SOME HYDROXYURETHANES AND THE SILVER SALTS OF THEIR ACYL DERIVATIVES.

A Thesis

by

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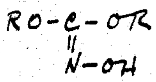
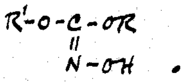
Introduction

Oximido carbonic esters, as a class of substituted derivatives of carbonic acid may be of two types: simple esters in which the two radicals are alike;



$RO-\underset{\substack{\| \\ N-OH}}{C}-OR$

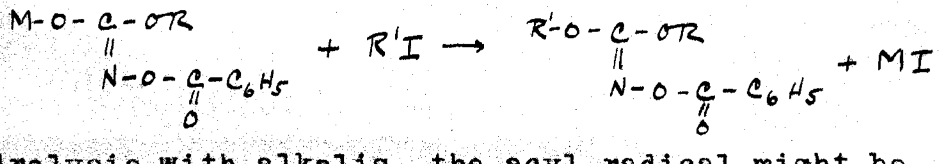
and mixed esters in which they are different:



$R'-O-\underset{\substack{\| \\ N-OH}}{C}-OR$.

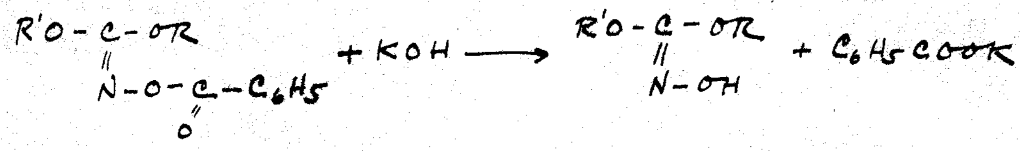
The latter class is interesting, since it offers the possibility of obtaining geometrical isomers, syn and anti forms. Some work was carried out in this laboratory by Jones and Oesper (1) with the hope of isolating these isomeric forms, and they tried several methods of preparing these mixed oximido esters, but no general satisfactory procedure was devised. It was found that the reactions expected, either did not occur, or that isomers of the desired materials were produced, or that unstable products were formed, which could not be isolated.

It seemed probable however, that the mixed oximido carbonic esters might be prepared by the following method: the salts of the acylated carbalkoxy hydroximic acids, when treated with alkyl halides, might be expected to give the corresponding acyl oximido carbonic esters.



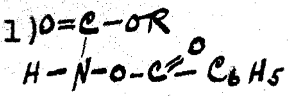
$$M-O-\underset{\substack{\| \\ N-O-\underset{\substack{\| \\ O}}{C}-C_6H_5}}{C}-OR + R'I \longrightarrow R'-O-\underset{\substack{\| \\ N-O-\underset{\substack{\| \\ O}}{C}-C_6H_5}}{C}-OR + MI$$

By hydrolysis with alkalis, the acyl radical might be eliminated.

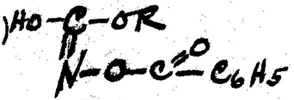


$$R'O-\underset{\substack{\| \\ N-O-\underset{\substack{\| \\ O}}{C}-C_6H_5}}{C}-OR + KOH \longrightarrow R'O-\underset{\substack{\| \\ N-OH}}{C}-OR + C_6H_5COOK$$

The formation of acylated derivatives of hydroxyurethane admits of the possibility of isomers; the oxam form (1) and the oxim form (2).

(1) 

$$\begin{array}{l}O=C-OR\\ \quad\;|\\ H-N-O-\overset{O}{\overset{\|}{C}}-C_6H_5\end{array}$$

(2) 

$$\begin{array}{l}HO-C-OR\\ \qquad\|\\ \qquad N-O-\overset{O}{\overset{\|}{C}}-C_6H_5\end{array}$$

The structure of the metallic derivatives of these esters admit also of two possibilities, the one in which the metal is bound to oxygen, the other, in which it is bound to nitrogen.

Tafel and Enoch (2) pointed out that the acid amides yield mercury and silver salts, as might be expected, from the replacable amido hydrogen atoms, but the alkyl derivatives obtained by interaction of these salts with alkyl halides, are not the expected nitrogen esters, but are the corresponding oxygen ethers. The structure of the sodium salt is claimed by Titherley (3) to be that of the normal amide, that is, with the metal attached to nitrogen. This contention is supported by the fact that these sodium derivatives do not readily react with alkyl halides, while, the sodium atom attached to oxygen of an hydroxyl group should readily yield alkyl derivatives. "Hence it must be supposed" states Titherley, "that the above amide sodium derivatives are true sodamide derivatives and not sodium salts of the type $R\begin{array}{l}=NH\\ -ONa\end{array}$. Whether the acid amides themselves are to be represented by the constitutional formula $R\begin{array}{l}=NH\\ -OH\end{array}$ or $R\begin{array}{l}-NH_2\\ =O\end{array}$ is a question to be explained probably only on the lines of tautomerism."

Titherley's(3) explanation, that the difference in color of the silver salts prepared by him and of those prepared by Tafel and Enoch is due to a difference in structure, the orange salt being $R-C\genfrac{}{}{0pt}{}{=O}{-NHAg}$, the white form $R-C\genfrac{}{}{0pt}{}{-OAg}{=NH}$ has been criticised by Freer and Sherman.(4) These investigators claim that the silver salts have the metal bound to oxygen, the sodium salts the metal bound to nitrogen, and that the difference in color of the silver salts of the same derivative cannot be attributed to structural differences.

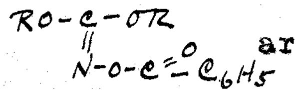
Further evidence, to support the general contention that the salts of the amides have the silver atom attached to oxygen, and sodium to the nitrogen atom is given by Blacher,(5) Comstock and Wheeler,(6) Wheeler and Walden.(7)

If the silver salts of the acylated hydroxyurethanes are analogous to the corresponding amide silver salts, then it should be possible to prepare the desired acylated mixed oximido esters by similar methods.

The results of the work of Jones and Oesper(8) showed the existence of two different types of silver salts of the acylated hydroxyurethanes, viz: yellow and white. These two forms, under proper conditions, may be converted into one another. Both forms, when pure, are perfectly stable and have the same empirical composition. The isoamyl and ethyl esters prepared from the yellow forms of the silver salts, by treatment with the corresponding halides, gave on hydrolysis, products, which indicated that the silver atom was attached to the nitrogen in all cases investigated. The behavior of the white forms of the silver salts towards alkyl halides was not investigated. It was therefore deemed desirable to study the behavior of the white silver salts towards halogen alkyls, in order to determine whether the two forms are tautomeric, or whether they are polymeric.

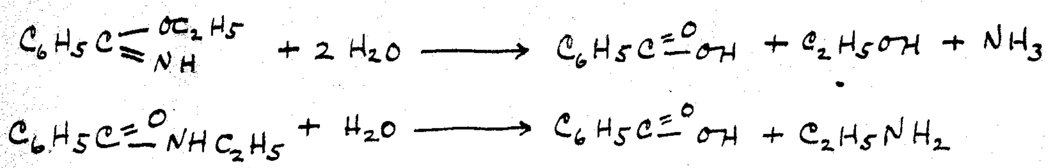
The substituted acyl drivatives of several hydroxyurethanes were prepared and studied with the hope that some of these compounds might yield silver salts, with the silver attached to the oxygen atom, and thus provide a means for preparing the mixed oximido esters. This paper constitutes a report of the preparation and investigation of a series of acyl and substituted acyl hydroxyurethanes and their corresponding silver salts, together with the alkyl derivatives obtained by treating the salts with ethyl iodide.

The hydroxyurethanes are usually prepared by treating the corresponding alkyl chlor carbonates in the presence of moist ether, with an equivalent of hydroxylamine hydrochloride or sulfate, and one or two equivalents respectively, of an alkali carbonate. The benzoyl esters of these derivatives can be prepared in one of two ways.

One method, an aqueous or ethereal solution of the hydroxamic acid is treated with benzoyl chloride in the presence of powdered potassium carbonate. In the preparation of the substituted acyl derivatives, the sodium salts of the hydroxamic acids are suspended in dry ether and treated with an equivalent of the acid chloride. The sodium salts of the hydroxamic acids are obtained by treatment of an alcoholic solution of the acid with an equivalent of sodium ethylate. The silver salts of these esters are precipitated from an alcoholic solution of the acyl derivative, to which an equivalent of ammonium hydroxide has been added, by the addition of an aqueous solution of an equivalent of silver nitrate. When treated in this way either yellow or white silver salts are obtained. In some cases, on addition of the first portion of the silver nitrate solution, a yellow precipitate forms and this turns white upon addition of the remainder of the silver nitrate solution. The silver salts of the benzoyl esters both yellow and white forms are very slightly soluble in ether, readily soluble in chloroform or benzene, and alcohol precipitates the yellow form of the salt from the solution, regardless of the original color of the salt. The silver salts of the substituted benzoyl esters which are discussed in this paper, are only moderately if at all soluble in chloroform and benzene, and attempts at purification by recrystallization were unsuccessful. In most cases these salts were purified by extraction of extraneous matter with ether. It has been found that the silver salts of the meta nitrobenzoyl esters of the several hydroxamic acids are white salts. When suspended in chloroform or benzene, these white salts yield yellow solutions. When suspended in ether, they remain unchanged. The silver salts of the para nitrobenzoyl esters of the acids studied, were all yellow with the exception of the one prepared from isoamyl hydroxamic acid, which precipitated yellow but immediately turned white. The preparation of the ethyl esters from the silver salts was accomplished by allowing the calculated weight of ethyl iodide to stand in contact with the silver salt in the presence of dry ether, chloroform, or ligroin. No evident reaction occurs when the silver salts suspended in ether are treated with the calculated weight of benzyl chloride. Reaction does occur however, if chloroform is used as solvent, and the reaction mixture refluxed for several days. All the benzyl derivatives, like the ethyl esters were aromatic oils at room temperature, showing no tendency to solidify even when allowed to stand in ice-salt mixtures for several hours. Compounds of the type  $RO-\underset{\underset{N-O-\overset{O}{\overset{\|}{C}}-C_6H_5}{\|}}{C}-OR$ are known, and are crystalline solids, while the isomeric derivatives which were isolated were oils, with no tendency to solidify. Hydrolysis data indicated, the oils were alkyl nitrogen esters. It was hoped that this distinction between the physical state of these isomeric esters would hold true throughout, but it has been found to be only apparent. The alkyl esters obtained from several of the silver salts of the para and meta nitrobenzoyl esters were well defined crystalline solids, but hydrolysis indicated that the alkyl group in each case was attached to nitrogen and not to oxygen. It may be possible, however, that the destinction is real and not merely apparent. That is, conditions for hydrolysis such as temperature, pressure, may not have been chosen so as to prevent rearrangement of the oximido esters to alkyl nitrogen derivatives before the hydrolysis actually began. Numerous examples of the transference of an alkyl group from an oxygen to a nitrogen atom are recorded in the literature while only a few instances for the reverse case are mentioned. For example Hoffman and Olshausen(9) and also Pomarew(10) found that normal cyanuric esters pass into the isocyanuric esters on gentle heating. Again, Wheeler and Johnson(11) showed that imino ethers rearrange to alkyl amides on heating with alkyl iodides. Wislecenus and Goldschmidt(12) noted many cases in which mere heating converted the imino ether into the amide. Several times in the course of this work, the products isolated from the reaction between the silver salt and ethyl iodide, consisted of an oil which solidified on standing for several hours in vacuo, or on cooling in an ice-salt mixture, and there is a remote possibility that this physical transformation was an external manifestation of a chemical rearrangement.

Entirely different products might be obtained if the silver salts were refluxed with alkyl halide, directly, or in the presence of a solvent other than ether. The present work with the exception of the preparation of the benzyl derivatives, has been limited to the preparation of the ethyl esters, under identical conditions already described, i.e., treatment of the silver salts with the calculated amount of ethyl iodide in ether, chloroform, or ligroin, at room temperature and in the dark for several days. Wheeler and Johnson(13) by slight variations in experimental conditions, obtained either the alkyl amide or the isomeric imido ester from the reaction between silver formanilid and ethyl iodide. Heating the silver salt and slightly less than the calculated amount of alkyl halide, in a sealed tube, produced the amide derivative, while gentle boiling of the reactants in an ether solution yielded an almost theoretical quantity of the expected imido ester. Wheeler, commenting on these experiments says: "These striking results show that the method of preparation of a compound proves nothing in regard to its structure and that arguments concerning structure based solely on the compounds formed in a reaction have no weight. In the sodium salts of the amides, the metal is universally represented as attached to nitrogen, simply because these salts give nitrogen alkyl compounds with alkyl halides. That the metal is attached to nitrogen in these compounds is improbable. The above reactions show that slight changes in conditions may produce opposite results, and the difference in conditions when alkyl halides act on sodium salts on the one hand, and on silver salts on the other, is certainly great--greater at least, than is necessary to produce the opposite results in the case of the same material, i.e., the silver salts."

When the silver salt of benzamide is treated with ethyl iodide the metal is replaced by the alkyl radical. The product formed is determined by the temperature at which reaction takes place. The substance obtained at room temperature yields ammonia, and therefore, is the imino ester derivative(1). The compound formed from the silver salt of benzamide and ethyl iodide at 100°C is a substitution product of the amide(2) in which the alkyl group is bound to the nitrogen. The hydrolysis of the two isomers is represented as follows:

I


II

$$\text{I}\quad C_6H_5C\genfrac{}{}{0pt}{}{-OC_2H_5}{=NH} + 2\,H_2O \longrightarrow C_6H_5C\overset{=O}{-OH} + C_2H_5OH + NH_3$$

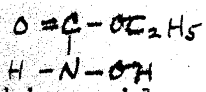
$$\text{II}\quad C_6H_5C\overset{=O}{-NHC_2H_5} + H_2O \longrightarrow C_6H_5C\overset{=O}{-OH} + C_2H_5NH_2$$

All the chemical evidence resulting from the present work indicates that there is no structural difference between the white and yellow modifications of the silver salts under investigation. In several cases identical products resulted from treatment of the silver salt with ethyl iodide in the presence of different solvents, which favor one or other forms of the silver salt. The white salts investigated, do not revert to the yellow form in the presence of ether. Since they are only moderately soluble in chloroform and benzene in most cases, molecular weight methods cannot be employed in determining whether the two forms of the silver salts are polymers. Some molecular weight values were determined on the silver salt of the benzoyl ester of carbamyloxy hydroxamic acid. The results of both ebullioscopic and cryoscopic methods indicated association of two or more molecules of the salt and furthermore, the values of the molecular weights increased with increasing concentrations of solutions. While this data has not been regarded as conclusive, evidence of polymerization, yet it may be considered as supporting in a general way the results of the present investigation.

It may be possible that the sodium salts or perhaps other metal salts of the acyl derivatives, such as the barium, zinc, cadmium, and lead salts may yield the corresponding alkyl oxygen derivatives, and these salts will be studied later. Attempts will also be made to prepare the higher carbalkyloxy hydroxamic acids containing larger aromatic radicals, such as triphenyl methyl, diphenyl methyl etc., in order to study the effect of such groups on the relative stability of the white and yellow forms of the silver salts. It seems highly probable that the two forms of the silver salts may be two physical modifications of the same substance, or polymeric forms.

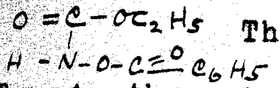
Experimental Part.

A. Derivatives of Carbethoxyhydroxamic Acid.



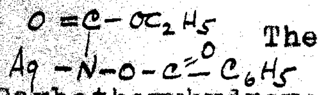
$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\ | \\ H-N-OH \end{array}$$

Carbethoxyhydroxamic Acid. Sixty-two grams of this acid were obtained from 56.7 grams of hydroxylamine sulfate and 95.4 grams anyhdrous potassium carbonate, by the method described by Jones.(14)



$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\ | \\ H-N-O-C\overset{O}{=}C_6H_5 \end{array}$$

The Benzoyl Ester of Carbethoxyhydroxamic Acid.(15) Twenty-three and seven tenths grams of a colorless oil with a strong odor of benzoyl chloride were obtained from 12 grams of carbethoxyhydroxamic acid, and 16 grams of benzoyl chloride, dissolved in ether, when treated with 7.9 grams potassium carbonate. This was not purified or analyzed, but converted into its corresponding silver salt.



$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\ | \\ Ag-N-O-C\overset{O}{=}C_6H_5 \end{array}$$

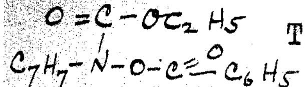
The Silver Salt of the Benzoyl Ester of Carbethoxyhydroxamic Acid.(16) Thirteen grams of the benzoyl ester dissolved in alcohol, neutralized with ammonium hydroxide, and an aqueous solution of 10 grams of silver nitrate produced a precipitate of the yellow silver salt. After recrystallization from chloroform and alcohol 14 grams of the pure salt were obtained. On analysis the following data was obtained.

(1). 0.2996 grams salt gave 0.1019 grams Ag.

(2). 0.3042 " " " 0.1031 " " .

Calc. for $C_{10}H_{10}O_4N\,Ag$: Ag, 34.15. Found: Ag (1) 34.08, (2) 33.9%

Attempts were made to convert several grams of this salt into its white modification by careful heating, but the results were unsuccessful. Even when suspended in absolute alcohol, reduction occurs. Ittwas hoped that the latter method would yield the white form of the silver salt.



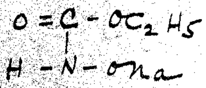
$$\begin{array}{l} \quad O=C-OC_2H_5 \\ \qquad\;\, | \\ C_7H_7-N-O-C(=O)-C_6H_5 \end{array}$$

The N-Benzyl Derivative of the Benzoyl Ester of Carbethoxyhydroxamic Acid. 12 grams of the silver salt and 4.8 grams of benzyl chloride were allowed to stand in the presence of 100 c.c. chloroform in the dark for two weeks. Only a small amount of silver chloride having formed the mixture was refluxed gently for 40 hours, after which reaction was complete. After removal of silver chloride and chloroform, a light yellow residual oil weighing 10.7 grams was obtained. After heating over a water bath, under diminished pressure to free it from traces of solvent, it was subjected to analysis, the following data was obtained:

0.2828 grams gave 11.5 c.c. N_2 at 27° and 746.7 mm.

Calc. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.44%.

This oil gave no indications of solidifying, even when kept for some time at -5°C. It boiled at 172 - 175° at 55mm., with slight decomposition.. It has a peppermint-like odor, is soluble in chloroform and alcohol, insoluble in ligroin and water. Attempts to prepare this derivative with ether as solvent were unsuccessful.



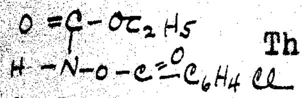
$\begin{array}{l} O=C-OC_2H_5 \\ \quad | \\ H-N-ONa \end{array}$

The Sodium Salt of Carbethoxyhydroxamic Acid. Sixteen grams carbethoxyhydroxamic acid dissolved in absolute alcohol and treated with an alcoholic solution of an equivalent quantity of sodium ethylate. A white crystalline precipitate separated on standing. After drying in a vacuum desiccator, analysis indicated the sodium content to be low. The salt is very hygroscopic, and after drying in a desiccator containing phosphorus pentoxide until constant weight had been obtained, the following analytical data was obtained:

(1). 0.5412 grams gave 0.2916 grams Na_2SO_4 .

(2). 0.5296 " " 0.2909 " " .

Calc. for $C_3H_6O_3NNa$:Na, 18.0. Found: Na (1) 17.45, (2) 17.78%. Jones(17) described the hydrated form of this salt. It is slightly soluble in alcohol, very soluble in water, insoluble in ether and ligroin.



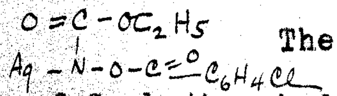
$\begin{array}{l} O=C-OC_2H_5 \\ \quad | \\ H-N-O-\overset{O}{C}-C_6H_4Cl \end{array}$

The para Chlorbenzoyl Ester of Carbethoxyhydroxamic Acid. Seven grams of the powdered sodium salt were suspended in dry ether and treated with an ethereal solution of 9.6 grams of para chlorbenzoyl chloride. Reaction takes place very readily and it was found best to add the solution of the acid chloride in small portions, cooling the reaction mixture with running water. After standing two days, the sodium chloride was removed by filtration, and the ether distilled off. A light yellow oil remained, which solidified on standing over night in an exhausted desiccator. The product was recrystallized from ether and ligroin, and melted at 75.5 -76.5° C. Yield 9 grams.

0.2224 grams gave 11.8 c.c. N_2 at 26°, and 737.6mm.

Calc. for $C_{10}H_{10}O_4NCl$: N, 5.75. Found: N, 5.75%.

This derivative is soluble in ether and alcohol, insoluble in ligroin and water.



$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\ | \\ Ag-N-O-C\overset{O}{=}C_6H_4Cl \end{array}$$

The Silver Salt of the para Chlorbenzoyl Ester of Carbethoxyhydroxamic Acid. 8.5 grams of the ester were dissolved in alcohol, treated with an equivalent quantity of ammonium hydroxide and an aqueous solution of 5.9 grams silver nitrate added. A bright yellow precipitate of the silver salt is obtained. This was separated by filtration, washed well with water, and dried on a porous plate in vacuo. While drying, the yellow salt changed rapidly to white through out the entire mass. The dried mass was extracted with ether to free it of any ester which had not reacted. Yield 10 grams. On analysis the following results were obtained:

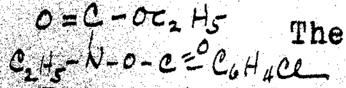
(1). 0.2037 grams gave 0.0624 grams Ag.

(2). 0.3318 " " 0.1016 " " .

Calc. for $C_{10}H_9O_4NClAg$: Ag, 30.78. Found: Ag (1) 30.63%

(2) 30.62%

This salt melts at 210° C with decomposition. It is slightly soluble in chloroform and benzene, insoluble in ligroin, ether, carbon tetrachloride and water.



$$\begin{array}{l} O=C-OC_2H_5 \\ \quad | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_4Cl \end{array}$$

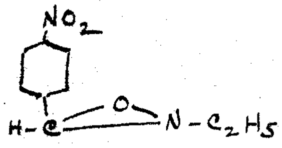
The N-Ethyl Derivative of the para Chlorbenzoyl Ester of Carbethoxyhydroxamic Acid. Ten grams of the white silver salt, suspended in anhydrous ether, together with 4.5 grams ethyl iodide were allowed to stand for several days, in the dark. The silver iodide was removed by filtration, ether distilled off, and 6.5 grams of a pale yellow oil remained.

0.4133 grams gave 20.6 c.c. N_2 at 29° C and 739.7 mm.

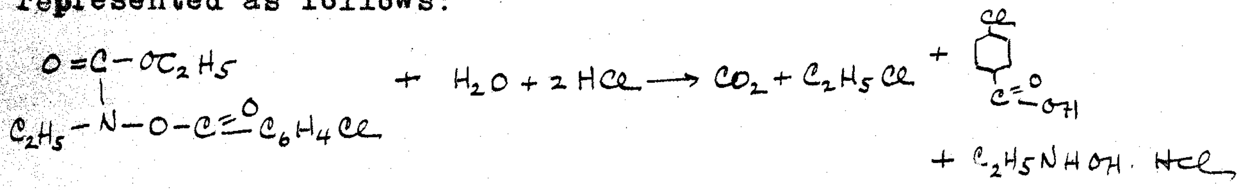
Calc. for $C_{12}H_{14}O_4NCl$: N, 5.16. Found: N 5.33%.

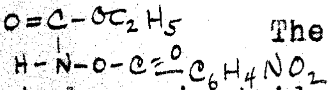
The product has a spicy odor, and gives no indications of solidifying even when cooled in an ice-salt mixture for some time.

Hydrolysis of the above N-Ethyl derivative with Hydrochloric Acid. Two grams of the above yellow oil were heated with 12 c.c. of concentrated hydrochloric acid in a sealed tube for one week at 105°C. Carbon dioxide and ethyl chloride escaped when the tube was opened. The contents of the tube were extracted with ether, and the residue obtained from the ether identified as para chlorbenzoic acid. The aqueous solution was evaporated in a steam bath, until a dark yellow oil remained. It was identified as B-ethyl hydroxylamine hydrochloride by condensing it with para nitrobenzaldehyde. The condensation product on recrystallization from ether and ligroin melted at 123 - 124° C which is in agreement with the value given by Hantzsch(18) and Behrend and Leuchs(19) for N-ethyl p-nitro isobenzaldoxime



Therefore the ethyl group was bound to nitrogen, since hydroxylamine would have been produced by the hydrolysis of the ethoxy derivative. The hydrolysis may be represented as follows:





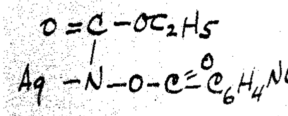
$O=C-OC_2H_5$ / $H-N-O-C(=O)-C_6H_4NO_2$

The meta Nitrobenzoyl Ester of Carbethoxyhydroxamic Acid. Five grams of sodium salt, suspended in anhydrous ether, on treatment with 7.3 grams meta nitrobenzoyl chloride gave after standing for three days, a light yellow oil which solidified on standing for several hours. This was recrystallized from ether and ligroin, and melted at 88.5 - 89° C. Yield 6.5 grams.

0.7349 grams gave 0.0977 grams NH_3

Calc. for $C_{10}H_{10}O_6N_2$: N, 11.03. Found : N, 10.95%.

The ester is soluble in ether and alcohol, insoluble in ligroin and water.



$O=C-OC_2H_5$ / $Ag-N-O-C(=O)-C_6H_4NO_2$

The Silver Salt of the meta Nitrobenzoyl Ester. 8.7 grams of the ester, dissolved in alcohol, were treated with an equivalent quantity of ammonium hydroxide and an equivalent of silver nitrate. A heavy white gelatinous precipitate of the silver salt was obtained. After washing with distilled water and drying in an amber desiccator, the dry salt was washed with ether and again dried. The following results were obtained on analysis:

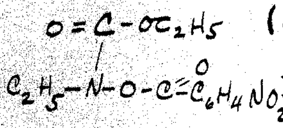
(1) 0.1135 grams gave 0.0335 grams Ag.

(2) 0.1020 " " 0.0300 " ".

Calc. for $C_{10}H_9O_6N_2Ag$: Ag, 29.89. Found (1) 29.60% Ag.

(2) 29.41% Ag.

The salt melts with decomposition at about 204° C. It is slightly soluble in chloroform and benzene yielding a yellow solution, insoluble in ether and ligroin.



$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\;\; | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

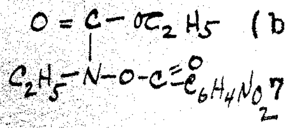
(a) The N-Ethyl derivative of meta Nitrobenzoyl Ester.. 9.5 grams of the silver salt suspended in ligroin and 4.1 grams ethyl iodide gave after standing in the dark for three weeks, 3.7 grams of a light yellow oil, which solidified after standing several hours. Recrystallization from ether and ligroin yielded crystals which melted at 67.5 - 68.5° C.

0.1496 grams gave 13.5 c.c. N_2 at 27° C, and 744 mm.

Calc. for $C_{12}H_{14}O_6N_2$: N, 9.93. Found, N 9.81%.

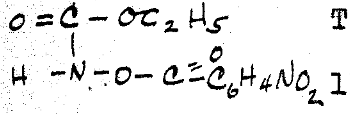
This derivative is soluble in ether, ligroin, insoluble in water.

Hydrolysis of (a))yielded B-ethyl hydroxylamine which was identified in the usual manner by condensation with para nitro-benzaldehyde. Therefore, the alkyl group is bound to nitrogen and not to oxygen.



$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\;\; | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

(b) The N-Ethyl derivative. Same as in (a). 7 grams of white silver salt were suspended in chloroform and treated with 3 grams ethyl iodide. The chloroform solution was yellow at the beginning of the reaction. After standing for ten days, 3.5 grams of a dark yellow oil were obtained. This solidified on standing, and on recrystallization yielded a mass of white crystals melting at 67 ° C. This is in agreement with the melting point of the product obtained in (a), and hence is identical with it. It was hoped that the reaction of the silver salt in the two solvents would yield different products.


$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\;| \\ H-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

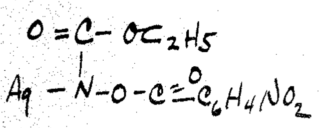
The para Nitrobenzoyl Ester.

11 grams carbethoxyhydroxamic acid and 19.4 grams para nitrobenzoyl chloride were dissolved in ether. To this mixture 7.3 grams powdered potassium carbonate were added in small portions. After standing for several hours, potassium chloride and ether were removed and a light yellow oil remained which solidified after standing for several hours. The yield, after recrystallization from ether and ligroin, was 12 grams. An analysis of the ester gave the following data:

0.0911 grams gave 9.0 c.c. N_2 at 25 ° C and 744.4 mm.

Calc. for $C_{10}H_{10}O_6N_2$: N, 11.03. Found, N 10.85 %.

This derivative is soluble in ether and alcohol, insoluble in water and ligroin. It melted at 92°C.


$$\begin{array}{l} O=C-OC_2H_5 \\ \quad\;| \\ Ag-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

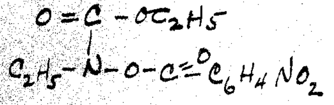
The Silver Salt of the para Nitrobenzoyl Ester.

11.6 grams of the ester dissolved in alcohol, treated with an equivalent quantity of ammonium hydroxide and an aqueous solution of 7.8 grams of silver nitrate. The yellow silver salt obtained, was dried in an amber desiccator, and then washed with ether. Yield 11.4 grams.

(1). 0.2232 grams gave 0.0678 grams Ag.
(2). 0.2354 " " 0.0713 " ".

Calc. for $C_{10}H_9O_6N_2Ag$: Ag, 29.90. Found (1) Ag, 30.35%
(2) ", 30.28%

The salt is insoluble in chloroform, benzene, alcohol, carbon tetrachloride, ether and water.



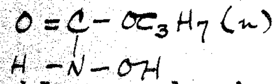
$\overset{O=C-OC_2H_5}{C_2H_5-N}-O-\overset{O}{C}-C_6H_4NO_2$

The N-Ethyl Derivative of the para Nitrobenzoyl Ester. 14.4 grams of the above silver salt suspended in ether were treated with 6.2 grams ethyl iodide. After standing in the dark for several days, reaction was complete and 8 grams of a light yellow oil were obtained. Attempts to solidify this oil by cooling were unsuccessful. When subjected to analysis the following data were obtained:

0.2956 grams gave 25.9 c.c. N_2 at 24°C and 743.6 mm.

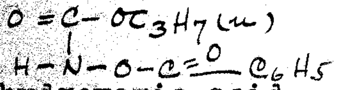
Calc. for $C_{12}H_{14}O_6N_2$: N, 9.93. Found N, 9.66%.

B. Derivatives of Carb n-propyloxyhydroxamic Acid.



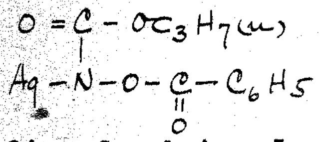
$\overset{O=C-OC_3H_7(n)}{H-N}-OH$

Carb n-propyloxyhydroxamic acid. 52 grams chlor carbonic n-propyl ester, 34.8 grams hydroxylamine sulfate, and 58.5 grams potassium carbonate produced 43.1 grams of the acid, by the method described by Jones(20) for the preparation of oxyurethane. Like the isomeric isopropyl derivative which is described by Jones and Oesper(21) it is an oil.



$\overset{O=C-OC_3H_7(n)}{H-N}-O-\overset{O}{C}-C_6H_5$

The Benzoyl Ester of Carb n-propyloxyhydroxamic acid. 10 grams of the acid, 11.8 grams redistilled benzoyl chloride were dissolved in ether, to which 5.8 grams powdered potassium carbonate was added in small portions. After standing over night, the potassium chloride and ether were removed and 17.8 grams of a yellow oil were obtained. It contained some benzoyl chloride as evidenced by its odor. Attempts to solidify the oil were without success. It is soluble in ether, alcohol, insoluble in ligroin and water. The oil was not analyzed but converted into the silver salt.



$$\begin{array}{l} O=C-OC_3H_7(n) \\ \quad\;\, | \\ Ag-N-O-\underset{\overset{\|}{O}}{C}-C_6H_5 \end{array}$$

The Silver Salt of the Benzoyl Ester.of

17.2 grams of the above ester were dissolved in alcohol, neutralized with ammonium hydroxide, and a solution of 13 grams silver nitrate added. A heavy yellow precipitate which had formed, was washed with distilled water and dried in an amber desiccator. The chloroform extract on cooling in an ice-salt bath yielded on addition of cold ligroin light yellow needles. Yield 19 grams. An analysis of the yellow salt gave the following data:

0.3181 grams gave 0.1035 grams Ag.

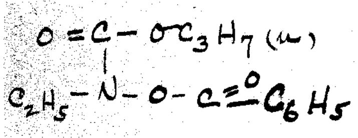
Calc. for $C_{11}H_{12}O_4NAg$: Ag, 32.67. Found Ag, 32.54%.

This salt when warmed to 132 - 133°C changes to the white form. It melts with decomposition at 174 - 175°C. About 1 gram when heated in a bath of boiling water, under diminished pressure for several hours changed completely to the white form. An analysis of the white modification yielded the following results:

0.2187 grams gave 0.0715 grams Ag.

Calc. for $C_{11}H_{12}O_4NAg$: Ag, 32.67. Found Ag, 32.69%.

Attempts to convert large quantities of the yellow salt into the white form by the above method were unsuccessful. The silver salt of the isomeric ester isolated and described by Jones and Oesper(22) melts at 144 - 145°C, and shows no transition point to a white form.



$$\begin{array}{l} O=C-OC_3H_7\,(n) \\ \quad\;\; | \\ C_2H_5-N-O-C{=}O\,C_6H_5 \end{array}$$

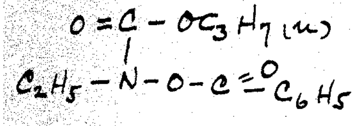
(a). Ethyl derivative of the Benzoyl Ester.

4 grams of the yellow silver salt suspended in ether, were treated with 1.9 grams ethyl iodide. The reaction mixture was allowed to stand in the dark several days until reaction was complete. After several hours contact with the halide ether solution, the silver salt turned white. The white solid could not have been the silver halide, for a portion of it when treated with dilute nitric acid, dissolved. 2.4 grams of a light yellow oil were obtained, which gave the following analytical data:

0.3451 grams gave 16.8 c.c. N_2 at 26°C and 745 mm.

Calc. for $C_{13}H_{17}O_4N$: N, 5.57. Found N, 5.33%.

The oil has a characteristic spicy odor, and on hydrolysis yielded B-ethyl hydroxylamine, indicating that the alkyl group was bound to nitrogen.



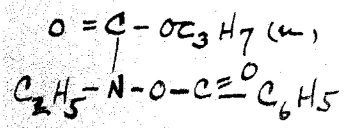
$$\begin{array}{l} \quad O{=}C{-}OC_3H_7(n) \\ \qquad | \\ C_2H_5{-}N{-}O{-}C{\overset{O}{=}}{-}C_6H_5 \end{array}$$

(b). Ethyl Derivative of Benzoyl Ester. Same as (a), but prepared from the white salt. 8 grams of the yellow silver salt were suspended in absolute alcohol over night. After that time, it was found that the salt had entirely reverted to the white modification. It was filtered off, washed with distilled water, and dried in vacuo. The white salt was then suspended in ligroin and 3.8 grams of ethyl iodide added. 5 grams of a light yellow oil with a spicy odor were obtained.

0.3288 grams gave 17.5 c.c. N_2 at 26°C and 737.6mm.

Calc. for $C_{13}H_{17}O_4N$: N, 5.57. Found N, 5.76%.

This derivative on heating with hydrochloric acid in a sealed tube gave B-ethyl hydroxylamine hydrochloride just as did (a) on hydrolysis. To eliminate any doubt that the white silver salt had been the reactant in both cases, since the products in (a) and (b) were identical, the same derivative was prepared in the presence of chloroform as a solvent which stabilizes the yellow salt.



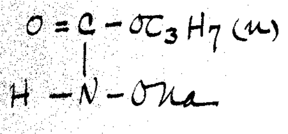
$$\begin{array}{l} \quad O{=}C{-}OC_3H_7(n) \\ \qquad | \\ C_2H_5{-}N{-}O{-}C{\overset{O}{=}}{-}C_6H_5 \end{array}$$

(c). Ethyl Derivative prepared as in (a) and (b) using chloroform as solvent. 5.3 grams of the silver salt and 2.5 grams ethyl iodide dissolved in chloroform yielded 3.7 grams of a light yellow oil with a spicy odor.

0.2992 grams gave 14.4 c.c. N_2 at 27°C and 743 mm.

Calc. for $C_{13}H_{17}O_4N$: N, 5.57. Found, N, 5.23%.

This oil, like the product obtained from (a) and (b) on hydrolysis, yielded B-ethyl hydroxylamine. Hence it is concluded that the two forms of the silver salts are alike structurally.



$$\begin{array}{l} O=C-OC_3H_7(n) \\ \quad\;\, | \\ H-N-ONa \end{array}$$

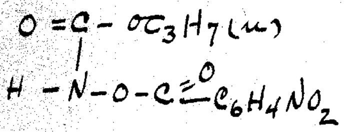
Sodium Salt of Carb n-propyloxyhydroxamic Acid

20 grams carbpropoxyhydroxamic were dissolved in absolute alcohol and treated with an alcoholic solution of sodium ethylate prepared from 3.9 grams metallic sodium. On standing for some time a heavy white precipitate separated. After drying on a porous plate over phosphorus pentoxide, it was analyzed. Yield 18 grams.

0.6242 grams gave 0.3313 grams Na_2SO_4.

Calc. for $C_4H_8O_3NNa$: Na, 16.3. Found Na, 17.2%.

This result is not unsatisfactory, since no method of purification was attempted. The value is probably high, due to the presence of a small quantity of sodium ethylate.



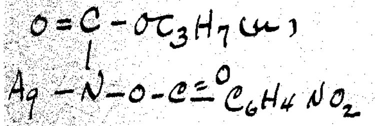
$$\begin{array}{l} O=C-OC_3H_7(n) \\ \quad\;\, | \\ H-N-O-\overset{O}{\overset{\|}{C}}-C_6H_4NO_2 \end{array}$$

The meta Nitrobenzoyl Ester.

8 grams of the above sodium salt suspended in ether, were treated with 10.5 grams meta nitrobenzoyl chloride. After standing for four days, a light yellow oil was obtained which solidified on standing. 10 grams of the pure material melting at 59-60°C, were obtained after recrystallization from ether and ligroin.

0.1524 grams gave 14.3 c.c. N_2 at 27°C and 750.5 mm.

Calc. for $C_{11}H_{12}O_6N_2$: N, 10.45. Found, N 10.30 %.



$$\begin{array}{l} O=C-OC_3H_7(n) \\ \quad | \\ Ag-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

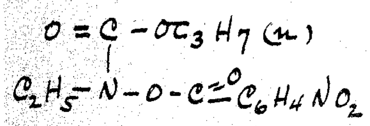
Silver Salt of the meta Nitrobenzoyl Ester.

11 grams of the above ester dissolved in alcohol, when treated with the equivalent of ammonium hydroxide, and an aqueous solution of 7 grams silver nitrate produced a heavy white precipitate. After drying on a porous plate in vacuo, the salt was extracted with ether, again dried and analyzed.

0.4083 grams gave 0.1158 grams Ag.

Calc. for $C_{11}H_{11}O_6N_2Ag$: Ag, 28.77. Found Ag, 28.36%

The salt is moderately soluble in chloroform, giving a yellow solution, slightly soluble in benzene, insoluble in ether. White salt gives no indications of changing to the yellow form on heating or in the absence of a suitable solvent.



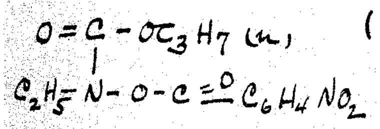
$$\begin{array}{l} O=C-OC_3H_7(n) \\ \quad | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

(a). N-Ethyl Derivative of the meta Nitrobenzoyl Ester. Ether as solvent.

5.5 grams of the silver salt suspended in ether were treated with 2.3 grams of ethyl iodide. 2.7 grams of a light yellow oil were obtained, which solidified on cooling. Recrystallization from ether and ligroin yielded a white mass of crystals which melted at 37.5 - 38.5°C.

0.1742 grams gave 15.3 c.c. N_2 at 28°C and 738.2 mm.

Calc. for $C_{13}H_{16}O_6N_2$: N, 9.46. Found N, 9.42%.

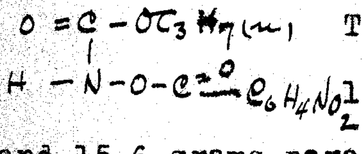


$$\begin{array}{l} O=C-OC_3H_7(n) \\ \quad | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

(b). The Ethyl Derivative as in (a) Chloroform as solvent.

6.2 grams of the silver salt suspended in chloroform were treated with

2.6 grams ethyl iodide. The reaction mixture was allowed to stand for several days. 3.8 grams of a dark colored oil which solidified on standing over night, were obtained. A portion of the crystals obtained were spread out on a porous plate and dried. The melting point of the dried crystals was 37 - 38°C which is in agreement with the melting point of the product obtained in (a). The major portion of the product obtained in (b) was recrystallized from ether and ligroin, and the melting point of the pure material was found to be 37 - 38°C. A mixture of the crystals before recrystallization in (b) together with some of the product described under (a) melted at the same temperature. Hydrolysis of the product obtained in (b) gave B-ethyl hydroxylamine. This proved that the alkyl group is bound to the nitrogen atom. Since it has been shown that the products in (a) and (b) are identical, it follows that the structure of the silver salt, both the yellow and the white form is the same, provided that direct replacement of the metal by alkyl group has occurred in (a) and (b). The conclusion is supported by the data obtained for the structure of the silver salt of the benzoyl ester of n-carbpropyloxyhydroxamic acid, which has already been discussed in this paper.



$$\begin{array}{l} \quad O=C-OC_3H_7(n) \\ \qquad\ \ | \\ H-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

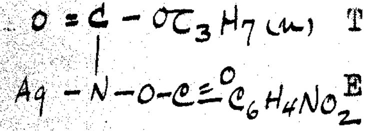
The para Nitrobenzoyl Ester.

10 grams of carbpropyloxyhydroxamic acid and 15.6 grams para nitrobenzoyl chloride were dissolved

in ether and 5.8 grams powdered potassium carbonate was added to the mixture in small portions. After standing over night, the reaction mixture was worked up and a light yellow oil remained, which solidified on standing. Recrystallization from ether and ligroin yielded 10 grams of the ester, which melted at 75 → 76° C.

0.2055 grams gave 19.6 c.c. N_2 at 27°C and 745.5mm.

Calc. for $C_{11}H_{12}O_6N_2$: N, 10.45. Found N, 10.40 %.



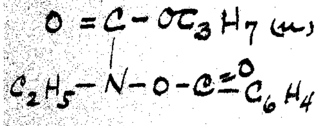
$$\begin{array}{l} O=C-OC_3H_7\,(n) \\ \quad\;\; | \\ Ag-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

The Silver Salt of the para Nitrobenzoyl Ester. 7.6 grams of the above ester dissolved in alcohol and neutralized with ammonium hydroxide, gave on addition of an aqueous solution of 4.8 grams silver nitrate, a heavy yellow precipitate. The dry salt was washed with ether, again dried and analyzed. Yield 10 grams.

0 .3412 grams gave 0.0975 grams Ag.

Calc. for $C_{11}H_{11}O_6N_2Ag$:Ag, 28.78. Found Ag, 28.57%.

The salt gave indications of decomposition at 204°C, and melted at 235°C. No evidence of change to the white modification was noted when heated.



$$\begin{array}{l} O=C-OC_3H_7\,(n) \\ \quad\;\; | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_4NO_2 \end{array}$$

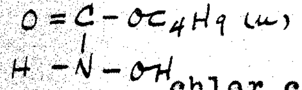
N-Ethyl Derivative of the para Nitrobenzoyl Ester. 7.2 grams of the silver salt suspended in ligroin were treated with 3 grams of ethyl iodide. After standing for two weeks, 4.5 grams of a light yellow oil was obtained. This solidified on standing several hours in an exhausted desiccator. Recrystallization from ether and ligroin, yielded a mass of crystals which melted at 43 - 44° C.

0.2099 grams gave 18.4 c.c. N_2 at 23° C and 747 mm.

Calc. for $C_{13}H_{16}O_6N_2$: N, 9.46. Found N, 9.76%.

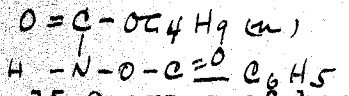
The compound is soluble in ether, chloroform, and benzene, insoluble in ligroin. Hydrolysis of this compound by heating in a sealed tube with hydrochloric acid, yielded B-ethyl hydroxylamine. Therefore the alkyl group was bound to nitrogen.

C. Derivatives of Carb n-butyloxyhydroxamic Acid.



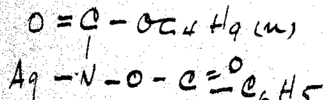
$$\begin{array}{l} O=C-OC_4H_9\ (n) \\ \ \ \ \ | \\ H-N-OH \end{array}$$

Carbbutyloxyhydroxamic acid. 40 grams chlor carbonic normal butyl ester, 24 grams hydroxylamine sulfate and 40.5 grams potassium carbonate were allowed to react in the usual manner, and 31.4 grams of a thick yellow oil was obtained. This derivative gave the characteristic test of a hydroxamic acid with ferric chloride, and has an odor characteristic of almond oil. This was not analyzed, but converted into its benzoyl ester.



$$\begin{array}{l} O=C-OC_4H_9\ (n) \\ \ \ \ \ | \\ H-N-O-C\overset{O}{=}C_6H_5 \end{array}$$

The Benzoyl Ester. 15 grams of the acid, 15.9 grams of benzoyl chloride dissolved in ether, were treated with 7.8 grams potassium carbonate. 24.4 grams of a colorless oil with a strong odor of benzoyl chloride remained. This was not analyzed, but converted into the silver salt.



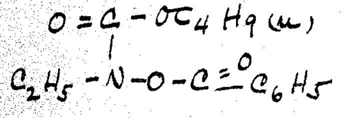
$$\begin{array}{l} O=C-OC_4H_9\ (n) \\ \ \ \ \ | \\ Ag-N-O-C\overset{O}{=}C_6H_5 \end{array}$$

The Silver Salt of the Benzoyl Ester. 24.4 grams of the above ester dissolved in alcohol, neutralized with ammonium hydroxide, on addition of a solution of 17.5 grams silver nitrate yielded a heavy yellow precipitate. The dry salt was recrystallized from ice-cold chloroform and ether. Yellow needles separated. An analysis of the salt gave the following data:

0.4155 grams gave 0.1304 grams Ag.

Calc. for $C_{12}H_{14}O_4NAg$: Ag, 31.37. Found Ag, 31.38%.

The salt melts with decomposition at 154 - 155°C. Unlike the isomeric silver salt of the benzoyl ester of carb isobutylhydroxamic acid which has been described by Jones and Oesper(23) as existing in two modifications, this salt undergoes no change to the white modification. It is insoluble in cold absolute alcohol, undergoing rapid reduction, moderately soluble in chloroform, very slightly soluble in ether, and insoluble in carbon tetrachloride.



$$\begin{array}{l} \quad O=C-OC_4H_9(n) \\ \qquad\quad | \\ C_2H_5-N-O-C\overset{O}{=}C_6H_5 \end{array}$$

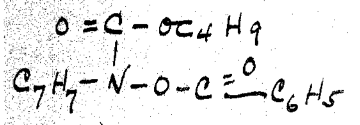
N-Ethyl Derivative of the Benzoyl Ester.

5 grams of the silver salt suspended in ligroin, when treated with 2.3 grams ethyl iodide, gave 2 grams of a light yellow oil with a spicy odor.

0.3375 grams gave 17.0 c.c. N_2 at 25°C and 747 mm.

Calc. for $C_{14}H_{19}O_4N$: N, 5.28. Found N, 5.55%.

This compound when hydrolyzed gave B-ethyl hydroxylamine, which proves that the alkyl group is bound to nitrogen.



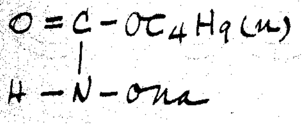
$$\begin{array}{l} \quad O=C-OC_4H_9 \\ \qquad\quad | \\ C_7H_7-N-O-C\overset{O}{=}C_6H_5 \end{array}$$

The N-Benzyl Derivative of the Benzoyl Ester.

4.7 grams of the silver salt and 1.7 grams benzyl chloride were dissolved in chloroform, and refluxed for forty hours. 4 grams of a light yellow oil with a very spicy odor was obtained. Attempts to solidify this compound were not successful. On analysis the following data was obtained:

0.3466 grams gave 13.2 c.c. N_2 at 25.5°C and 755 mm.

Calc. for $C_{19}H_{21}O_4N$: N, 4.28. Found N, 4.23%.



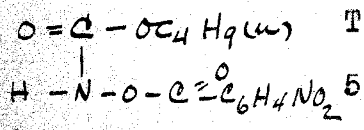
$$\begin{array}{l} O=C-OC_4H_9(n) \\ \quad\;| \\ H-N-ONa \end{array}$$

Sodium Salt of the Acid.

16 grams of the acid dissolved in absolute alcohol when treated with a solution of sodium ethylate, made by dissolving 2.7 grams metallic sodium in excess alcohol, produced a heavy white crystalline precipitate after standing several hours in an ice-salt bath. After drying over phosphorus pentoxide, 13 grams of the salt remained.

0.7405 grams gave 0.3463 grams Na_2SO_4.

Calc. for $C_5H_{10}O_3Na$: Na, 14.83. Found Na, 15.14%.
The compound is slightly soluble in alcohol, insoluble in ether.



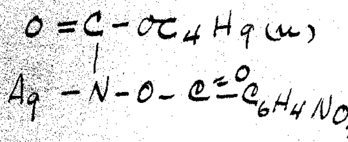
$$\begin{array}{l} O=C-OC_4H_9(n) \\ \quad\;| \\ H-N-O-\overset{O}{\overset{\|}{C}}-C_6H_4NO_2 \end{array}$$

The meta Nitrobenzoyl Ester.

5.7 grams of the above sodium salt suspended in absolute ether and 6.8 grams of meta nitrobenzoyl chloride added. The reaction was allowed to stand for about two days and then refluxed for 2 or 3 hours. The oil produced by the reaction solidified on standing. Recrystallization from ether and ligroin yielded 7 grams of the ester. It is soluble in ether and alcohol, insoluble in ligroin, chloroform and water. Melting point 44° C.

0.1857 grams gave 17 c.c. N_2 at 26°C and 741.2 mm.

Calc. for $C_{12}H_{14}O_6N_2$: N, 9.93. Found N, 9.97%.



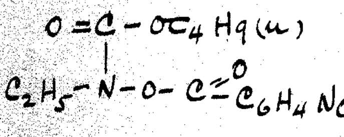
$$\begin{array}{l} O{=}C{-}OC_4H_9(n) \\ \quad\; | \\ Ag{-}N{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_4NO_2 \end{array}$$

The Silver Salt of the meta Nitrobenzoyl Ester. 6 grams of the above ester dissolved in alcohol, neutralized with ammonium hydroxide, and 3.6 grams of silver nitrate produced a heavy white gelatinous precipitate. The dry salt was then extracted with ether and dried again. Yield 6 grams. When subjected to analysis the following data were obtained:

0.3603 grams salt gave 0.0980 grams Ag.

Calc. for $C_{12}H_{13}O_6N_2Ag$: Ag, 27.73. Found Ag, 27.2%.

This salt is soluble in chloroform, giving a yellow solution, which on the addition of ligroin pricipitates the white salt. It is slightly soluble in benzene, giving a yellow solution, insoluble in carbon tetrachloride and ligroin. Spontaneous evaporation of a chloroform solution of this salt yielded the white modification.



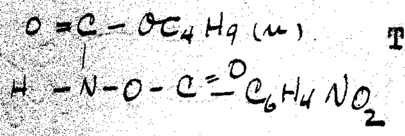
$$\begin{array}{l} O{=}C{-}OC_4H_9(n) \\ \qquad\;\; | \\ C_2H_5{-}N{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_4NO_2 \end{array}$$

N-Ethyl Derivative of the meta Nitrobenzoyl Ester. 5 grams of the white silver salt suspended in ether, were treated with 2 grams ethyl iodide, and allowed to stand 10 days. The residual oil solidified on standing over night in a desiccator. Recrystallization from ether and ligroin yielded 2.5 grams of a white powder which melted at 56.5 - 57.5°C. An analysis of the product gave the following result:-

0.1594 grams gave 13.4 c.c. N_2 at 26°C and 747 mm.

Calc. for $C_{14}H_{18}O_6N_2$: N, 9.02. Found N, 9.22%.

This compound when hydrolyzed gave B-ethylhydroxylamine.

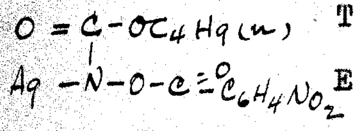


$$\begin{array}{l} O=C-OC_4H_9(n) \\ \quad\; | \\ H-N-O-C(=O)-C_6H_4NO_2 \end{array}$$

The para Nitrobenzoyl Ester. 4.5 grams of the sodium salt of carb n-butyloxyhydroxamic acid were suspended in ether, treated with 5.4 grams of para nitrobenzoyl chloride and the mixture allowed to stand several days. After recrystallization from ether and ligroin 6.3 grams of the ester were obtained. The compound melts at 74 - 75°C.

0.1817 grams gave 16.5 c.c. N_2 at 25.5°C and 748 mm.

Calc. for $C_{12}H_{14}O_6N_2$: N, 9.93. Found N, 10%.

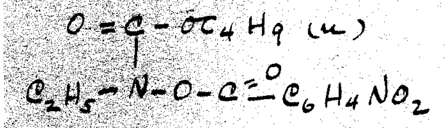


$$\begin{array}{l} O=C-OC_4H_9(n) \\ \quad\;\; | \\ Ag-N-O-C(=O)-C_6H_4NO_2 \end{array}$$

The Silver Salt of the para Nitrobenzoyl Ester. An alcoholic solution of 5.6 grams of the above ester was neutralized with ammonium hydroxide and treated with an aqueous solution of 3.3 grams silver nitrate. During the addition of the first portion of the silver solution, a yellow silver salt precipitated. Addition of the remainder of the silver nitrate caused the yellow precipitate to change to the white form. The white silver salt was dried on a porous plate over night, and then extracted with ether to remove any unreacted ester which might have been present. The yield was 7 grams.

0.4325 grams gave 0.1192 grams Ag.

Calc. for $C_{12}H_{13}O_6N_2Ag$: Ag, 27.73. Found Ag, 27.56%. This salt is insoluble in ether, and alcohol, and slightly soluble in chloroform giving a faint yellow color to the solution. It is the only silver salt of several of the para nitrobenzoyl esters that were studied, which is precipitated in the white form directly from a solution of its ester.



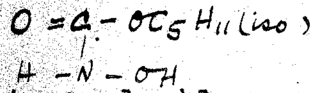
$$\begin{array}{l} O=C-OC_4H_9\ (n) \\ \quad\ | \\ C_2H_5-N-O-C\overset{O}{=}-C_6H_4NO_2 \end{array}$$

N-Ethyl Derivative of the para Nitrobenzoyl Ester. To 6.3 grams of the silver salt suspended in ether, 2.5 grams ethyl iodide was added. After standing for two weeks, the silver iodide was removed and the ether distilled off. 4 grams of a light yellow oil with a very pungent odor remained. All attempts to solidify this oil were without success. On analysis the following results were obtained.

0.3494 grams gave 29.4 c.c. N_2 at 25°C and 740.4 mm.

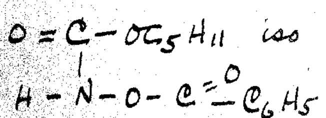
Calc. for $C_{14}H_{18}O_6N_2$: N, 9.03. Found N, 9.19%.

D. Derivatives of Carbisoamylhydroxamic Acid.



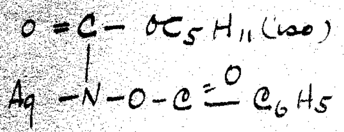
$$\begin{array}{l} O=C-OC_5H_{11}\ (iso) \\ \quad\ | \\ H-N-OH \end{array}$$

Carbisoamylhydroxamic Acid. 50 grams of isoamyl chlor carbonate were added in small portions to a mixture of 27.3 grams hydroxylamine sulfate and 45.8 grams powdered potassium carbonate, suspended in moist ether. After reaction is complete the product was isolated by the usual procedure. 42 grams (theory 48 grams) of a light yellow oil, with an odor characteristic of isoamyl alcohol, were obtained.



$$\begin{array}{l} O=C-OC_5H_{11}\ iso \\ \qquad | \\ H-N-O-C\overset{O}{=}-C_6H_5 \end{array}$$

Benzoyl Ester of Carbisoamylhydroxamic Acid. 12 grams of the acid and 5.6 grams of potassium carbonate dissolved in water, was treated with 11.5 grams benzoyl chloride added in small portions. The ester was extracted with ether and 18 grams of a colorless oil, with a slight odor of benzoyl chloride were obtained on evaporation of the ether. This was not analyzed, but converted into the silver salt.



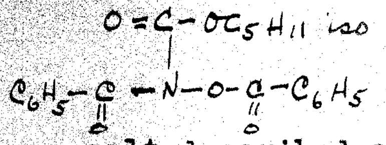
$$\begin{array}{l} O=C-OC_5H_{11}(iso) \\ \quad | \\ Ag-N-O-C(=O)-C_6H_5 \end{array}$$

Silver Salt of the Benzoyl Ester. 18 grams of the ester dissolved in alcohol, neutralized with ammonium hydroxide, were treated with 12.3 grams silver nitrate. The heavy white precipitate of silver salt was dried on a porous plate, and recrystallized from chloroform and alcohol. The recrystallized product was the yellow form. An analysis gave the following data:

0.3340 grams gave 0.1003 grams Ag.

Calc. for $C_{13}H_{16}O_4NAg$: Ag, 30.13. Found Ag, 30.00%

While giving no indications of transformation to a white form, this salt when heated slowly showed a change of the orange-yellow crystals to a light yellow, about 88 C and at higher temperatures, no further change was noted until melting occurred at 141 - 142°C. The salt is reduced when suspended in absolute alcohol. The above data did not correspond with that recorded by Jones and Oesper(24) for the silver salt of the benzoyl ester of carbisoamylhydroxamic acid, and therefore it was thought advisable to prepare the dibenzoyl derivative in order to further compare the present results with those already published.



$$\begin{array}{l} \qquad O=C-OC_5H_{11}\ iso \\ \qquad\quad | \\ C_6H_5-\underset{O}{\overset{}{\underset{\|}{C}}}-N-O-\underset{O}{\underset{\|}{C}}-C_6H_5 \end{array}$$

Dibenzoyl Derivative of Carbisoamylhydroxamic Acid. 2.5 grams of the silver salt described above, on treatment with 1 gram benzoyl chloride in the presence of absolute ether gave after standing the dark for several days a yellow oil.. This solidified after short time and when recrystallized from warm ligroin yielded crystals melting at 65°C as compared with 69 - 70°C given by Jones and Oesper (25) for presumably the same material. An analysis of this derivative gave the following data:

0.2134 grams gave 7.9 c.c. N_2 at 26°C and 746.7 mm.

Calc. for $C_{20}H_{21}O_5N$: N, 3.94. Found N, 4.06%.

The solid has a characteristic sweetish odor. Discrepancy in these melting points indicated that the compounds were derivatives of different parent alcohols. The boiling point of the alkyl chlor carbonate used in these experiments was found to be 151 - 154°C, a value in agreement with that given in Beilstein (26) for the isoamyl derivative, and therefore the data given in this paper is the correct data for the derivatives of carbisoamylhydroxamic acid, that given by Jones and Oesper (27) is for isomeric derivatives. None of the material used by them is available, and a solution of these discordant results must await further investigation.

Summary and Conclusion.

The present investigation was undertaken with the hope of determining whether the existence of the chromisomeric silver salts of acylated hydroxyurethanes is a case of isomeric or polymeric tautomerism. The results of Jones and Oesper(28) seemed to suggest that the colored forms of the silver salts were isomers, and that the white form might by treatment with alkyl halide, lead to the formation of the acylated mixed oximido esters. In this work several new hydroxamic acids as well as their benzoyl esters and substituted nitro and chlor benzoyl esters, their silver salts, and alkyl derivatives, have been prepared and studied. The hydrolysis of the ethyl derivatives regardless of the color of the silver salts used in their preparation, invariably yielded B-ethyl hydroxylamine hydrochloride. This indicates that the alkyl group was bound to the nitrogen in all cases. Assuming that direct replacement of the metal atom occurs,, and there is no reason to believe the contrary, in the study of these derivatives, it follows that there is no difference in the structure of the two forms of the silver salts, when such exists. This leads to the conclusion that these colored modifications are polymers and not isomers. It was intended to repeat the work of Jones and Oesper(29) on the determination of molecular weights of the silver salt of the benzoyl derivative of carbisoamylhydroxamic acid.

which they described with the hope of confirming association of simple molecules in the case of one colored form of this derivative, and not the other, or perhaps association complexes in both forms, but of different degrees. Unfortunately, this phase of the work could not be realized as it was found that it was not the silver salt of the benzoylated isoamyl hydroxamic acid, but of some other isomeric salt. The silver salts which have just been prepared do not permit of molecular weight determinations because of their low solubility. A study of the silver salts of acylated carbalkyloxyhydroxamic acid containing large aromatic radicals will be undertaken, with the hope that further data will confirm our present contentions. Other salts such as the barium, lead, cadmium, and zinc derivatives and their alkyl derivatives will be prepared and studied, in an effort to determine whether the metal in these salts is attached to nitrogen as is the silver salts. Should the other metals be bound to oxygen, then there exists the possibility of preparing mixed oximide esters.

Acknowledgment.

In conclusion, I desire to express my appreciation of the friendly aid of Dr. Ralph E. Oesper, at whose suggestion, this work was undertaken initiated, and who gave assistance and suggestions throughout the entire course of this investigation.

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