made. These are all colorless compounds and therefore have the lactoid structure. Tetrachloroeosin itself has only been obtained in the *colorless lactoid* modification.

7. As examples of the derivatives of the colored quinoid form of tetrachloroeosin, the hydrate and the dipotassium salt have been prepared.

8. The introduction of four bromine atoms into the molecule of tetrachlorofluorescein increases the acidity of the compound, as is shown by the behavior of tetrachloroeosin toward gaseous ammonia and toward strong solutions of the alkalies.

9. Indications of the existence of the two possible isomeric tetrachlorofluoresceins have been obtained.

10. The absorption and fluorescence spectra of solutions of fluorescein tetrachlorofluorescein, eosin, and tetrachloroeosin have been studied. The theory of Stark and Meyer and of Kauffmann that the benzene nucleus is the seat of fluorescence, is apparently confirmed.

ITHACA, N. Y.

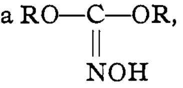
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

OXIMIDOCARBONIC ESTERS AND RELATED COMPOUNDS.

BY LAUDER WILLIAM JONES AND RALPH E. OESPER.

Received February 20, 1914.

The experiments described in this paper were begun several years ago, but were interrupted before any definite conclusions were arrived at. Some time ago, the work was resumed; and, in view of the fact that, recently, Houben and Schmidt[1] have published an account of experiments in which they have duplicated some of our unpublished results, it seemed desirable that a preliminary announcement of our experiments should appear at this time.

The oximidocarbonic esters, *i. e.*, compounds of the formula  $RO-\underset{\underset{NOH}{\|}}{C}-OR$, may be of two types: simple esters in which the two radicals are alike; and mixed esters in which they are different. The latter type is especially interesting, since it offers the possibility of obtaining geometrical stereoisomers in *syn-* and *anti*-modifications. This work was undertaken in the hope of isolating these stereoisomers, and, also, with the intention of investigating their behavior when they are subjected to the action of reagents which bring about the Beckmann rearrangement of oximes, etc.

We found that the preparation of the simple oximido esters offered no special difficulties, since they could be obtained from imidocarbonic esters by the action of hydroxylammonium chloride.

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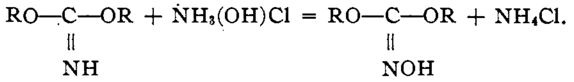
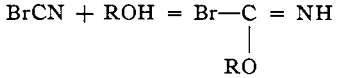
[1] Houben and Schmidt, *Ber.*, 46, 2458 (1913).



$$\underset{\underset{NH}{\|}}{RO\text{—}C\text{—}OR} + NH_3(OH)Cl = \underset{\underset{NOH}{\|}}{RO\text{—}C\text{—}OR} + NH_4Cl.$$

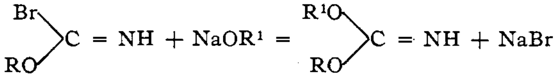
By this method Houben and Schmidt have recently prepared the diethyl and the dimethyl derivatives. The simple imidocarbonic esters are obtained by the action of bromocyanogen on a mixture of an alcohol and its sodium alcoholate. This reaction may be represented by the following equations:

(I)



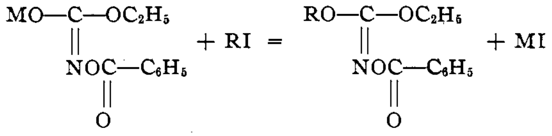
$$BrCN + ROH = \underset{\underset{RO}{|}}{Br\text{—}C} = NH$$

(II)



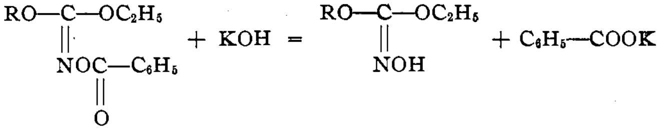
In this way Nef[1] prepared the diethyl and diphenyl esters, and Hantzsch[2] the di-*p*-bromophenyl ester. When sodium phenolate was allowed to react with bromocyanogen in the presence of ethyl alcohol, Nef[3] observed that the ethylphenyl ester, as well as the diphenyl derivative, resulted. This is obvious, since any alcohol may take part in the second stage of the process represented above. At first glance this would seem to afford a method of preparing the mixed imidocarbonic esters, but a mixture of two, and possibly three, substances might result, and their separation would be practically impossible, since these compounds cannot be distilled without considerable decomposition.

It seemed probable that the mixed oximido esters might be prepared by the following method: The salts of the acyl derivatives of hydroxyurethane,[4] when treated with alkyl halides, might be expected to give acylated oximidocarbonic esters:



$$\underset{\underset{\underset{\underset{O}{\|}}{NOC\text{—}C_6H_5}}{\|}}{MO\text{—}C\text{—}OC_2H_5} + RI = \underset{\underset{\underset{\underset{O}{\|}}{NOC\text{—}C_6H_5}}{\|}}{RO\text{—}C\text{—}OC_2H_5} + MI$$

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



$$\underset{\underset{\underset{\underset{O}{\|}}{NOC\text{—}C_6H_5}}{\|}}{RO\text{—}C\text{—}OC_2H_5} + KOH = \underset{\underset{NOH}{\|}}{RO\text{—}C\text{—}OC_2H_5} + C_6H_5\text{—}COOK$$

However, the acylated derivative of hydroxyurethane may exist in two possible tautomeric forms:

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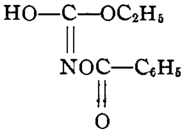
[1] Nef, *Ann.*, **287**, 313, 319 (1895).

[2] Hantzsch and Mai, *Ber.*, **28**, 2469 (1895).

[3] Nef, *Loc. cit.*, 321.

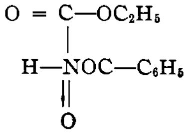
[4] Jones, *Am. Chem. J.*, **20**, 49 (1898).

(I)

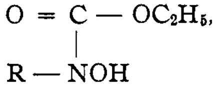
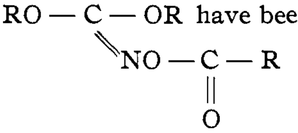
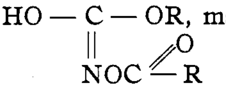


$$\begin{array}{l} HO-C-OC_2H_5 \\ \quad\ \ \| \\ \quad\ \ NOC-C_6H_5 \\ \qquad\quad \| \\ \qquad\quad O \end{array}$$

(II)



$$\begin{array}{l} O = C-OC_2H_5 \\ \qquad\ | \\ H-NOC-C_6H_5 \\ \qquad\ \| \\ \qquad\ O \end{array}$$

If the *silver salts* correspond to Formula (I), then the reaction outlined above would lead to the desired compounds; but if they react according to type (II) isomeric derivatives,  $\begin{array}{l} O = C - OC_2H_5 \\ \qquad\ | \\ R - NOH \end{array}$, 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 the ethyl group or the isoamyl group was introduced, we have found that the silver salts gave rise to *nitrogen esters;* the resulting compounds, when hydrolyzed with hydrochloric acid, yielded β-substituted hydroxylamines, which 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  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,  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[2] have been formed to rearrange to give alkyl amides. After these compounds have been investigated more fully, our results will be presented in a later article.

When the *sodium salt* of the benzoyl ester of hydroxyurethane was allowed to react with ethyl iodide in the presence of alcohol, a liquid was obtained which boiled constantly within one degree. But the figures of

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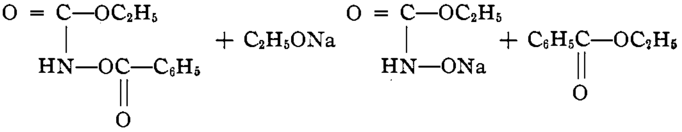
[1] Tafel and Enoch, *Ber.*, 23, 104 (1890); Meyer and Jacobson, *Lehrbuch*, Vol. I, p. 615.

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

the analysis did not agree with the values calculated for the ethyl derivative; and, on investigation, the liquid was found to be a mixture of *o*-ethyl hydroxyurethane and benzoic ethyl ester. During the process, alcoholysis had taken place to give the sodium salt of hydroxyurethane and benzoic ethyl ester, and the reaction had proceeded as follows:[1]

(I)



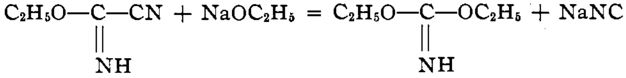
$$\begin{array}{l} O=C-OC_2H_5 \\ \;\;| \\ HN-OC-C_6H_5 \\ \qquad\;\; \| \\ \qquad\;\; O \end{array} + C_2H_5ONa \qquad \begin{array}{l} O=C-OC_2H_5 \\ \;\;| \\ HN-ONa \end{array} + \begin{array}{l} C_6H_5C-OC_2H_5 \\ \qquad \| \\ \qquad O \end{array}$$

(II)

$$\begin{array}{l} O=C-OC_2H_5 \\ \;\;| \\ HN-ONa \end{array} + C_2H_5I \qquad \begin{array}{l} O=C-OC_2H_5 \\ \;\;| \\ HN-OC_2H_5 \end{array} + NaI.$$

The action of the alcohol-free salt will be studied later. However, since the silver salts gave nitrogen alkyl derivatives, the sodium salts will probably do the same, so that this method, in its present form at least, does not seem to be practicable for the preparation of the oximidocarbonic esters.

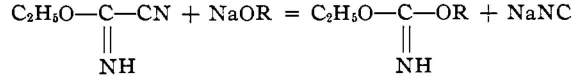
A reaction described by Nef[2] offered a method for the preparation of the mixed imidocarbonic esters. By the action of sodium ethylate on cyanimidocarbonic ethyl ester, he obtained imidocarbonic ethyl ester.



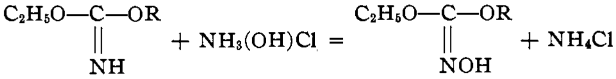
$$\begin{array}{c} C_2H_5O-\underset{\underset{\displaystyle NH}{\|}}{C}-CN \end{array} + NaOC_2H_5 = \begin{array}{c} C_2H_5O-\underset{\underset{\displaystyle NH}{\|}}{C}-OC_2H_5 \end{array} + NaNC$$

By using other alcoholates in place of sodium ethylate, the desired imido compounds may be obtained, which, on treatment with hydroxylammonium chloride, would give the mixed oximidocarbonic esters.

Thus:



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

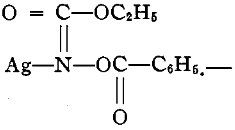


$$C_2H_5O-\underset{\underset{\displaystyle NH}{\|}}{C}-OR + NH_3(OH)Cl = C_2H_5O-\underset{\underset{\displaystyle NOH}{\|}}{C}-OR + NH_4Cl$$

Experimental Part

Derivatives of Hydroxyurethane.

The Silver Salt of the Benzoyl Ester of Hydroxyurethane,



$$Ag-\underset{}{N}(-C(=O)OC_2H_5)-O\underset{\underset{\displaystyle O}{\|}}{C}-C_6H_5.—$$

Seven and four-tenths grams of sodium hydroxide were mixed with 37 g. of the benzoyl ester of hydroxyurethane dissolved in alcohol, and 30 g. of silver nitrate dissolved in water were added. The heavy, yellow precipi-

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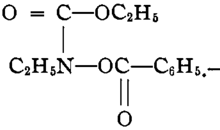
[1] Compare Titherly, *J. Chem. Soc.*, **79**, 392 (1901).

[2] Nef, *Loc. cit.*, p. 286.

tate was separated by filtration, washed with a small amount of water, and then with alcohol. It was dried on a clay plate placed in an amber desiccator. The salt is rather sensitive to light and is best prepared in the dark.

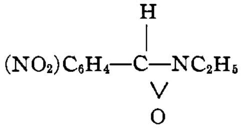
Preparation of the N-Ethyl Derivative of the Benzoyl Ester of Hydroxyurethane,  $\overset{O=C-OC_2H_5}{\overset{|}{C_2H_5N}}-O\underset{\underset{O}{\|}}{C}-C_6H_5$.—Twenty-seven grams of ethyl iodide were added to 50 g. of the silver salt suspended in ether, and the mixture was allowed to stand in the dark for two weeks. At the end of this time the bright yellow color of the silver salt had disappeared. The silver iodide was separated by filtration and washed with ether. After shaking the ether solution with a solution of sodium thiosulfate to remove the small quantity of iodine that had separated, it was dried with fused sodium sulfate and freed from ether by distillation. The light yellow oil which remained was fractionated *in vacuo.* After three fractionations, 10 g. were obtained which boiled with slight decomposition between 188–190°, under a pressure of 25 mm.

0.1526 g. gave 8.64 cc. N_2 at 29° and 743 mm.

Calc. for $C_{12}H_{15}O_4N$: N, 5.90. Found, N, 6.09.

The substance was an oil with a spicy odor. It was nearly insoluble in water, but soluble in most organic solvents.

Hydrolysis of the Ethyl Derivative by Hydrochloric Acid.—Three and seven-tenths grams of the oil were heated with 10 cc. of concentrated hydrochloric acid in a sealed tube for six hours at 105°. When the tube was opened, carbon dioxide and ethyl chloride escaped. The contents of the tube were extracted wlth ether, and 1.4 g. (calculated 1.5 g.) of benzoic acid were obtained when the ether was evaporated. The water solution was concentrated over a water bath until a thick yellow oil remained which would not solidify even at —10°. It was identified as β-ethyl hydroxylammonium chloride by condensing it with para-nitrobenzaldehyde. The condensation product melted at 123°, which agrees with the value given by Hantzsch[1] for N-ethyl-*p*-nitroisobenzaldoxime,



$$(NO_2)C_6H_4-\overset{\overset{H}{|}}{C}\underset{\underset{O}{\vee}}{-}NC_2H_5$$

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:

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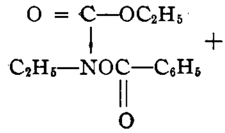
[1] Hantzsch and Hillard, *Ber.*, 31, 2066 (1898).



$$\begin{array}{l} O = C\text{—}OC_2H_5 \\ \quad | \\ C_2H_5\text{—}NOC\text{—}C_6H_5 \\ \qquad \| \\ \qquad O \end{array} + H_2O + 2HCl = CO_2 + C_2H_5Cl + C_6H_5COOH + C_2H_5\text{—}NH_2(OH)Cl$$

The Action of Ethyl Iodide on the Sodium Salt of the Benzoyl Ester of Hydroxyurethane.—To a solution of 35 g. of benzoyl ester of hydroxyurethane in alcohol, 3.8 g. of sodium, dissolved in alcohol, and 26 g. of ethyl iodide were added. After two weeks the alcohol was removed by distillation and the mixture of oil and crystals which remained was extracted with ether. After washing the ether with water, it was dried with sodium sulfate and distilled. A colorless oil was obtained which was fractionated *in vacuo*, 24 g. of a clear colorless liquid, boiling at 108–109° at 25 mm., resulting.

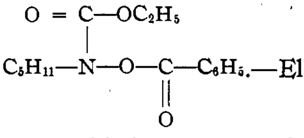
The figures which the analysis of the oil gave did not agree with the values calculated for the ethyl derivative; and, on a further investigation, it was found that the oil consisted of a neutral and an acid portion. It was dissolved in ether and shaken with a solution of sodium hydroxide. The neutral portion was found to be ethyl benzoate, boiling at 213°. The alkaline solution was acidified and extracted with ether. A clear, colorless liquid was obtained which boiled between 96–7° at 17 mm. When treated with phosphorus pentachloride and then with water and alkalies, it gave a base whose chloride melted at 127°. This chloride formed a chloroplatinate which melted with decomposition between 174–176°.

0.096 g. gave 0.0352 g. Pt.

Calc. for $(C_2H_5ONH_3)_2PtCl_6$: Pt, 36.65. Found: Pt, 36.66.

These results showed that the compounds under consideration were derivatives of α-ethylhydroxylamine.

The acid portion was therefore *o*-ethyl hydroxyurethane. It was found to be identical with the ethyl derivative described by Jones.[1] The origin of these products was explained above.

Preparation of N-Isoamyl Derivative of the Benzoyl Ester of Hydroxyurethane,  $\begin{array}{l} \qquad O = C\text{—}OC_2H_5 \\ \qquad\quad | \\ C_5H_{11}\text{—}N\text{—}O\text{—}C\text{—}C_6H_5 \\ \qquad\qquad\qquad \| \\ \qquad\qquad\qquad O \end{array}$.—Eleven and nine-tenths grams of isoamyl iodide were added to 19 g. of the silver salt of the benzoyl ester of hydroxyurethane suspended in ether. After two weeks the silver iodide was removed and the product was treated in the manner described under the ethyl derivative. After three fractionations, 16 g. of a yellow oil, boiling, with slight decomposition, between 203–205° at 30 mm., were obtained.

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[1] Jones, *Loc. cit.*, p. 46.

0.1562 g. gave 7.9 cc. N_2 at 31° and 745 mm. Calc. for $C_{15}H_{21}O_4N$: N, 5.01. Found: N, 5.10.

The substance resembled the ethyl derivative described above in all of its properties.

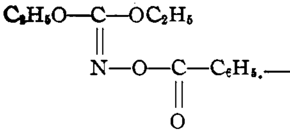
The Hydrolysis of the N-Isoamyl Derivative with Hydrochloric Acid.—Three grams of the oil were heated with 10 cc. of concentrated hydrochloric acid in a sealed tube for three hours at 110°. Carbon dioxide and ethyl chloride escaped on opening the tube. One and two-tenths grams of benzoic acid (calculated 1.3 g.) were extracted with ether and the water gave brownish crystals when evaporated. These crystals were dissolved in alcohol and a turbid suspension was produced by the addition of ether. An alcoholic solution of platinic chloride precipitated a yellow solid substance, which was analyzed.

0.0960 g. gave 0.0310 g. of Pt. Calc. for $(C_5H_{11}NH_2OH)_2PtCl_6$: Pt, 31.63. Found: Pt, 32.29.

In this case, also, the alkyl group was bound to nitrogen.

Derivatives of Oximidocarbonic Esters.

Preparation of the Benzoyl Ester of Oximidocarbonic Ethyl Ester,

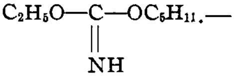


$C_2H_5O-\underset{\underset{N-O-\underset{\underset{O}{\|}}{C}-C_6H_5}{\|}}{C}-OC_2H_5$.—Three and one-tenth grams of sodium bicarbonate were added to 5 g. of oximidocarbonic ethyl ester[1] dissolved in 10 g. of water. Five and one-tenth grams of benzoyl chloride were added in small portions, the flask being cooled with running water. A colorless oil separated which soon solidified to a mass of white crystals. These were collected on a filter, dried, and recrystallized from chloroform and ligroin. They formed fine needles which melted at 148°.

0.2716 g. gave 14.9 cc. N_2 at 29° and 745 mm. Calc. for $C_{12}H_{15}O_4N$: N, 5.90. Found: N, 5.91.

The compound was soluble in benzene, in alcohol and in chloroform, not very soluble in ether, and insoluble in ligroin and in water. Several crystals were added to the ethyl derivative obtained from the silver salt described above, but the oil showed no tendency to solidify, which proved that the latter was not the oxygen ester existing as an undercooled liquid.

Preparation of Imidocarbonic Ethyl Isoamyl Ester,



$C_2H_5O-\underset{\underset{NH}{\|}}{C}-OC_5H_{11}$.—Five and three-tenths grams of sodium were treated with the equivalent quantity (20 g.) of isoamyl alcohol in the presence of ether.[2] Twenty-

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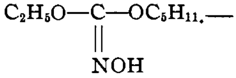
[1] Houben and Schmidt, *Loc. cit.*

[2] Brühl, *Ber.*, **37**, 2066 (1904).

two and five-tenths grams of cyanimidocarbonic ethyl ester, prepared from bromocyanogen, potassium cyanide, and alcohol[1] were added to the suspended alcoholate. Heat was developed, the solution became yellow, and sodium cyanide was precipitated. The reaction mixture was heated for two hours in a flask connected with a reflux condenser, and enough water was added to dissolve the sodium cyanide. After the water solution had been extracted with ether several times, the ether was dried with calcium chloride. Thus, 32 g. of a light yellow oil, possessing a strong basic odor, were obtained when the ether was evaporated. Even at a pressure of 25 mm. the compound could not be distilled without considerable decomposition. Therefore, no analysis of the substance was attempted. Its identity was established by converting it into the corresponding oximido derivative.

Preparation of Oximidocarbonic Ethyl Isoamyl Ester,



$C_2H_5O\text{—}\underset{\underset{NOH}{\|}}{C}\text{—}OC_5H_{11}$.—

Eight and four-tenths grams of hydroxylamine, dissolved in a small amount of water, were added to 20 g. of the imido ester dissolved in 20 cc. of ether. The mixture was shaken thirty minutes, the water layer was drawn off, extracted several times with ether, and the ether dried with sodium sulfate. Twenty grams of a reddish yellow oil were obtained when the ether evaporated. When cooled to —15°, white crystals appeared which melted when they were spread out on a cold clay plate.

0.1754 g. gave 12.8 cc. N_2 at 24.5° and 742 mm. Calc. for $C_8H_{17}O_3N$: N, 7.99. Found: N, 8.01.

When freshly prepared, the substance was practically odorless but, on standing, the odor of isoamyl alcohol became apparent. The oil was insoluble in water, but soluble in alkalies, and in most organic solvents.

CINCINNATI, OHIO.

FRIEDEL AND CRAFTS' REACTION—THE PREPARATION OF ORTHOBENZOYL-BENZOIC ACID AND BENZOPHENONE.

BY C. R. RUBIDGE AND N. C. QUA.

Received February 20, 1914.

Orthobenzoyl-benzoic acid had been prepared by several investigators but was first prepared by means of the reaction between phthalic anhydride, benzene and aluminium chloride, by Friedel and Crafts.[2] Heller[3] showed that the aluminium chloride was not a catalytic agent and that a good yield depended on the phthalic anhydride and the aluminium chloride being used in the proportion of their formula weights(using Al_2Cl_6).

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

[2] *Ann. chim. phys.*, [6] **14**, 446 (1888).

[3] *Z. angew. Chem.*, **19**, 669 (1906).