g. of hydroxylammonium chloride, and 36.5 g. of potassium carbonate produced 21 g. of thick yellow oil which was very soluble in water. This was not analyzed but was converted into its benzoyl ester.

The Benzoyl Ester of Carbmethoxydroxamic Acid,



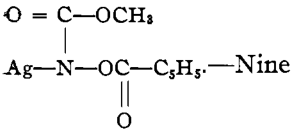
$$\begin{array}{l} O{=}C{-}OCH_3 \\ \quad | \\ H{-}N{-}OC{-}C_6H_5. \\ \qquad\quad \| \\ \qquad\quad O \end{array}$$

—To 9 g. of carbmethoxyhydroxamic acid and 6.8 g. of potassium carbonate dissolved in water, 13.8 g. of benzoyl chloride were added in small portions. A colorless oil separated which soon solidified. After recrystallization from warm chloroform and ligroin, it formed white needles melting at 82°. The yield was 12.5 g.

0.2550 g. gave 17 cc. N_2 at 29° and 746 mm.
Calc. for $C_9H_9O_4N$: N, 7.18. Found: N, 7.16%.

The compound was soluble in ether, in chloroform and in alcohol, but insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbmethoxyhydroxamic Acid,



$O = C—OCH_3$, $Ag—N—OC—C_5H_5$ ($C=O$ below)

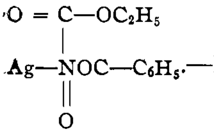
.—Nine grams of the benzoyl ester described above were dissolved in alcohol and the equivalent quantity of ammonium hydroxide was added to it. When this solution was treated with 7.8 g. of silver nitrate dissolved in water, a bright yellow precipitate was formed which was separated by filtration, washed with alcohol and water, and dried on a porous plate. Yield, 11 g.

0.4870 g. gave 0.1735 g. Ag.
Calc. for $C_9H_8O_4NAg$: Ag, 35.74. Found: Ag, 35.62%.

The salt melted at 149–150°, was very stable toward light, and was the only one of the silver salts investigated which was not soluble in chloroform or in benzene.

II. Derivatives of Carbethoxyhydroxamic Acid.

The Silver Salt of the Benzoyl Ester of Carbethoxydroxamic Acid,



$O = C—OC_2H_5$, $Ag—NOC—C_6H_5$ ($C=O$ below)

.—Forty grams of this salt[1] were obtained by the action of 30 g. of silver nitrate on 37 g. of the benzoyl ester of carbethoxyhydroxamic acid. After the salt was dried, it was dissolved in warm chloroform, the solution filtered and cooled to —5°. Alcohol was then added and a mass of bright yellow needles was precipitated. These were collected on a filter, and dried on a porous plate.

0.3540 g. gave 0.1210 g. Ag.
Calc. for $C_{10}H_{10}O_4NAg$: Ag, 34.15. Found: Ag, 34.18%.

The salt was readily soluble in chloroform and in benzene, but only slightly soluble in ether and insoluble in alcohol. When heated to 156–157°, the yellow color faded and a pure white salt resulted which darkens rapidly if the temperature was raised beyond this point. The salt melted with decomposition at 174°. The white form was stable at room temperature though it was much more sensitive to light than the yellow variety was. On ignition, a sample gave the following values:

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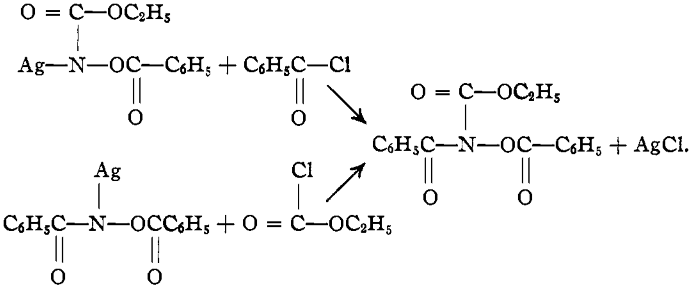
[1] Jones, *Loc. cit.*, p. 49.

0.4356 g. gave 0.1489 g. Ag.
Calc. for $C_{10}H_{10}O_4NAg$: Ag, 34.15. Found: Ag, 34.18%.

The behavior of the yellow silver salt when treated with ethyl iodide or with isoamyl iodide was described in the previous paper,[1] and it will suffice to point out here that the products obtained had the alkyl bound to nitrogen. Samples of these materials which had *not been distilled* gave the same products when hydrolyzed showing that no rearrangement had taken place during the distillation.

Structure of the Yellow Silver Salt.—Provided direct replacement of the metal occurred, the formation of these products indicates that the silver salt has the silver bound to nitrogen. If this be true, it is evident that the compound produced by the action of chlorocarbonic ester on the silver salt of dibenzhydroxamic acid should be identical with the substance formed by the action of benzoyl chloride on the silver salt under discussion. These reactions are shown by the following equations:



$$\mathrm{Ag{-}\overset{O=C-OC_2H_5}{\overset{|}{N}}{-}O\underset{\underset{O}{\|}}{C}{-}C_6H_5 + C_6H_5\underset{\underset{O}{\|}}{C}{-}Cl \searrow}$$

$$\mathrm{C_6H_5\underset{\underset{O}{\|}}{C}{-}\overset{O=C-OC_2H_5}{\overset{|}{N}}{-}O\underset{\underset{O}{\|}}{C}{-}C_6H_5 + AgCl.}$$

$$\mathrm{C_6H_5\underset{\underset{O}{\|}}{C}{-}\overset{Ag}{\overset{|}{N}}{-}O\underset{\underset{O}{\|}}{C}C_6H_5 + O = \overset{Cl}{\overset{|}{C}}{-}OC_2H_5 \nearrow}$$

(*a*) *Action of Benzoyl Chloride on the Silver Salt of Carbethoxyhydroxamic Acid.*—Eleven and five-tenths grams of the silver salt, suspended in ether, were treated with 5 g. of benzoyl chloride. After standing four hours, the silver chloride was separated by filtration, and the ether was removed by distillation. Eight grams of a colorless oil remained, which slowly deposited prismatic crystals. When recrystallized from ether and ligroin, the compound melted at 71–72°.

(*b*) *Action of Chlorocarbonic Ethyl Ester on the Silver Salt of Dibenzhydroxamic Acid.*—Five grams of the silver salt of dibenzhydroxamic acid[2] were treated with 1.5 g. of chlorocarbonic ethyl ester in the presence of ether. After two weeks, the silver chloride and the unchanged silver salt were removed by filtration, and the liquid evaporated *in vacuo*. After standing for several days, the odor of the ester had disappeared, and the remaining oil slowly solidified. The crystals melted at 71–72°, and a mixture of the products of the reactions described under (*a*) and (*b*) melted at the same temperature.

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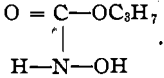
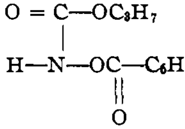
[1] Jones and Oesper, THIS JOURNAL, 36, 729 (1914).

[2] Lossen, *Ann.*, 161, 360 (1872).

The same product, therefore, resulted in both of these reactions, and it was identical with the dibenzoyl ester of carbethoxyhydroxamic acid described by Jones,[1] who prepared it from the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid and benzoyl chloride.

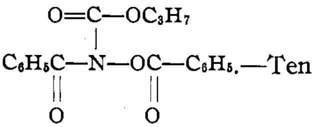
III. Derivatives of Carbpropyloxyhydroxamic Acid.

Carbpropyloxyhydroxamic Acid,  $\begin{array}{l} O=C-OC_3H_7 \\ \quad\;| \\ H-N-OH \end{array}$.—Twenty-five grams of chlorocarbonic propyl ester were added to a mixture of 14.2 g. of hydroxylammonium chloride and 28 g. of potassium carbonate. 22.5 g. of a thick colorless oil were obtained which were converted into the benzoyl ester.

Benzoyl Ester of Carbpropyloxyhydroxamic Acid,  $\begin{array}{l} \quad O=C-OC_3H_7 \\ \qquad\quad | \\ H-N-OC-C_6H_5 \\ \qquad\qquad \| \\ \qquad\qquad O \end{array}$.—Twenty-seven grams of a colorless oil were obtained by the action of 20 g. of carbpropyloxyhydroxamic acid, 11.5 g. of potassium carbonate and 23.5 g. of benzoyl chloride. All attempts to solidify the oil were unsuccessful. Accordingly, it was dissolved in alcohol, neutralized with ammonium hydroxide and 21 g. of silver nitrate were added to the solution. A bright yellow precipitate was obtained. This was crystallized from chloroform and alcohol, and formed yellow needles which melted at 144–145°.

0.4360 g. gave 0.1418 g. Ag.
Calc. for $C_{11}H_{12}O_4NAg$: Ag, 32.67. Found: Ag, 32.52%.

When heated, this salt showed no indication of changing to a white modification.

Dibenzoyl Ester of Carbisopropyloxyhydroxamic Acid,  $\begin{array}{l} \quad O=C-OC_3H_7 \\ \qquad\quad | \\ C_6H_5C-N-OC-C_6H_5 \\ \qquad \| \qquad\quad \| \\ \qquad O \qquad\quad O \end{array}$.—Ten grams of the silver salt described above were suspended in ether and 4.2 g. of benzoyl chloride were added. The reaction was completed in three days. The silver chloride was removed by filtration and the ether evaporated *in vacuo.* Nine grams of a thick oil remained which slowly deposited transparent cubical crystals. These crystals, when recrystallized from chloroform and ligroin, melted at 78–89°.

0.2822 g. gave 11.4 cc. N_2 at 28° and 745 mm.
Calc. for $C_{18}H_{17}O_5N$: N, 4.28. Found: N, 4.36%.

This compound was soluble in ether, in chloroform and in alcohol, but it was insoluble in cold ligroin and in water.

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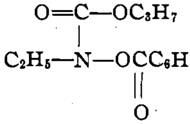
[1] Jones, *Loc. cit.*, p. 50.

The N-Ethyl Derivative of the Benzoyl Ester of Carbpropyloxyhydroxamic Acid,



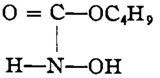
$C_2H_5-\overset{\overset{O=C-OC_3H_7}{|}}{N}-O\underset{\underset{O}{\|}}{C}C_6H_5$. — Fifteen grams of the silver salt described above were suspended in ether, and 7 g. of ethyl iodide were added. After standing two weeks in the dark, the silver iodide was removed, and the other evaporated *in vacuo.* Nine grams of a light yellow oil with a spicy odor remained.

0.2402 g. gave 12.2 cc. N_2 at 22.5° and 735 mm.
Calc. for $C_{13}H_{17}O_4N$: N, 5.53. Found: N, 5.57%.

When heated in a sealed tube with hydrochloric acid, β-ethyl hydroxylammonium chloride was obtained. This was identified by condensing it with *p*-nitrobenzaldehyde.[1] The product obtained showed that the alkyl group was bound to nitrogen.

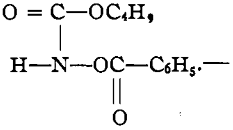
IV. Derivatives of Carbisobutyloxyhydroxamic Acid.

Carbisobutyloxyhydroxamic Acid,



$H-\overset{\overset{O=C-OC_4H_9}{|}}{N}-OH$ —Twenty-five grams of chlorocarbonicisobutyl ester, 12.8 g. of hydroxylammonium chloride and 25 g. of potassium carbonate produced 21 g. of a colorless oil which was not very soluble in water. When treated with copper acetate solution it produced a crystalline green precipitate which was not affected when boiled with water.

Benzoyl Ester of Carbisobutylhydroxamic Acid,



$H-\overset{\overset{O=C-OC_4H_9}{|}}{N}-O\underset{\underset{O}{\|}}{C}-C_6H_5$.— A colorless oil was produced by the action of 19 g. of benzoyl chloride, 9.4 g. of potassium carbonate and 18 g. of carbisobutyloxyhydroxamic acid. This was dissolved in ether and extracted with dilute sodium hydroxide. The alkaline solution was cooled to 5° and carbon dioxide was passed with the solution. A crystalline precipitate appeared. When recrystallized from warm chloroform and ligroin it formed needles melting at 43–44°. Yield, 19 g.

0.2944 g. gave 16.5 cc. N_2 at 28° and 751 mm.
Calc. for $C_{12}H_{15}O_4N$: N, 5.90. Found: N, 6.09%.

The compound was soluble in ether, in chloroform and in alcohol, but was insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbisobutyloxyhydroxamic Acid,

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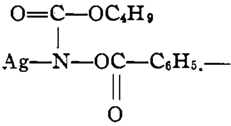
[1] Hantzsch and Hillard, *Ber.*, 31, 2066 (1898).



$\mathrm{Ag{-}N(C(=O){-}OC_4H_9){-}OC(=O){-}C_6H_5}$.—An alcoholic solution of 21.5 g. of the benzoyl derivative was treated with one equivalent of ammonium hydroxide, and then with an aqueous solution of 15 g. of silver nitrate. A bright yellow precipitate was formed which immediately became colorless where it was in contact with the solvent. The interior of the precipitate was still yellow after standing five minutes. The precipitate was collected on a filter, thoroughly washed with alcohol, and dried on a porous plate placed in an amber desiccator. After standing over night, the entire mass had blackened. This material was extracted with warm chloroform, the solution cooled to —5° and an excess of alcohol added. Bright yellow needles were precipitated.

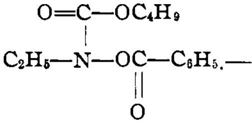
0.2492 g. gave 0.0784 g. Ag.
Calc. for $C_{12}H_{14}O_4NAg$: Ag, 31.37. Found: Ag, 31.46%.

When warmed to 80–82°, the yellow crystals become white. The white mass softened slightly at 144° and finally melts at 158°. The white form did not change to the yellow form at room temperature. A sample of the white salt, on ignition, gave the following values:

0.4230 g. gave 0.1325 g. Ag.
Calc. for $C_{12}H_{14}O_4NAg$: Ag, 31.37. Found: Ag, 31.32%.

The conversion of the yellow form into the white form took place very slowly at 40°, but the change occurred only in certain parts of the mass and the rest of the material remained yellow. Furthermore, the change appeared to commence in the interior of these regions and to spread outward, which would seem to indicate that the phenomenon is not of a photochemical nature. The most curious effect, however, was observed if the portion of the white form was rubbed against a hard surface with a porcelain spatula. Where it was rubbed, a bright yellow streak appears which immediately becomes colorless again. The rapidity of the reversion to the white form seemed to be influenced by the intensity of the light, for the change was almost instantaneous in direct sunlight, slower in diffused light, while if the salt is rubbed in the dark it remains yellow until brought into the light. No explanation of this peculiar behavior is offered.

The N-Ethyl Derivative of the Benzoyl Ester of Carbisobutyloxyhydroxamic Acid,

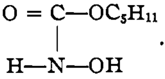


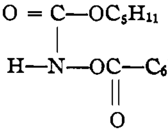
$\mathrm{C_2H_5{-}N(C(=O){-}OC_4H_9){-}OC(=O){-}C_6H_5}$.—Twenty-one and five-tenths grams of the yellow silver salt described above were suspended in ether, and 10 g. of ethyl iodide added. The reaction was complete after two weeks. A bright yellow oil with a spicy odor was obtained when the ether was evaporated. Yield, 14 g.

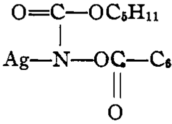
0.3096 g. gave 15.6 cc. at 29° and 740 mm.
Calc. for $C_{14}H_{19}O_4N$: N, 5.28. Found: N, 5.37%.

When heated in a sealed tube with concentrated hydrochloric acid for six hours at 110°, β-ethyl hydroxylammonium chloride was obtained, showing that this was the nitrogen derivative.

V. *Derivatives of Carbisoamyloxyhydroxamic Acid.*

Carbisoamyloxyhydroxamic Acid,  $\begin{array}{c} O = C{-}OC_5H_{11} \\ | \\ H{-}N{-}OH \end{array}$.—Twenty-five grams of chlorocarbonicisoamyl ester, 11.5 g. of hydroxylammonium chloride and 22.8 g. of potassium carbonate were allowed to react in the usual manner, and 23 g. of a thick, light yellow oil were obtained. The compound had a slight odor suggestive of isoamyl alcohol and was only slightly soluble in water. Copper acetate produced a green crystalline precipitate from an alcoholic solution which was not affected when boiled with water.

The Benzoyl Ester of Carbisoamyloxyhydroxamic Acid,  $\begin{array}{l} \quad\;\; O = C{-}OC_5H_{11} \\ \qquad\quad | \\ H{-}N{-}\underset{\overset{\|}{O}}{C}{-}C_6H_5. \end{array}$ —All attempts to obtain this compound in the solid state were fruitless. The product of the reaction of carbisoamyloxyhydroxamic acid, potassium carbonate and benzoyl chloride was a colorless oil, which, when dissolved in sodium hydroxide and precipitated by carbon dioxide, remained liquid even when thoroughly dried and cooled to —10° for several hours. It was very easily hydrolyzed by dilute alkalies, and the yield was extremely poor if the compound was purified in this way.

Silver Salt of Carbisoamyloxyhydroxamic Acid,  $\begin{array}{l} \quad\;\; O{=}C{-}OC_5H_{11} \\ \qquad\quad | \\ Ag{-}N{-}O\underset{\overset{\|}{O}}{C}{-}C_6H_5. \end{array}$ —The silver salt was precipitated from an alcoholic solution of the benzoyl ester in the form of bright yellow curds which turn white immediately. After drying the salt over night, it was dissolved in warm chloroform and reprecipitated by alcohol in the form of bright yellow needles.

0.4506 g. gave 0.1354 g. Ag.
Calc. for $C_{13}H_{16}O_4NAg$: Ag, 30.13. Found: Ag, 30.06%.

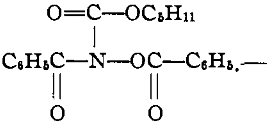
When heated to 40°, the salt turned white in patches, and at about 75°, the change was rapid and complete. If the temperature was raised still higher, no further change occurred until the salt melted at 141–142°. The white form, on ignition, gave the following results:

0.3632 g. gave 0.1090 g. Ag.
Calc. for $C_{13}H_{16}O_4NAg$: Ag, 30.13. Found: Ag, 30.01%.

This white form showed no tendency to revert to the yellow modification, even in contact with a particle of the latter at —10°. On one occasion, however, the yellow form was precipitated as usual from a chloroform solution by alcohol, and as soon as the crystals were separated from the solvent by filtration they began to turn white. However, the change was localized, and after two weeks the yellow and the white forms still existed side by side. We have never been able to duplicate this change at room temperature.

As was stated above, it seemed possible that molecular weight determinations might throw some light on the nature of this color change. The figures obtained in freezing benzene gave values which varied from 739 to 1514 depending on the concentration of the solution, and the values in boiling benzene, using Menzies[1] method, were of the same order. The value for the simple salt is 538.

Dibenzoyl Derivatives of Carbisoamyloxyhydroxamic Acid,



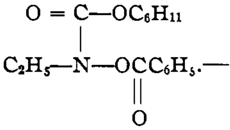
$$C_6H_5\underset{\underset{O}{\|}}{C}—\overset{\overset{O=C—OC_5H_{11}}{|}}{N}—O\underset{\underset{O}{\|}}{C}—C_6H_5.$$

—Eight grams of the silver salt described above were treated with 3.1 g. of benzoyl chloride. The reaction was completed after 2 weeks and 5 g. of a colorless oil were obtained on evaporating the ether. After standing in an exhausted desiccator for 10 days, clear prismatic crystals were deposited, which, after recrystallization from warm ligroin, melted at 69–70°.

0.3050 g. gave 11 cc. N_2 at 26° and 749.5 mm.
Calc. for $C_{20}H_{21}O_5N$: N, 3.94. Found: N, 3.95%.

The compound is soluble in ether, in chloroform and in alcohol, slightly soluble in ligroin and insoluble in water.

The Ethyl Derivative of the Benzoyl Ester of Carbisoamyloxyhydroxamic Acid,



$$C_2H_5—\overset{\overset{O\,=\,C—OC_6H_{11}}{|}}{N}—O\underset{\underset{O}{\|}}{C}C_6H_5.$$

—Eleven grams of the yellow salt and 4.8 g. of ethyl iodide were allowed to react in the presence of ether for two weeks. A light yellow oil remained when the ether evaporated.

0.4323 g. gave 20 cc. N_2 at 25° and 745 mm.
Calc. for $C_{15}H_{21}O_4N$: N, 5.01. Found: N, 5.06%.

It gave β-ethylhydroxylamine upon hydrolysis.

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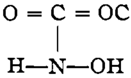
[1] Menzies, THIS JOURNAL, 32, 1615 (1910).

VI. *Derivatives of Carbbenzyloxyhydroxamic Acid.*

Carbbenzyloxyhydroxamic Acid,



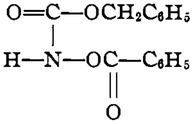
$$\begin{array}{l} O = C = OCH_2C_6H_5 \\ \quad\ | \\ H—N—OH \end{array}$$

.—Forty grams of chlorocarbonic benzyl ester, 16.2 g. of hydroxylammonium chloride and 32.4 g. of potassium carbonate produced a thick yellow oil which solidified on standing over night. When recrystallized from chloroform and ligroin, the compound was obtained in shining scales melting at 65°. Yield, 30 g.

0.2530 g. gave 19.4 cc. N_2 at 28° and 747.5 mm.
Calc. for $C_8H_9O_3N$: N, 8.38. Found: N, 8.29%.

The compound was insoluble in ether, in alcohol and in chloroform, somewhat soluble in water and insoluble in cold ligroin.

The Benzoyl Ester of Carbbenzyloxyhydroxamic Acid,



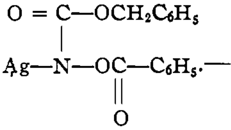
$$\begin{array}{l} \qquad\ O{=}C—OCH_2C_6H_5 \\ \qquad\quad\ | \\ H—N—OC—C_6H_5 \\ \qquad\qquad\ \| \\ \qquad\qquad\ O \end{array}$$

—Eighteen and five-tenths grams of carbbenzyloxyhydroxamic acid were treated with 7.46 g. of potassium carbonate and 15.6 g. of benzoyl chloride. An oil separated which was soon solidified. When recrystallized from warm alcohol and ligroin it formed white needles melting at 109–110°.

0.2944 g. gave 13.6 cc. N_2 at 23.5° and 748.5 mm.
Calc. for $C_{15}H_{13}O_4N$: N, 5.16. Found: N, 5.12%.

The compound was soluble in alcohol, in ether and in chloroform, and insoluble in water and in cold ligroin.

The Silver Salt of the Benzoyl Ester of Carbbenzyloxyhydroxamic Acid,



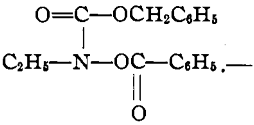
$$\begin{array}{l} O = C—OCH_2C_6H_5 \\ \quad\ \ | \\ Ag—N—OC—C_6H_5 \\ \qquad\quad\ \| \\ \qquad\quad\ O \end{array}$$

.—Sixteen grams of the benzoyl ester, when treated with ammonium hydroxide and 10.3 g. of silver nitrate gave a yellow precipitate which immediately turned white. When recrystallized from chloroform and alcohol it formed bright yellow needles which melted at 150–151°.

0.3583 g. gave 0.1025 g. Ag.
Calc. for $C_{15}H_{21}O_4NAg$: Ag, 28.67. Found: Ag, 28.61%.

The salt became white when heated, but the transition temperature was so near the melting point that it was not possible to isolate the white form in this way.

Ethyl Derivative of the Benzoyl Ester of Carbbenzyloxyhydroxamic Acid,



$$\begin{array}{l} \quad O{=}C—OCH_2C_6H_5 \\ \qquad\ | \\ C_2H_5—N—OC—C_6H_5 \\ \qquad\qquad\ \| \\ \qquad\qquad\ O \end{array}$$

.—Eight grams of the silver salt described above were allowed to react with 2.3 g. of ethyl iodide for one week. 5 g. of a light yellow oil were obtained.

0.4658 g. gave 20 cc. N_2 at 21° and 745 mm.
Calc. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.81%.

Summary.

1. In the course of experiments which had in view the preparation of mixed oximidocarbonic esters, RO.C(NOH).OR′ several new hydroxyurethanes, including the methyl, isopropyl, isobutyl, isoamyl and benzyl derivatives were prepared, and their benzoyl esters studied.

2. The silver salts of some of these benzoyl esters were obtained in two modifications, white and yellow, of the same composition and mutually transformable. While the methyl, ethyl and isopropyl derivatives were prepared only as yellow salts, the compounds with larger radicals, *viz.*, isobutyl, isoamyl, and benzyl, were obtained in two forms.

3. These silver salts have been found to yield derivatives with the alkyl groups bound to *nitrogen* instead of to *oxygen*. This unforseen reaction prevented us from obtaining the acyl derivatives of mixed oximidocarbonic esters, which would otherwise have resulted from the action of various alkyl halides upon these silver salts.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

THE ISOLATION OF CRYSTALLINE *dl*-GLYCERIC ALDEHYDE FROM A SYRUP OBTAINED BY THE OXIDATION OF GLYCEROL.

BY EDGAR J. WITZEMANN.

Received August 7, 1914.

dl-Glyceric aldehyde is a compound of considerable importance. In the various more or less theoretical discussions of the break-down and synthesis of the hexoses, either in the chemical laboratory or in the living organism, *dl*-glyceric aldehyde, along with dihydroxyacetone, assumes a prominent place. The collection of facts with regard to its behavior in the body has been retarded by the difficulty of obtaining sufficient quantities with which to work. The only method now known of preparing the pure substance is that of Wohl, and this method is extremely laborious. For physiological experiments in man, quantities are required which make Wohl's method well nigh prohibitive. The method of Fenton and Jackson is simple and undoubtedly gives a large yield of glyceric aldehyde, although admixed with impurities. Dr. R. T. Woodyatt, of this laboratory, sometime ago published a preliminary report on the use of glyceric aldehyde, prepared according to the latter method, in diabetes mellitus.[1] The nature of these results was such as to emphasize the necessity of determining

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[1] *J. Am. Med. Assoc.*, **55**, 2109–2112 (1910).