acetate from the reaction of phenyl bromide with mercuric acetate is important, as it is the first case of the formation of a *meta* mercury compound by direct mercuration. (c) Whether or not *ortho* and *meta* compounds are formed from phenyl chloride and phenyl iodide has not yet been determined.

3. The replacement of mercury by a nitro group has been carried out with *p*- and *o*-chloro-, and *p*- and *o*-bromo-phenylmercuric acetates. This reaction was not so simple with the *meta*-chloro- and bromo-mercury compounds. The limits of this reaction are being studied with other mercury compounds.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

MERCURY DERIVATIVES OF SALICYLALDEHYDE AND THE NITRO-SALICYLALDEHYDES[1]

BY FRANK C. WHITMORE AND EDMUND BURRUS MIDDLETON[2]

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Aromatic aldehydes cannot, as a rule, be mercurated by mercuric acetate because of its oxidizing action. At the time the present work was done the only mercurated aromatic aldehyde was a mercury vanillin of undetermined structure.[3] More recently the 3 hydroxybenzaldehydes have been mercurated.[1a] Definite mercuration products have also been obtained from vanillin.[4] Salicylaldehyde was chosen for the present study because of its resistance to oxidation and because of the activating effect of the phenolic hydroxyl.

Salicylaldehyde reacts readily with two molecular proportions of mercuric acetate in alcohol to form 3,5-diacetoxymercuri-salicylaldehyde. No oxidation takes place, as shown by the absence of mercurous acetate and metallic mercury from the products. The dichloromercuri compound is made in the usual way from an acetic acid solution of the acetate and a chloride solution. Even when only 1 molecular proportion of mercuric acetate is used the chief product is the dimercurated compound, although a small amount of a monomercurated product can be obtained from the

[1] Presented at the Birmingham Meeting of the American Chemical Society, April, 1922. Since the presentation of this paper an article has appeared by Henry and Sharp on the mercury derivatives of the three hydroxybenzaldehydes. (a) *J. Chem. Soc.*, **121**, 1055 (1922).

[2] Research Fellow under a grant from the U. S. Interdepartmental Social Hygiene Board, General M. W. Ireland, Chairman. Some of the compounds prepared are being investigated pharmacologically under the direction of Dr. A. S. Loevenhart of the Department of Pharmacology of the University of Wisconsin.

[3] "Realenzyklopaedie für Pharmazie," vol. VII, p. 100.

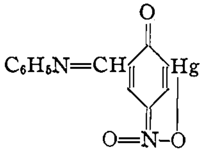
[4] Paolini, *Gazz. chim. ital.*, **51**, II, 188 (1921); *C. A.*, **16**, 557 (1922).

reaction mixture. Since phenol can be changed to monomercurated products by adding mercuric acetate to an excess of phenol without a solvent[5] it seemed likely that salicylaldehyde might be mercurated in the same way. Such, however, was found not to be the case. The failure is apparently due to the fact that the mercuration products of salicylaldehyde are insoluble in an excess of the parent substance, while those of phenol are soluble in the excess of phenol.

In order to obtain a monomercurated aldehyde easily, the mononitro-salicylaldehydes are used. Mercuration by mercuric acetate in alcohol readily gives 3-acetoxymercuri-5-nitro-salicylaldehyde and 5-acetoxymercuri-3-nitro-salicylaldehyde. The corresponding chloromercuri compounds are prepared in the usual way.

The mercurated salicylaldehydes dissolve in aqueous alkali. The alkaline solutions, precipitated by dil. hydrochloric acid, give the chloromercuri compounds. The alkali salts in the case of the nitro compounds can be recrystallized from hot water. They are highly colored, indicating a quinoid-acinitro structure.[6]

The mercurated salicylaldehydes condense with primary aromatic amines forming colored Schiff's bases. Diacetoxymercuri-salicylaldehyde has been condensed in this way with aniline, *p*-toluidine, *p*-aminobenzoic acid and anthranilic acid. The mercurated nitro-salicylaldehydes, both acetates and chlorides, have been condensed with these amines. In the case of the acetoxymercuri compounds, one molecule of acetic acid is lost. Since this loss occurs only with the nitro compounds the products are probably anhydrides or inner salts formed between the acinitro and hydroxymercuri groups.[4] Thus the product of the condensation of 3-acetoxymercuri-5-nitro-salicylaldehyde with aniline would be as follows.



The corresponding chloromercuri compound condenses with amines without anhydride formation. As would be expected the products are less highly colored than the anhydrides.

The mercurated salicylaldehydes react with hydroxylamine and with phenylhydrazine, giving metallic mercury. The Perkin reaction with acetic anhydride and sodium acetate gives tarry products from which no pure substance has been obtained.

With potassium iodide the mercurated salicylaldehydes behave like

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[5] This Journal, **43**, 622 (1921).

[6] Compare the work of Hantzsch and Auld on the mercurated nitrophenols. *Ber.*, **39**, 1117 (1906).

the mercurated phenols, losing mercury with the formation of the unmercurated aldehydes, potassium mercuric iodide and potassium hydroxide. The instability of the C–Hg linkage in these compounds is due to the presence of the phenolic hydroxyl. When the latter is protected by acetyl, methyl or ethyl, the decomposition by iodides follows a different course. The properties and reactions of such derivatives of the mercurated salicylaldehydes are being studied by one of us (M.).

Experimental Part

3,5-Diacetoxymercuri-salicylaldehyde.—Ten g. of salicylaldehyde and 52 g. of mercuric acetate (2 molecular proportions) are dissolved in 500 cc. of 50% alcohol containing 5 cc. of acetic acid. After the mixture has been heated for 1 hour on the steam-bath it is cooled and filtered. The crude diacetate obtained weighs 32 g. On standing overnight 10 g. more separates. Addition of sodium chloride solution to the filtrate precipitates 8 g. of crude dichloromercuri-salicylaldehyde. The diacetate is insoluble in all ordinary organic solvents except glacial acetic acid in which it is soluble in the proportions of about 1:5 in the boiling solution and 1:10 in the cold. It separates in needles which melt with decomposition at 234° (uncorr.). The crude material melts with decomposition at about 225°.[7] It is soluble in aqueous sodium hydroxide. Boiling with alcoholic potassium iodide removes all the mercury as potassium mercuric iodide forming salicylaldehyde and potassium hydroxide. The diacetate reacts with hydroxylamine and with phenylhydrazine as an oxidizing agent, forming metallic mercury.

Analyses.[8] Calc. for $C_{11}H_{10}O_6Hg_2$: Hg, 62.8. Found: Hg, 6.24, 62.8.

The *dichloromercuri* compound is insoluble in organic solvents and does not melt at 270°.

Analysis. Calc. for $C_7H_4O_2Cl_2Hg_2$: Hg, 67.7. Found: 67.8.

3(?)-Chloromercuri-salicylaldehyde.—Attempts to make this substance by mercuration of an excess of salicylaldehyde without a solvent failed, apparently because of the insolubility of the mercurated products in the salicylaldehyde. Ten g. of salicylaldehyde in 2 liters of water is treated with 26 g. of mercuric acetate (1 molecular proportion) and the mixture is stirred mechanically. As soon as the solution no longer gives a test for inorganic mercury with sodium hydroxide it is filtered. Three g. of the diacetate is thus obtained. Addition of sodium chloride solution to the filtrate gives 19 g. of a mixture of mono- and dichloromercuri compounds. Repeated extractions with boiling alcohol remove 5 g. of a pure monochloromercuri-salicylaldehyde; m. p., 189–190°. Suspended in chloroform and treated with 1 molecular proportion of iodine it gives an iodo-salicylaldehyde; m. p., 52–58°. This is apparently the 3-iodo-salicylaldehyde which is reported to melt at 55°. The residue insoluble in hot alcohol appeared by analysis to be a mixture of dichloromercuri- and monochloromercuri-salicylaldehydes. The latter is probably the 5-chloromercuri compound. No method of separating this mixture has been found.

Analysis. Calc. for $C_7H_5O_2ClHg$: Hg, 56.3. Found: 56.4.

Nitration of Salicylaldehyde.[9]—3-Nitro- and 5-nitro-salicylaldehydes were prepared according to the method described by Miller.

3-Acetoxymercuri-5-nitro-salicylaldehyde.—Twelve g. of 5-nitro-salicylaldehyde and 23 g. of mercuric acetate dissolved in 400 cc. of alcohol containing 5 cc. of acetic acid are heated 1 hour on the steam-bath. The precipitate is filtered, washed and dried;

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[7] Henry and Sharp give the melting point as 133°.

[8] For method of analysis see note, THIS JOURNAL, **44,** 1548 (1922).

[9] Miller, *Ber.,* **20,** 1928 (1887).

yield, 26 g. It is crystallized from glacial acetic acid, the only organic solvent in which it is appreciably soluble. It forms pale yellow crystals which do not melt at 260°. It dissolves in aqueous sodium hydroxide to give a yellow solution.

Analyses. Calc. for $C_9H_7O_6NHg$: Hg, 47.1. Found: 47.1, 47.1.

5-Acetoxymercuri-3-nitro-salicylaldehyde.—Four g. of 3-nitro-salicylaldehyde and 7 g. of mercuric acetate are treated as described above. The product weighs 9 g. It is recrystallized from glacial acetic acid. It does not melt at 260°.

Analysis. Calc. for $C_9H_7O_6NHg$: Hg, 47.1. Found: 46.9.

3-Chloromercuri-5-nitro-salicylaldehyde.—Ten g. of the corresponding acetate dissolved in dil. sodium hydroxide solution and acidified with dil. hydrochloric acid precipitates 8 g. of the chloride. The substance is insoluble in organic solvents and does not melt at 260°.

Analyses. Calc. for $C_7H_4O_4NClHg$: Hg, 49.9. Found: 49.1, 49.3.

Condensation of Mercurated Salicylaldehydes with Aromatic Amines

Schiff's bases are obtained by heating the mercurated salicylaldehydes with an excess of aniline or *p*-toluidine. Similar compounds are obtained from the aminobenzoic acids by refluxing the latter in alcohol. Less pure products can be obtained by refluxing the aldehydes with the aminobenzoic acids in acetic acid.

3,5-Diacetoxymercuri-salicylal-aniline.—Five g. of the mercurated aldehyde dissolved in 10 cc. of hot aniline and cooled gives 5.5 g. of a brick-red amorphous product which is insoluble in organic solvents and does not melt at 260°. The crude product is washed thoroughly with benzene and dried at 100° for analysis.

Analyses. Calc. for $C_{17}H_{15}O_5NHg_2$: Hg, 56.2. Found: 56.2, 56.8.

3,5-Diacetoxymercuri-salicylal-*p*-toluidine.—The preparation and properties of this substance are similar to those of the aniline compound.

Analyses. Calc. for $C_{18}H_{17}O_5NHg$: Hg, 55.1. Found: 54.6, 54.9.

3,5-Diacetoxymercuri-salicylal-*p*-aminobenzoic Acid.—Five g. of the aldehyde yields 5.5 g. of a deep red, insoluble powder which does not melt at 250°.

Analysis. Calc. for $C_{18}H_{15}O_7NHg_2$: Hg, 52.9. Found: 53.0.

The substance is soluble in dil. alkali. Precipitation by acetic acid gives a product richer in mercury (56.7%). This may consist of anhydride or a partly hydrolyzed product in which one of the acetoxymercuri groups has been changed to an hydroxymercuri group.[10]

3,5-Diacetoxymercuri-salicylal-anthranilic Acid.—The preparation and properties of this substance are similar to those of the *p*-aminobenzoic acid compound.

Analysis. Calc. for $C_{18}H_{15}O_7NHg_2$: Hg, 52.9. Found: 52.3.

3(?)-Chloromercuri-salicylal-aniline.—Two g. of the alcohol-soluble monochloromercuri-salicylaldehyde dissolved in 4 g. of hot aniline gives on cooling 2 g. of flat, yellow plates which are insoluble in organic solvents; m. p., 182–184°.

Analysis. Calc. for $C_{13}H_{10}ONClHg$: Hg, 46.4. Found: 46.5.

Anhydride of 3-Hydroxymercuri-5-nitrosalicylal-aniline.—Five g. of 3-acetoxymercuri-5-nitro-salicylaldehyde dissolved in 8 cc. of hot aniline and cooled gives a deep red amorphous product which is insoluble in organic solvents but is soluble in alkali. It does not melt at 250°. Analyses show that 1 molecule of acetic acid has been lost during the condensation or during the drying of the product. This probably takes place between the acinitro and acetoxymercuri groups.[6]

Analyses. Calc. for $C_{13}H_8O_3N_2Hg$: Hg, 45.5; C, 35.4. Found: Hg, 45.6; C, 35.0.

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[10] White, THIS JOURNAL, **42**, 2363 (1920).

A similar product is formed from aniline and 5-acetoxymercuri-3-nitro-salicylaldehyde.

3-Chloromercuri-5-nitrosalicylal-aniline.—Three g. of the aldehyde dissolved in 8 cc. of hot aniline and cooled gives an orange-red product which is insoluble and does not melt.

Analyses. Calc. for $C_{13}H_9O_3N_2ClHg$: Hg, 42.1. Found: 42.5, 42.8.

Summary

1. Mercuration of salicylaldehyde by mercuric acetate gives mainly a dimercurated product with only small amounts of a monomercurated aldehyde.
2. The two nitro-salicylaldehydes give normal mercuration products.
3. The mercurated salicylaldehydes lose all their mercury when treated with potassium iodide, hydroxylamine or phenylhydrazine.
4. The mercurated salicylaldehydes form Schiff's bases with aromatic amines.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE]

THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS. II

BY ROGER F. BRUNEL

Received March 14, 1923

Using the methods described by Brunel, Crenshaw and Tobin,[1] the additional alcohols, methylpropyl, diethyl, and dipropyl carbinols have now been purified, and additional specimens of several alcohols formerly investigated have been prepared.

The temperatures have now been followed during the distillations with the 12-junction, copper-constantan thermo-element and are, therefore, more reliable as determinations of the boiling points than those formerly obtained in the boiling-point apparatus subsequent to distillation.[2] In the case of the alcohols whose constants are redetermined, 2 of the boiling points now found are exactly the same; that of methyl-*iso*butyl carbinol, formerly given as only approximate, proves to have been 0.03° low; while that of *n*-propyl alcohol was 0.015° high.

As stated by Brunel, Crenshaw and Tobin, the junctions of the thermo-element were at first soldered, but later brazed. Only the hot junctions, however, were brazed, and at the beginning of the present work it was necessary to braze the cold junctions also. The fixed points were, therefore, redetermined with the following results (cold junctions at 0°): $Na_2SO_4.10H_2O$, transition point 32.384°, 15781 μv; $SrCl_2.6H_2O$, transition

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[1] Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).

[2] The use of the boiling point apparatus was necessary in the former work because the thermo-element was not installed until the distillation of the alcohols was completed.