

Summary.

Guanidine nitrate may be obtained in excellent yield by heating dicyandiamide for 2 hours at 160° with slightly more than 2 molecules of ammonium nitrate, using either the dry materials alone or the materials and water in an autoclave.

CAMBRIDGE, 39, MASSACHUSETTS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

AN INDIRECT METHOD OF PREPARATION OF ORGANIC MERCURIC DERIVATIVES AND A METHOD OF LINKING CARBON TO CARBON.

Preliminary Report.¹

BY MORRIS S. KHARASCH.²

Received July 5, 1921.

The study of organic metallic derivatives is of considerable importance not only because of the use they can be put to synthetically, but also of the opportunity they afford to attack, from an entirely different angle, problems of great theoretical moment. The methods at our disposal suitable to the preparation of any type of mercury compound are, however, rather limited. The main difficulty arises from the fact that mercury never orients *meta* to the group already present in the molecule in the case of a mono substituted benzene derivative. Even in such compounds as nitrobenzene and benzoic acid the mercury orients to the *ortho* and not the *meta* position. This is rather significant if taken in conjunction with the fact that in the mercurization of a compound containing an electronegative group the *para* compound is formed in much larger quantity than the *ortho*.

It is, therefore, quite evident that one has to develop indirect methods of preparing mercury derivatives, otherwise the scope of investigation is necessarily limited, especially in the case of compounds containing one or more electropositive groups.

In a recent paper Kharasch and Chalkley³ have shown that the sulfinic acid method can be used for introducing mercury in any desired position in the benzene molecule, by the use of the corresponding sulfinic acid, the mercury taking the place of the SOOH radical. Unfortunately the preparation of the corresponding sulfinic acids is at times exceedingly difficult, and the writer has, therefore, been led to a search for a simpler and less time consuming method.

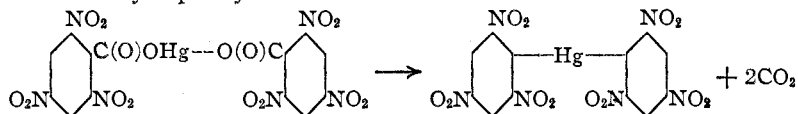
¹ Read before the Organic Division of the American Chemical Society at the Rochester Meeting, March 1921.

² National Research Fellow in Organic Chemistry.

³ Kharasch and Chalkley, THIS JOURNAL, 43, 607 (1921).

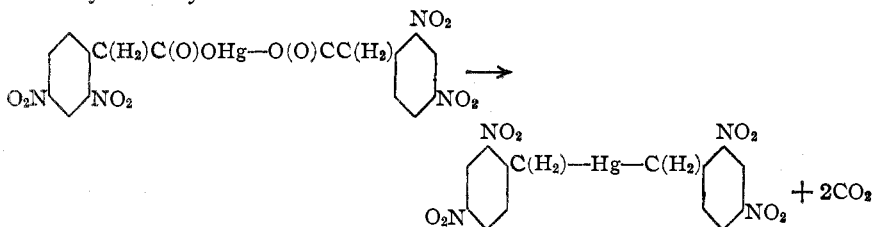
The fact that certain carboxylic acids split off carbon dioxide upon heating has suggested a method of attack, namely, heating the dry mercury salt of the acid or a solution of the latter in pyridine. The present paper deals only with the preparation of certain mercury compounds prepared by heating the dry mercury salts, and is merely a preliminary report on the subject.

It was found that when the mercury salt of 2,4,6-trinitro-benzoic acid was heated to 210°, a gas, which was later proved to be carbon dioxide, was given off. When the reaction was studied quantitatively, it was found that the amount of carbon dioxide lost corresponded to 2 molecules for every molecule of the mercury salt of the trinitro-benzoic acid. The product thus formed is undoubtedly 2,2',4,4',6,6'-hexanitro-mercury-diphenyl:



Analysis and the qualitative reactions of the compound seem to bear out this contention.

In the same way the mercury salt of 2,4-dinitro-phenylacetic acid upon heating decomposes into carbon dioxide and 2,2',4,4'-tetranitro-mercury-dibenzyl



The 2,2',4,4'-tetranitro-mercury-dibenzyl is insoluble in the common organic solvents; it is soluble, however, in pyridine from which it is precipitated out with ligroin. Care must be taken not to heat the pyridine solution, since this leads to the precipitation of mercury. This is characteristic also of the mercury salts of compounds which lose carbon dioxide readily. Thus the writer and A. P. Locke have found that the mercury salt of triphenyl-acetic acid when heated in pyridine solution gives rise to triphenyl-methyl peroxide.⁴ While the dry mercury salt of triphenyl-acetic

⁴ The reaction probably proceeds in two stages, as indicated by the equations given below:

1. $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{C}(\text{O})\text{---O---Hg---O---C}(\text{O})\text{C}(\text{C}_6\text{H}_5)_3 \longrightarrow (\text{C}_6\text{H}_5)_3\text{C---Hg---C}(\text{C}_6\text{H}_5)_3 + 2\text{CO}_2$
2. $(\text{C}_6\text{H}_5)_3\text{C---Hg---C}(\text{C}_6\text{H}_5)_3 \longrightarrow 2(\text{C}_6\text{H}_5)_3\text{C} + \text{Hg} \downarrow \xrightarrow{+\text{O}_2} (\text{C}_6\text{H}_5)_3\text{C---O---O---C}(\text{C}_6\text{H}_5)_3$

In the second stage of the reaction the mercury oxidizes the carbon and we get triphenyl-methyl which combines with the oxygen of the air to give triphenyl-methyl peroxide.

acid when heated gives rise to different products. This behavior of mercury salts of mono- and di-carboxylic acids, which lose carbon dioxide readily, in pyridine solution is under investigation and will be reported soon. The following types of compounds are under investigation at the present time as to the behavior of their mercury salts in pyridine solution and other solvents and upon dry heating: the phenylene oxydicarboxylic acids, the phenyl-paraffin-ketone carboxylic acids, the phenylketone mono and dicarboxylic acids, phenyl-alcohol dicarboxylic acids, the phenylene-ketone dicarboxylic acids, various substituted malonic acids, and other acids which lose carbon dioxide at their melting points or at slightly higher temperatures.

In the case of aromatic carboxylic acids which do not lose carbon dioxide readily, the mercury usually becomes attached to a carbon of the benzene ring. Although this has been known for a long time no systematic study has been undertaken as to the effect of the group already present in the molecule on the orientation of the mercury. Thus Dimroth has shown that when the mercury salt of benzoic acid was heated the mercury enters *ortho* to the carboxyl group. However, in the case of salicylic acid the mercury became attached to the carbon which is *ortho* to the hydroxyl group. The writer has investigated a number of substituted carboxylic acids, and although the work, so far as concerns the positions taken by the entering mercury, is not complete as yet, nevertheless it all points to the following rule: in the case of negatively substituted aromatic acids the mercury usually enters *ortho* to the negative group, irrespective of the position of the carboxyl group, while in the case of a positively substituted aromatic acid the mercury enters *ortho* to the carboxyl group.⁵

Thus, when the mercury salt of anisic acid is heated the mercury enters *ortho* to the methoxy group, as shown by the fact that when the mercury compound thus formed is treated with a solution of potassium periodide it gives 3-iodo-4-methoxybenzoic acid. In the same way in 3-nitro-4-methoxybenzoic acid and 3-nitro-4-hydroxybenzoic acid⁶ the mercury enters *ortho* to the negative group, methoxy and hydroxyl respectively. Other substituted carboxylic acids such as *o*- and *m*-nitrobenzoic acids, 3,5-dinitro- and 2,4-dinitro-benzoic acids, the nitrosalicylic acids (2-nitrosalicylic acid [OH = 1] and 4-nitrosalicylic acid) have also been investigated, but the position taken by the entering mercury has not been established as yet, since the corresponding halogen derivatives of some of them are not recorded in the literature and it is necessary to prepare them by some other means. This work is now in progress.

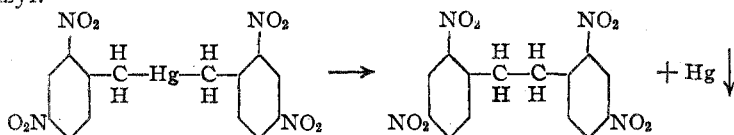
m- and *o*-nitrobenzoic acids and other nitrobenzoic acids such as nitroanisic acid, besides giving rise to mercury compounds, in which the mercury

⁵ This is not rigidly correct as will be brought out in a subsequent paper.

⁶ Kharasch, *THIS JOURNAL*, 43, 1203 (1921).

is attached to a carbon of the benzene ring, also split off carbon dioxide especially at temperatures above 200°. Thus upon heating *o*-nitrobenzoic acid two products were obtained; one of them was found to be mercurized *o*-nitrobenzoic acid, and the other, insoluble in alkali, gave rise to nitrobenzene-*o*-mercuric chloride upon treatment with alcohol saturated with hydrogen chloride. This work is almost complete and will be reported soon.

The above mentioned method for the preparation of mercury compounds by heating the mercury salt of an acid, which loses carbon dioxide readily, would thereby enable us to replace a carboxyl group by a halogen and it is also hoped that it would have a much wider application in that by heating the mercury compound, thus formed, in the dry state or in some solvent the mercury would oxidize one of the carbons and thereby link the two carbons together. This would be especially possible in the case of the compounds where the mercury would be attached to the aliphatic residue. This observation has been made by Wolff,⁷ incidentally, in the case of mercury dibenzyl which was found to go over into dibenzyl and metallic mercury when heated slightly above its melting point, and the writer has also observed it in the case of 2,2',4,4'-tetranitro-mercury-dibenzyl.



The writer and F. W. Stavely are engaged at the present time in working out the details and applications of this method of linking carbon to carbon.

Experimental Part.

The Preparation of the Mercuric Salt of 2,4-Dinitro-phenylacetic acid.—It was found more advantageous in the preparation of the mercury salts of the substituted aromatic acids to treat a water solution of the acids with mercuric acetate, rather than by double decomposition of the sodium salts with mercuric chloride.

To a solution of 4.5 g. of 2,4-dinitro-phenylacetic acid, in 450 cc. of hot water (70°), a solution of 3.2 g. of mercuric acetate in 50 cc. of water was added in small portions, the whole being well stirred. An immediate precipitate resulted and was at once collected on a filter, washed well with water and dried *in vacuo* over sulfuric acid. Yield, 6 g. For analysis the salt was dried to constant weight *in vacuo* at 100°.

Analysis. Subs., 0.1844: N₂, 14.00 cc. (16° and 733.2 mm.). Calc. for C₁₆H₁₀O₁₂N₄Hg:N, 8.59. Found: 8.66.

The compound is of a very light yellow color. When treated with sodium hydroxide solution it soon turns it dark, comparable with the behavior of 2,4-dinitro-phenyl-acetic acid. It is soluble in pyridine imparting to it a yellow color, but after a while the solution turns dark and, if warmed, metallic mercury separates. The compound has no melting point, but loses carbon dioxide when heated at 180-190° and goes over into the compound described immediately below.

⁷ Wolff, *Ber.*, 46, 64 (1913).

The Preparation of 2,2',4,4'-Tetranitro Mercury Dibenzyl.—When the dry mercury salt of 2,4-dinitro-phenyl-acetic acid was heated to 180° a vigorous evolution of carbon dioxide took place and a yellow solid remained. The amount of carbon dioxide lost, as estimated by the loss in weight of the test-tube, in which the compound was contained, corresponded to two molecules for every molecule of the mercury salt of 2,4-dinitro-phenyl-acetic acid. The melting point of the compound thus obtained is 215°. After washing with acetone, in which the substance is insoluble, the melting point was raised to 235°.

For analysis the compound was dissolved in pyridine and filtered from the small amount of mercury with which it is contaminated. It was then precipitated with ligroin, and dried to constant weight *in vacuo* over sulfuric acid.

Analysis. Subs., 0.1280: N₂, 11.30 cc. (22° and 732.5 mm.). Calc. for C₁₄H₁₀O₈N₄Hg: N, 9.97. Found: 9.83.

The compound is insoluble in all common organic solvents except pyridine and is precipitated from a solution of the latter by ligroin as a bright red powder. When the pyridine solution of the compound is heated mercury separates. It is insoluble in sodium hydroxide and also does not change color when heated with it. It melts with decomposition rather sharply at 235°, with separation of mercury.

The Preparation of the Mercuric Salt of 2,4,6-Trinitrobenzoic Acid.—To a solution of 5.2 g. of 2,4,6-trinitrobenzoic acid dissolved in 350 cc. of hot water, a solution of 3.4 g. of mercuric acetate in 20 cc. of water, was added. A beautiful white compound separated. The whole was then cooled, and the precipitate collected on a filter, washed several times with small amounts of cold water and dried *in vacuo* over sulfuric acid. Yield 6.1 g.

For analysis the substance was dried to constant weight *in vacuo* at 100°.

Analysis. Subs., 0.1078: N₂, 11.50 cc. (21° and 737.8 mm.). Calc. for C₁₄H₄O₁₆N₆Hg: N, 11.81. Found: 12.03.

The salt gives the same reactions with sodium hydroxide as does trinitrobenzoic acid. It begins to give off carbon dioxide at 210° and goes over into the compound described below.

The Preparation of 2,2',4,4',6,6'-Hexanitro Mercury Diphenyl.—The mercury salt of 2,4,6-trinitrobenzoic acid contained in a test-tube, was heated to 210°, by immersing the latter in a sulfuric acid bath, and kept at that temperature until no more carbon dioxide was evolved. The loss in weight corresponds quantitatively to two molecules of carbon dioxide for every molecule of the mercury salt. The contents of the test-tube were then extracted with acetone. Most of the substance goes in solution and can be obtained in fairly pure condition by concentrating the acetone extract, decanting the mother liquor from the precipitate formed, and washing the latter with ether. It is best, however, to recrystallize it from a mixture of acetone and alcohol.

For analysis the substance was dried *in vacuo* at 100°.

Analyses. Subs., 0.5005: HgS, 0.1832. Subs., 0.1755: N₂, 21.00 cc., (22° and 724.5 mm.). Calc. for C₁₂H₁₄O₁₂N₆Hg: N, 13.43; Hg, 31.23. Found: N, 13.27; Hg, 31.57.

The compound is white and crystalline with a faint suggestion of yellow. It is soluble in acetone, very slightly soluble in alcohol and almost insoluble in ether. It dissolves in pyridine imparting to the solution a pink color, and when heated in it, the pink color changes immediately to a green-purple. Upon exposing the solution to the air it becomes yellow and a precipitate separates which is insoluble in acetone. It melts rather sharply at 272°, and the melt does not separate any mercury when heated to 295°.

When suspended in water and treated with potassium periodide or potassium per-

bromide the mercury is not removed from the benzene ring even in the course of 10 days, as evidenced by the fact that the compound can be recovered unchanged. However, with mercuric chloride the reaction is normal. This anomalous behavior with potassium periodide is perhaps due to the fact that water does not moisten the compound.

The Preparation of 2,4,6-Trinitro-phenyl-mercuric chloride.—To 0.8 g. of 2,2',4,4',6,6'-hexanitro-mercury-diphenyl, suspended in 50 cc. of alcohol, 0.35 g. of mercuric chloride was added, and the whole was heated on the hot plate for 3 hours. The unchanged 2,2',4,4',6,6'-hexanitro mercury diphenyl was filtered off (0.25 g.), and the filtrate evaporated to dryness. Weight, 0.75 g. It was crystallized from alcohol.

For analysis the compound was dried *in vacuo* at 100°.

Analysis. Subs., 0.1937 : N₂, 16.20 cc. (22° and 732.9 mm.). Calc. for C₆H₂O₆N₃ ClHg: N, 9.38. Found: 9.33.

The compound is of an exceedingly light yellow color so that it appears to be almost white. It is soluble in alcohol, ether and acetone. It melts at 202° to a clear liquid.

Preparation of 2,4,6-Trinitro-iodo-benzene and 2,2',4,4',6,6'-Hexanitro-diphenyl.—To a suspension of 1.1 g. of 2,4,6-trinitro-phenyl-mercuric chloride in 30 cc. of water, 7 cc. of solution of potassium periodide (0.1 g. of iodine per cc.), and 5 g. of potassium iodide were added. The mixture was then agitated on the shaking machine for one hour and the precipitate collected on a filter. It was then washed well with water and dried in the oven at 100°. When completely dry the precipitate was extracted with ether. A residue remained which melted at 240° and is probably as 2,2',4,4',6,6'-hexanitro-diphenyl. The ether extract was evaporated to dryness. A very light yellow compound was thus obtained. It melted at 164–165° and was identified as 2,4,6-trinitro-iodo-benzene.

Summary.

1. It has been shown that when the mercury salts of certain carboxylic acids are heated, carbon dioxide is split off and the mercury takes the place originally occupied by the carboxyl groups.

2. The preparation of the mercury salts of 2,4-dinitro-phenylacetic acid and 2,4,6-trinitrobenzoic acid is given as well as the compounds derived from them: 2,2',4,4'-tetranitro mercury dibenzyl, 2,2',4,4',6,6'-hexanitro mercury diphenyl, and 2,4,6-trinitro-phenyl-mercuric chloride.

3. It has been shown that when 2,4,6-trinitro-phenyl-mercuric chloride is treated with potassium periodide it gives rise to 2,4,6-trinitro-iodo-benzene, and presumably to 2,2',4,4',6,6'-hexanitro-diphenyl.

CHICAGO, ILLINOIS.