In our hands Bertram's procedure for the preparation of esters of aconityl anil[26] did not lead to the isolation of the products sought. However, when, after esterification is complete, the alcohol is distilled in a vacuum at a low temperature, and the residue washed first with a little ether and then with water, recrystallization of the residue from benzene gives a pure product. A comparison of the methyl and ethyl esters made in this way with our products established their identity.

## Summary

1. A new method of making anhydrides is given in connection with the preparation of methylene-citric anhydride.
2. The symmetrical structure of methylene-citric anhydride is established.
3. The formation of the unsymmetrical anil of citric acid from *sym.*-methylene-citric anhydride is cleared up.
4. Contrary to patent literature it is found that methylene-citric anhydride reacts with alcohols to form mono- and not dialkyl esters of methylene-citric acid.
5. A method of preparation of symmetrical dialkyl and unsymmetrical mono-alkyl esters of citric acid, using methylene-citric anhydride, is suggested.
6. The preparation of the anil of aconitic acid from the anil of citric acid is described and an analogy in structure definitely established.
7. A modification of the method of making aconitic anhydride is given.

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

# SOME NEW HYDROXY-URETHANS AND CHROMO-ISOMERIC SILVER SALTS OF THEIR ACYL DERIVATIVES. III[1]

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The previous papers of this series[2] have contained studies of the reversibly transformable yellow silver salts of the benzoylated carbo-alkyloxy-hydroxamic acids, with the view of determining whether they corresponded to the isomeric forms I and II.

$$\underset{\text{I}}{\text{RO.CO.N(Ag)OCOC}_6\text{H}_5} \rightleftharpoons \underset{\text{II}}{\text{RO.C(OAg):N.OCOC}_6\text{H}_5}$$

The alkyl derivatives formed by interaction of alkyl iodides with either the white or yellow silver salts gave betasubstituted hydroxylamines

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[26] Ref. 17, p. 1617.

[1] This communication is an abstract of part of a thesis submitted by Walter Broker in partial fulfilment of the requirements for the degree of Master of Arts at the University of Cincinnati.

[2] (a) Jones and Oesper, THIS JOURNAL, **36**, 2208 (1914); (b) **36**, 726 (1914). (c) Oesper and Cook, *ibid.*, **47**, 422 (1925).

when hydrolyzed and compelled the conclusions that the salts were not isomers but that both forms corresponded to Structure I.

We have now prepared derivatives of carbo-aryloxy-hydroxamic acids and in some instances white and yellow silver salts have been isolated, but again both forms react as though the metal were "bound to nitrogen," and the substitution of aromatic radicals for the aliphatic ones has furnished no evidence in favor of Structure II and the two forms of the silver salts are, probably, polymers of Structure I.

The hydroxamic acids, their benzoyl esters, silver salts and ethyl-N derivatives of the benzoyl esters were prepared by methods previously described.[2c] Better yields of the benzoyl esters are obtained by refluxing ether solutions of the hydroxamic acid and benzoyl chloride in the presence of the equivalent quantity of potassium carbonate, than by the ordinary Schotten-Baumann procedure.

Table I summarizes the data concerning the series of compounds we have studied.

Table I

Compounds Studied

| | Parent alcohol R—O—H | Hydroxamic acid ROCO.NHOH | | | Benzoyl ester ROCO.N(H)OCOC$_6$H$_5$ | | |
|---|---|---|---|---|---|---|---|
| | | M. p. °C. | % N Calcd. | % N Found | M. p. °C. | % N Calcd. | % N Found |
| 1 | $C_6H_5OH$ | 102.5 | 9.15 | 9.10 | 105.5 | 5.45 | 5.41 |
| 2 | *o*-$CH_3C_6H_4OH$ | 116 | 8.38 | 8.14 | 76.5 | 5.16[a] | 5.27 |
| 3 | *m*-$CH_3C_6H_4OH$ | 67.5 | 8.38 | 8.08 | 102.5 | 5.16 | 5.17 |
| 4 | *p*-$CH_3C_6H_4OH$ | 99 | 8.38 | 8.08 | 92 | 5.16[b] | 5.00 |
| 5 | *p*-$ClC_6H_4OH$ | 127 | 7.47 | 7.49 | 100 | 4.80 | 4.90 |
| 6 | *o*-$ClC_6H_4OH$ | 119 | 7.47 | 7.41 | ... | .. | .. |
| 7 | *m*-$NO_2C_6H_4OH$ | 130.5 | 14.14 | 13.91 | 99 | 9.27 | 9.37 |

| | Parent alcohol R—O—H | Silver salt of benzoyl ester RO.CO.N(AgOCOC$_6$H$_5$ | Ethyl-N derivative RO.CO.N(C$_2$H$_5$)OCOC$_6$H$_5$ | | |
|---|---|---|---|---|---|
| | | Color | M. p. °C. | % N Calcd. | % N Found |
| 1 | $C_6H_5OH$ | w → y → w | 45 | 4.91 | 4.88 |
| 2 | *o*-$CH_3C_6H_4OH$ | y → w | oil | 4.68 | 4.73 |
| 3 | *m*-$CH_3C_6H_4OH$ | w | oil | 4.68 | 4.69 |
| 4 | *p*-$CH_3C_6H_4OH$ | w | oil | 4.68 | 4.52 |
| 5 | *p*-$ClC_6H_4OH$ | w | .. | .. | .. |
| 6 | *o*-$ClC_6H_4OH$ | .. | .. | .. | .. |
| 7 | *m*-$NO_2C_6H_4OH$ | .. | .. | .. | .. |

[a] The dibenzoyl ester from the silver salt and benzoyl chloride, recrystallized from benzene and ligroin; m. p., 54.5°. Calcd. for $C_{22}H_{17}O_6N$: N, 3.73. Found: 3.83.

[b] Dibenzoyl ester, m. p. 90°, from ether and ligroin. Calcd.: N, 3.75. Found: 3.83.

The Silver Salt of the benzoyl ester of carbophenoxy-hydroxamic acid was white when first precipitated, and rapidly became light yellow. After the mother liquor had been removed and the substance washed with water, the color reverted to white. The salt was soluble in boiling chloroform depositing yellow needles on cooling; m. p., 150–155°, with decomposition.

*Anal.* Calcd. for $C_{14}H_{10}O_4NAg$: Ag, 29.63. Found: 29.62.

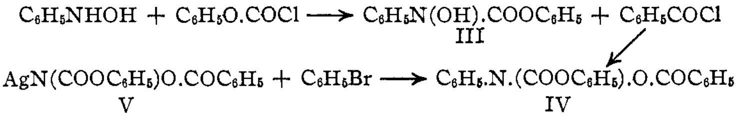
Since reaction with ethyl iodide indicated that the metal was bound to nitrogen, it seemed that the following reactions would furnish an independent proof of the structure. β-Phenylhydroxylamine was allowed to react with phenyl chlorocarbonate in the presence of potassium carbonate and ether. The product, after recrystallization from benzene, melted at 124°.

*Anal.* Calcd. for $C_{13}H_{11}O_3N$: N, 6.11. Found: 6.17.

The phenyl-N ester of carbophenoxy-hydroxamic acid (III) when treated with benzoyl chloride in the presence of sodium hydroxide, yielded the phenyl-N ester of the benzoyl ester of carbophenyloxy-hydroxamic acid (IV) which, recrystallized from benzene, melted at 93°.

*Anal.* Calcd. for $C_{20}H_{15}O_4N$: N, 4.20. Found: 3.99.

Substance IV is identical with the compound yielded by the action of phenyl bromide on a chloroform solution of the silver salt of the benzoyl ester of carbophenoxy-hydroxamic acid (V) and the position of the silver as bound to nitrogen is assured. These reactions may be represented as follows.



$$C_6H_5NHOH + C_6H_5O.COCl \longrightarrow \underset{\text{III}}{C_6H_5N(OH).COOC_6H_5} + C_6H_5COCl$$

$$\underset{\text{V}}{AgN(COOC_6H_5)O.COC_6H_5} + C_6H_5Br \longrightarrow \underset{\text{IV}}{C_6H_5.N.(COOC_6H_5).O.COC_6H_5}$$

The silver salt of the benzoyl ester of carbotolyloxy-hydroxamic acid is yellow when first precipitated, but turns white when washed with water and dried. It is soluble in chloroform and hot benzene. Ligroin precipitates the white form from chloroform solution, while alcohol precipitates the yellow modification. The white form was suspended in ether, the yellow in chloroform, and ethyl iodide added to each. The resulting ethyl derivatives appeared identical and both yielded β-ethyl-hydroxylamine when hydrolyzed by concd. hydrochloric acid. All the other silver salts were observed in the white modification only and invariably yielded N-ethyl esters when treated in the usual way.

## Summary

The study of the yellow and white silver salts of the benzoyl esters of carbo-alkyloxy-hydroxamic acids has been extended to analogous carbo-aryloxy-hydroxamic acids and indicates that in both of the chromo-isomeric silver salts the metal is "bound to nitrogen."

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