of the physicists and it seems quite certain that at some future time our theories of chemical combination must be brought into harmony with the known facts about spectral lines, absorption bands, color and other phenomena of light and radiation.

CAMBRIDGE, ENGLAND   WILLIAM A. NOYES
Received September 4, 1923

A Method for Reproducing Graphs in Quantity.—Graphs, etc., are plotted with waterproof india ink on the ordinary graph (or coördinate) paper. This is dipped in a saturated solution of purified, colorless paraffin oil (such as Stanolind-Liquid Paraffin) in chloroform and allowed to stand for $1/2$ to 1 minute. It is then removed from the solution and allowed to drain as long as convenient. The excess of oil is wiped off and the sheet allowed to dry in the air until ready to use.

Using paper thus prepared, as a negative, photographic copies can be made on any of the bromide or blue print papers by direct printing. The bromide reproductions are particularly satisfactory and resemble photostats.

EVANS MEMORIAL   W. C. GREENE
BOSTON, MASSACHUSETTS   R. S. HUNT
Received September 14, 1923

THE BEHAVIOR OF MERCURIC SALTS OF ORGANIC ACIDS TOWARD HEAT[1]

BY MORRIS S. KHARASCH[2] AND FREDERICK W. STAVELEY[3]

In a previous communication Kharasch[4] called attention to the fact that mercuric salts of certain aromatic carboxylic acids when heated split off carbon dioxide and the mercury becomes attached to the carbon originally bound to the carboxyl group. That reaction is applicable only to those aromatic carboxylic acids which split off carbon dioxide at their respective melting points or at slightly higher temperatures. In the case of the mercury salts of aromatic carboxylic acids, which do not split off carbon dioxide

[1] Read before the Organic Division of the American Chemical Society at the Pittsburgh Meeting, September, 1922.
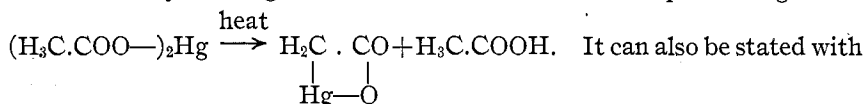
[2] National Research Fellow in Organic Chemistry.

[3] The material presented here is used by F. W. Staveley in his dissertation presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Chicago.

[4] Kharasch, THIS JOURNAL, 43, 2238 (1921).

readily, the mercury usually becomes attached to a carbon of the benzene ring.[5]

The extent to which these reactions find their parallel in the aliphatic series has been the subject of an extensive investigation by Kharasch and various collaborators. The present communication deals primarily with the behavior toward heat of various substituted acetic acids. In selecting the compounds for this work, we were guided by the following considerations. We wanted to ascertain, first, the behavior toward heat of mercuric salts of substituted acetic acids not containing a replaceable hydrogen atom on the α carbon atom; second, whether in phenylated acetic acids the velocity of mercuration of the benzene nucleus is greater than that of the α carbon atom; third, the behavior of mercuric salts of substituted acetic acids that decompose readily into carbon dioxide and hydrocarbon.

The only work known to the writers which has been carried out on the behavior of mercuric salts of aliphatic acids toward heat is that of Dimroth.[6,7] This author claims to have obtained a mercurated acetic acid by heating mercuric acetate, the reaction proceeding thus:

$$(H_3C.COO\text{---})_2Hg \xrightarrow{\text{heat}} \underset{\underset{Hg\text{---}O}{\mid\qquad\quad\mid}}{H_2C\ .\ CO} + H_3C.COOH.$$ It can also be stated with

a fair degree of certainty that most of the mercury salts of aliphatic acids containing one or more hydrogen atoms on the α carbon atom would behave in the same way, the mercury replacing one of the hydrogen atoms of the α carbon atom.[8] However, when the hydrogen atoms on the α carbon atom are replaced by other groups, the reaction that takes place depends upon the character of the substituting radicals. Thus far, the investigation in this direction with salts of acids which do not split off carbon dioxide readily, has been confined to the study of various substituted acetic acids, namely, trimethyl-, trichloro-, phenyl-, diphenyl- and triphenylacetic acids.

In the case of the mercury salt of trimethylacetic acid, no change takes place when it is heated in a vacuum to 240° for 20 minutes, except that some of the salt distils. Thus, the salt still gives a precipitate of yellow mercuric oxide when treated with sodium hydroxide, and its behavior in other ways

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[5] It is usually assumed that in substituted benzoic acids the mercury enters *ortho* to the carboxyl group. (See Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., 1921, p. 295, for references.) However, this is not rigidly correct. Thus, by heating the mercury salt of *p*-nitrobenzoic acid the mercury enters not only *ortho* to the carboxyl group, but also *meta* to it. This latter product has been overlooked by previous investigators.

[6] Dimroth, *Ber.*, 35, 2870 (1902).

[7] The behavior of mercuric cyanide when heated is discussed later in the paper.

[8] The mercury salts of methyl-, dimethyl- and ethylacetic acids have been found to give products of that type. They will be reported by one of us (Kh.) in connection with another investigation.

resembles that of mercury trimethylacetate. Similarly, when the salt is heated above its melting point in the air, no change can be detected by chemical means.

However, when all three hydrogen atoms of acetic acid are replaced by chlorine atoms, as in the case of trichloro-acetic acid, an entirely different reaction takes place. It must also be stated at the outset that our experience with the mercuric salt of trichloro-acetic acid is not in agreement with that of the previous investigator[9] of this salt. We could not isolate the mercury salt by dissolving mercuric oxide in a water solution of trichloro-acetic acid, although it must have been formed, since the solution gave a precipitate of mercuric oxide when treated with sodium hydroxide. The solution of the salt, however, was found to be unstable and when heated, or concentrated in a vacuum, or even allowed to stand for any length of time, mercurous chloride separated, and carbon dioxide was evolved.[10,11]

If we replace the hydrogen atoms in acetic acid by phenyl groups, instead of methyl or chloro, the decomposition reactions which the mercury salts undergo upon heating are different. Thus, when the mercury salts of phenyl- and diphenylacetic acids are heated slightly above their melting points, the mercury does not replace a hydrogen atom of the α carbon atom, but one of the benzene ring. In that respect this reaction resembles the mercuration of aromatic acids by the dry heating of the salts of the latter compounds. In the case of triphenylacetic acid the reaction is more complicated; one of the products of the reaction is, however, a nucleus-mercurated triphenylacetic acid.[12] In no case is any product formed which contains the mercury on the α carbon atom. It appears, thus, that in

[9] Clermont, *Compt. rend.*, 76, 774 (1874).

[10] The reaction undoubtedly proceeds in two or more stages, the decomposition in the molecule beginning with the mercury oxidizing the carbon, and thus giving rise to the following products: $(Cl_3C.COO—)_2Hg \xrightarrow{H_2O} 2 (Cl_3C.COOHg) + Cl_3C.COOH + (Cl_3C.OH) + CO_2$. The trichlorocarbinol thus formed decomposed immediately into phosgene and hydrogen chloride. The decomposition of the former product in water then proceeds in the usual manner. The non-formation of chloroform in this reaction precludes the possibility that hexachloro-mercury dimethyl is an intermediate product in this reaction.

[11] This behavior of the mercuric salt of trichloro-acetic acid is somewhat similar to that of the mercuric salt of oxalic acid (from the electronic point of view the two acids are similar) since the mercuric salt of the latter acid when treated with ammonium chloride breaks down when warmed, into ammonium oxalate, carbon dioxide and mercurous chloride. [Souchay and Lennsen, *Ann.*, 102, 42 (1857).] The ferric salt of oxalic acid is also known only in solution [Doberiner, *Ann.*, 122, 113 (1862). Lemoine, *Compt. rend.*, 116, 982 (1893)] and it decomposes very readily into ferrous oxalate and carbon dioxide. The behavior of the salts of these easily oxidizable acids is under investigation by one of us.
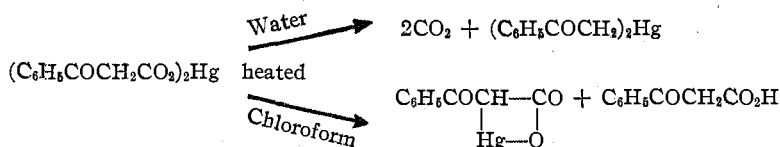
[12] This is most interesting in view of the fact that in pyridine solution the salt decomposes into triphenylmethyl and metallic mercury. See Ref. 4.

the case of phenylated acetic acids, the velocity of mercuration of the nucleus is much greater than that of the side chain.[13]

From the considerations thus far developed it is quite evident what course the decomposition of a mercury salt of a substituted acetic acid of a given type would take. However, there is another factor involved in these decompositions, namely, the ease with which the acid loses carbon dioxide when heated. This is a very important factor, and the relative quantities of the products of the decomposition are largely dependent upon this factor. Of the acids thus far investigated, dimethyl- and diethylaceto-acetic acid and benzoylacetic acid might be mentioned. These acids were all selected because of their similarity, since all are substituted acetic acids, and lose carbon dioxide very readily. As anticipated, the mercuric salts of dimethyl- and diethylaceto-acetic acids when thoroughly dried and heated in a vacuum at 90° split off carbon dioxide, and the mercury became attached to the carbons originally bound to the carboxyl groups. This type of decomposition is illustrated below by that of the mercuric salt of

diethylaceto-acetic acid: $[CH_3CO.C(C_2H_5)_2.CO_2]_2Hg \xrightarrow{\text{heat}} 2CO_2 + [CH_3-CO.C(C_2H_5)_2-]_2Hg$.
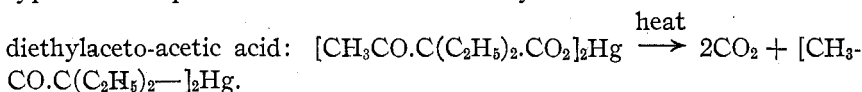
In the case of benzoylacetic acid, which contains two labile α hydrogen atoms, the reaction may be made to go in either of two directions which depend upon the conditions under which the experiment is carried out. When the acid is heated with mercuric oxide in alcohol, carbon dioxide is evolved, and mercury-*bis*-benzoylmethane is obtained. If the reaction is carried out in chloroform, no carbon dioxide is lost, the mercury going to the α carbon atom. The two processes may be illustrated by the following equations.

$$(C_6H_5COCH_2CO_2)_2Hg \quad \begin{array}{c} \xrightarrow{\text{Water}} \quad 2CO_2 + (C_6H_5COCH_2)_2Hg \\ \text{heated} \\ \xrightarrow{\text{Chloroform}} \quad \underset{\overset{|}{Hg}—\overset{|}{O}}{C_6H_5COCH—CO} + C_6H_5COCH_2CO_2H \end{array}$$
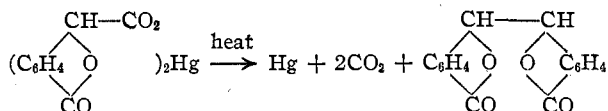
In the methylated and ethylated aceto-acetic acids, where the labile α hydrogen atoms are replaced by alkyl groups, only the tendency to split off carbon dioxide was observed.

In the case of the acids previously mentioned where, upon heating the mercury salts, the mercury takes the place originally held by the carboxyl group, there is also a great tendency for the mercury to split out and link the two carbons. This usually takes place at temperatures slightly higher than those at which the decomposition of the mercury salt into the mercury-*bis* compound occurs although some compounds such as mercury-

[13] The experimental data are not recorded in this paper, for the position of the mercury in the ring has not been definitely established, but will be reported in a later paper.
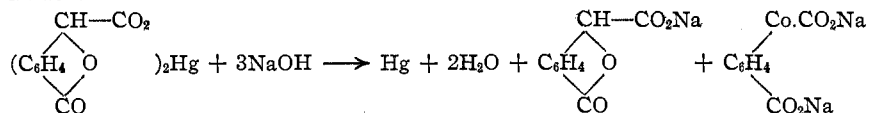
bis-acetodiethyl methane and the corresponding dimethyl compound lose mercury spontaneously when kept for a few days. Again, in the case of the mercuric salt of phthalide carboxylic acid, we were not able to isolate the intermediate mercury compound, the salt decomposing when heated into carbon dioxide, metallic mercury and dihydrophthalide.[14,15]

$$\text{(C}_6\text{H}_4 \underset{\text{CO}}{\overset{\text{CH---CO}_2}{\diamond}} \text{O} \big)_2\text{Hg} \xrightarrow{\text{heat}} \text{Hg} + 2\text{CO}_2 + \text{C}_6\text{H}_4 \underset{\text{CO}}{\overset{\text{CH-----CH}}{\diamond}} \text{O} \quad \text{O} \underset{\text{CO}}{\diamond} \text{C}_6\text{H}_4$$

Similar linking undoubtedly took place when the mercuric salts of diethyl- and dimethylaceto-acetic acids were distilled in a vacuum. The isolation of these ketones, and a thorough study of the linking of the carbon to carbon by means of these mercury derivatives will be continued by Kharasch and Mildred W. Grafflin.

Mercury carbon compounds differ very widely in their stability toward various reagents such as sodium hydroxide and ammonium sulfide.[16] If we neglect, for the time being, the aromatic mercuri-organic derivatives, which will be discussed in greater detail in a paper by Kharasch and Chalkley, we may consider the mercury aliphatic compounds to be of the

[14] An exceedingly interesting reaction takes place when the mercuric salt of phthalide carboxylic acid is treated with sodium hydroxide; metallic mercury separates and from the solution two acids can be isolated; phthalide carboxylic acid and its oxidation product phthalonic acid. It appears, thus, that in alkaline solution one-half of the phthalide carboxylic acid is oxidized to phthalonic acid, leading thus to the products isolated.

$$\text{(C}_6\text{H}_4 \underset{\text{CO}}{\overset{\text{CH---CO}_2}{\diamond}} \text{O} \big)_2\text{Hg} + 3\text{NaOH} \longrightarrow \text{Hg} + 2\text{H}_2\text{O} + \text{C}_6\text{H}_4 \underset{\text{CO}}{\overset{\text{CH---CO}_2\text{Na}}{\diamond}} \text{O} + \text{C}_6\text{H}_4 \overset{\text{Co.CO}_2\text{Na}}{\underset{\text{CO}_2\text{Na}}{\diamond}}$$

This rather striking behavior is very readily comprehended since phthalide carboxylic acid is a γ lactone, which we should expect to be quite susceptible to oxidation.

[15] The chemistry of the decomposition of the keto carboxylic acid when heated will be reported by one of us in connection with the photochemical decomposition of mercuric salts of other keto acids, such as pyruvic acid.

[16] The speed of reaction of bridged mercury compounds with mercuric chloride is also of great significance in regard to the stability of the mercury-carbon union in the bridged compounds. Mercury-*bis*-acetodiethyl and -dimethyl methane react almost instantly with mercuric chloride, in the following manner: $[\text{H}_3\text{C.CO.C(C}_2\text{H}_5)_2\text{---}]_2\text{-}$ $\text{Hg} + \text{HgCl}_2 \longrightarrow \text{H}_3\text{C.CO.C(C}_2\text{H}_5).\text{HgCl}$. The reaction of mercury-*bis*-aceto-diethyl methane and mercuric chloride is taken for illustration. These compounds constitute the first definite mercury compounds of an alkylated acetone in which it is quite certain that the mercury is attached to a carbon atom. Some of the products of acetone, and substituted acetones, described in the literature are simply mixtures of various compounds, and there is absolutely no ground for assigning to a compound a formula such as the following: $5(\text{Me})_2\text{CO.8HgSO}_4.12\text{HgO}$ [Denigès, *Ann. chim. phys.* [8] **12**, 401 (1907)]. It is merely an attempt on the part of the investigator to fit his analytical figures to a formula.

same kind as the inorganic compounds, but differing from them in being less ionized. Naturally, it is the degree of ionization of these derivatives that determines whether a compound will give a test with sodium hydroxide or ammonium sulfide. It is understood, of course, that the degree of ionization of the mercury from the carbon is a function of the constitution of the molecule. Thus, while mercuric chloride, a representative inorganic compound, gives an immediate precipitate of mercuric oxide when treated with sodium hydroxide, mercuric cyanide does not. Ammonium sulfide, however, precipitates mercuric sulfide from both substances, on account of the extraordinary insolubility of mercuric sulfide. Similarly, the mercury derivatives of substituted acetones, the bridged as well as the unbridged, do not give a test for mercuric ions with sodium hydroxide, but ammonium sulfide gives an immediate precipitate of mercuric sulfide. It is noteworthy in this connection that mercuric cyanide and the bridged compounds, prepared from substituted acetoacetic acid, react very readily with mercuric chloride. Thus, soon after the solutions were mixed, sodium hydroxide failed in either case to give a test for mercuric ions. The reactions of these aliphatic mercury compounds thus parallel those of mercuric cyanide.

The decomposition of mercuric cyanide into metallic mercury and cyanogen when heated is also of great significance in this connection. It is merely an intramolecular oxidation-reduction reaction between the mercury and the carbon, and is thus quite similar to the decompositions which the aliphatic bridged mercury compounds, previously discussed, undergo when heated. The analogy in chemical behavior of mercuric cyanide and the bridged mercury aliphatic compounds indicates quite strongly that the former has a nitrile and not an isocyanide structure. This view also seems to be in accord with other facts known about mercuric cyanide. The notion certainly deserves consideration, in view of the facts advanced for its support, and will be more thoroughly discussed later.

The investigations along the various lines outlined in the paper are being continued at the University of Maryland.

Experimental Part

Mercury-*bis*-benzoylmethane, $(C_6H_5COCH_2)_2Hg$.—To 1.3 g. of benzoylacetic acid dissolved in 50 cc. of 95% alcohol, 5 g. of yellow mercuric oxide was added. The whole was then heated to boiling, and filtered. The residue was boiled with 20 cc. of alcohol and filtered. The two filtrates were combined, diluted with water, and cooled in an ice-bath. A faintly yellow precipitate separated which was washed with water and dried on a porous plate; m. p., 159.5°; yield, 0.8 g.

Analysis.[17] Subs., 0.2624: HgS, 0.1386. Calc. for $C_{16}H_{14}O_2Hg$: Hg, 45.72. Found: 45.56.

The compound is white. It is soluble in hot alcohol and crystallizes as the solution cools. It is soluble in acetone but insoluble in water or ether.

[17] Unless otherwise indicated all samples for analysis were dried to constant weight in a vacuum over sulfuric acid.

An alcoholic solution of the compound does not give mercuric oxide when treated with sodium hydroxide; however, ammonium sulfide gives an immediate precipitate of mercuric sulfide.

When mercury-*bis*-benzoylmethane is treated with mercuric chloride it forms the compound described immediately below.

Benzoylmethyl-mercuric Chloride, $C_6H_5COCH_2HgCl$.—To 0.32 g. of mercury-*bis*-benzoylmethane, dissolved in 10 cc. of hot 95% alcohol, 0.2 g. of mercuric chloride was added, and the mixture heated on the water-bath until it no longer gave a test for mercuric ion when sodium hydroxide was added. It was then diluted with water and cooled in ice. The precipitate was collected on a filter, washed with water, and dried on a porous plate; m. p., 146°; yield, 0.3 g. The compound thus obtained was found to be identical with that prepared by direct mercuration of acetophenone, the constitution of which has been definitely established as benzoylmethyl-mercuric chloride (phenacyl-mercuric chloride).[6]

Anhydro-α-hydroxy-mercuribenzoyl Acetic Acid, C_6H_3CO—CH—CO—O—Hg.—

An excess of yellow mercuric oxide was added to 3 g. of benzoyl-acetic acid dissolved in 50 cc. of chloroform. The mixture was kept at the boiling temperature of chloroform for a minute and then filtered. When the filtrate was evaporated to dryness a white solid remained. To remove unchanged benzoylacetic acid, the product obtained above was extracted twice with ether. It was then dried in a vacuum over sulfuric acid; yield, 1.3 g.

Analysis. Subs., 0.4706: HgS, 0.3027. Calc. for $C_9H_6O_3Hg$: Hg, 55.32. Found: 55.47.

The compound is white. It is slightly soluble in cold chloroform, very soluble in hot, and insoluble in ether; it is insoluble in water, but readily soluble in sodium hydroxide. The compound decomposes at about 290°. When treated with dil. hydrochloric acid, benzoylacetic acid and mercuric chloride are formed. The compound does not give an immediate violet coloration with an alcoholic ferric chloride solution but, if it is first acidified with hydrochloric acid, an immediate violet coloration characteristic of benzoylacetic acid is obtained.

Mercuric Phthalide-Carboxylate, $(C_6H_4COOCHCOO)_2Hg$.—To 1 g. of phthalide carboxylic acid, dissolved in 200 cc. of hot water, 0.89 g. of mercuric acetate, dissolved in a small amount of water, was added. A heavy white precipitate was obtained which was collected on a filter, washed with cold water and then with a small amount of alcohol and ether. It melted, with decomposition, at 195°.

Analyses. Subs., 0.3277, 0.5667, 0.4674: HgS, 0.1380, 0.2336, 0.1942. Calc. for $C_{18}H_{10}O_8Hg$: Hg, 36.16. Found: 36.32, 35.55, 35.83.

The compound is easily soluble in hot acetone and insoluble in cold alcohol and ether. When it is treated with sodium hydroxide, metallic mercury separates.

Action of Sodium Hydroxide on the Mercuric Salt of Phthalide Carboxylic Acid

To 5 g. of mercuric phthalide carboxylate 10 cc. of sodium hydroxide (6 N) was added. An immediate precipitation of metallic mercury took place. The mixture was filtered and the filtrate shaken with charcoal, to remove traces of finely divided mercury, and then filtered again. After that, the filtrate did not contain any mercury. It was acidified with dil. sulfuric acid and extracted several times with ether. On evaporation of the ether an oil was obtained which solidified after standing for some time. The compound was easily soluble in water; m. p., 100°; yield, 1.2 g. The compound thus

obtained was extracted with chloroform and the insoluble portion was treated with a very small amount of water and allowed to crystallize slowly, after which the crystals were again extracted with chloroform. The residue dried on a porous plate, melted at 140°. Phthalonic acid prepared by the oxidation of naphthalene melted at 145°, and a mixture of the phthalonic acid with the above product melted at 140°. Both products gave a red coloration when treated with concd. sulfuric acid and benzene containing thiophene.

The chloroform filtrates were combined, evaporated to dryness, and the solid residue was extracted twice with small amounts of water. The residue was dried on a porous plate. This product melted at 144.5°. Phthalide carboxylic acid prepared by reducing phthalonic acid melted at 151°, and a mixture of the two melted at 150°. This product gave only a faint pink coloration with concd. sulfuric acid and benzene containing thiophene.

When mercuric-phthalide carboxylate is heated to 195°, it melts and decomposes, metallic mercury separates and the compound described immediately below is formed.

Preparation of Dihydrophthalide from the Mercuric Salt of Phthalide Carboxylic Acid

One g. of the well-dried mercuric salt of phthalide carboxylic acid was heated to 195° when it decomposed with the separation of metallic mercury. When cold the solid was extracted with hot glacial acetic acid. As the filtrate was cooled, a yellow solid separated which was collected on a filter and washed with water. The product was then dried in a vacuum over sulfuric acid; m. p., 250°; yield, 0.36 g.

Pure dihydrophthalide prepared from phthalic anhydride, mixed with this compound was found not to depress the melting point.

Mercurous Benzoylformate, $C_6H_5CO.CO_2Hg$.—Benzoylformic acid was dissolved in 175 cc. of 80% alcohol, and 40 g. of yellow mercuric oxide was added. The mixture was boiled for a few minutes and filtered. As the filtrate cooled, a white precipitate separated which was collected on a filter.

Analysis. Subs., 0.1597: HgS, 0.1063. Calc. for $C_8H_5O_3Hg$: Hg, 57.40. Found: 57.45.

The compound is white. When it is treated with sodium carbonate or sodium hydroxide, metallic mercury separates. The same observation was made when pyridine was used as a solvent for the compound. This is characteristic of mercurous salts. The compound is only slightly soluble in boiling alcohol. When acidified with dil. sulfuric acid and extracted with ether, the ether extract upon evaporation gave a white solid which melted at 57°. Benzoylformic acid melts at 62° and was found not to depress the melting point of this compound. When the substance was heated the odor of benzaldehyde was noticeable.

Mercuric Benzoylformate, $(C_6H_5CO.CO_2)_2Hg$.—To 12.6 g. of benzoylformic acid dissolved in 500 cc. of water, a solution of 13.4 g. of mercuric acetate in 100 cc. of water was added slowly and the mixture was constantly stirred. A white precipitate was obtained which was collected on a filter and washed with water; m. p., 164°; yield, 15 g.

Analysis. Subs., 0.1779: HgS, 0.0867. Calc. for $C_{16}H_{10}O_6Hg$: Hg. 40.23. Found: 42.03.

The compound is white. It is soluble in pyridine and nitrobenzene, but only slightly soluble in water. When it was heated to 180° mercury separated, carbon dioxide was evolved and benzoic acid was formed. After it had been refluxed in nitrobenzene, a solid was obtained which had no definite melting point but decomposed at about 200°, and when treated with sodium hydroxide or pyridine metallic mercury separated from it. This is characteristic of mercurous salts.

Mercuric-α,α-diethyl-aceto-acetate, [CH$_3$CO.C(C$_2$H$_5$)$_2$.CO$_2$]$_2$Hg.—To 8.5 g. of α,α-diethyl-aceto-acetic acid, dissolved in 50 cc. of 30% alcohol, 9.2 g. of mercuric acetate, dissolved in a small amount of water, was slowly added and the mixture constantly stirred. The precipitate was collected on a filter, washed with water and then with a small amount of alcohol. The product thus obtained melted at 103° with decomposition; yield, 7 g.

Analysis. Subs., 0.1649: HgS, 0.0754. Calc. for C$_{16}$H$_{26}$O$_6$Hg: Hg, 38.97. Found: 39.43.

The compound is easily soluble in pyridine and hot alcohol. It is not very soluble in ether or cold nitrobenzene but dissolves in hot nitrobenzene, metallic mercury separating at the same time. When the compound is heated to its melting point carbon dioxide is evolved and the product described immediately below is formed.

Mercury-*bis*-aceto-diethylmethane, (CH$_3$CO.C(C$_2$H$_5$)$_2$—)$_2$Hg.—When mercuric-α,α-diethyl-aceto-acetate was heated in a vacuum to 85°, the compound melted, carbon dioxide was evolved and later the melt solidified. When the loss in weight corresponded to two molecular equivalents of carbon dioxide, the reaction was considered complete. The solid was then dissolved in acetone and the solution filtered. Upon slow evaporation of the solvent, a white solid separated which was dried on a porous plate. It melted at 109° with decomposition. The yield was almost quantitative.

For analysis the compound was dried as quickly as possible in a vacuum over phosphorus pentoxide.

Analysis. Subs., 0.1319: HgS, 0.0736. Calc. for C$_{14}$H$_{26}$O$_2$Hg: Hg, 47.00. Found: 48.11.

The compound is soluble in acetone, chloroform and benzene, but insoluble in water. It is unstable and decomposes rapidly, with the separation of metallic mercury, into an oil which has an odor somewhat resembling that of camphor. This instability explains the high value obtained for mercury. When an alcoholic solution of the compound was treated with ammonium sulfide a precipitate of mercuric sulfide was formed immediately.

When this substance is treated with mercuric chloride, the compound described immediately below is formed.

Aceto-diethyl-methyl-mercuric Chloride, (CH$_3$CO.C(C$_2$H$_5$)$_2$—)HgCl.—To 1.75 g. of mercury-*bis*-aceto-diethylmethane dissolved in 15 cc. of 95% alcohol was added a solution of 1.12 g. of mercuric chloride in 30 cc. of warm alcohol. The solution was cooled in a freezing mixture, and a white solid separated; m. p., 77°; yield, 0.85 g.

Analysis. Subs., 0.3618: HgS, 0.2408. Calc. for C$_7$H$_{13}$OClHg; Hg, 57.44. Found: 57.40.

The compound crystallizes slowly from alcohol. In the above preparation, shortly after the mercuric chloride was added to the mercury-*bis*-aceto-diethylmethane, no mercuric ions could be detected by the addition of sodium hydroxide. The compound gave, however, an immediate precipitate of mercuric sulfide with ammonium sulfide.

Mercuric Dimethyl-aceto-acetate, [CH$_3$CO.C(CH$_3$)$_2$.CO$_2$]$_2$Hg.—To 40 g. of mercuric acetate dissolved in 150 cc. of water was slowly added 29 g. of α,α-dimethyl-aceto-acetic acid, dissolved in 100 cc. of 30% alcohol. A thick paste formed immediately. More water was then added and the mixture was well stirred; the precipitate was collected on a filter and washed well with water. When dried on a porous plate the compound melted at 100°, with decomposition; yield, 15.5 g.

Analysis. Subs., 0.4237: HgS, 0.2206. Calc. for C$_{12}$H$_{18}$O$_6$Hg: Hg, 43.74. Found: 44.80.

The compound is white and is insoluble in water. When heated to 100°, it melts with decomposition, carbon dioxide is evolved and metallic mercury separates. With

sodium hydroxide a yellow precipitate of mercuric oxide is obtained. When it is heated to 90° in a vacuum, the product does not melt but carbon dioxide is evolved and the compound described immediately below is formed.

Mercury-*bis*-aceto-dimethyl-methane, [CH₃CO.C(CH₃)₂—]₂Hg.—When mercuric $\alpha,\dot{\alpha}$-dimethyl-aceto-acetate was heated in a vacuum at 90° it lost two molecular equivalents of carbon dioxide as indicated by an equivalent loss in weight. The solid was then extracted with acetone at room temperature and the acetone evaporated in a vacuum over sulfuric acid. A white solid remained which melted at 120° with decomposition. The yield was almost quantitative.

For analysis the compound was dried as rapidly as possible in a vacuum over phosphorus pentoxide.

Analysis. Subs., 0.3355: HgS, 0.2094. Calc. for $C_{10}H_{18}O_2Hg$: Hg, 54.11. Found: 53.83.

The compound is soluble in acetone and alcohol, and very slightly soluble in ether. It may be crystallized from toluene or xylene. No mercuric oxide formed upon the addition of sodium hydroxide, but upon the addition of ammonium sulfide an immediate precipitate of mercuric sulfide was obtained. The compound is unstable and rapidly decomposes with the separation of metallic mercury. When the compound (5 g.) was distilled in a vacuum at 90°, 1.3 g. of an oil was obtained which gave only a faint test for mercury and had an odor resembling that of camphor.

When mercury-*bis*-aceto-dimethyl-methane is treated with mercuric chloride the product described below is formed.

Aceto-dimethyl-methyl-mercuric Chloride, CH₃CO.C(CH₃)₂—HgCl.—A solution of 1.4 g. of mercuric chloride dissolved in 30 cc. of 95% alcohol was added to 1.8 g. of mercury-*bis*-aceto-dimethyl-methane in 15 cc. of alcohol. The mixture was refluxed for five minutes. As it cooled, beautiful white crystals with a metallic luster separated; m. p., 124.5°; yield, 1.1 g.

Analyses. Subs., 0.3127, 0.2934: HgS, 0.2229, 0.2116. Calc. for C_5H_9OClHg: Hg, 62.49. Found: 61.48, 62.20.

The compound is soluble in hot alcohol. When treated with sodium hydroxide it does not give a precipitate of mercuric oxide, but ammonium sulfide gives an immediate precipitate of mercuric sulfide.

Mercuric Trimethylacetate, [(CH₃)₃C.CO₂]₂Hg.—Trimethylacetic acid was dissolved in sodium hydroxide and the calculated amount of mercuric nitrate was added. A yellow product separated which was purified by crystallization from hot chloroform. Long, beautiful white needles were thus obtained which melted at 235°. The yield was good.

Analysis. Subs., 0.2855: HgS, 0.1629. Calc. for $C_{10}H_{18}O_4Hg$: HgS, 49.81. Found: 49.21.

The compound is soluble in hot chloroform and pyridine, but is very slightly soluble in carbon tetrachloride. When it was boiled in nitrobenzene, the color of the solution gradually became darker and metallic mercury separated. When it was heated to 240° in a vacuum, there was no evolution of carbon dioxide.

The Action of Mercuric Oxide on Trichloro-acetic Acid

1. Freshly distilled trichloro-acetic acid was dissolved in water and treated with an excess of yellow mercuric oxide and the solution filtered. When the filtrate was allowed to stand at room temperature (or concentrated in a vacuum) a mercurous salt was formed, as proved by the fact that it gave a precipitate of metallic mercury when treated with sodium hydroxide or pyridine. This mercurous salt is mercurous chloride, as is shown by the following analysis.

Analysis. Subs., 0.6908: HgS, 0.6647. Calc. for HgCl: Hg, 84.96. Found: 82.99.

When the filtrate from trichloro-acetic acid and mercuric oxide was heated to 60–65°, mercurous chloride precipitated and the acidity of the solution increased and reached a constant value after 30 minutes; at the end of that time all of the mercuric salt originally present had been converted into mercurous chloride.

2. A chloroform solution of freshly distilled trichloro-acetic acid was treated with yellow mercuric oxide containing a little water and the insoluble portion collected on a filter. The filtrate upon evaporation gave a white solid which was identified as mercuric chloride. Mercurous chloride was identified as part of the insoluble portion.

Summary and Conclusions

1. The behavior of mercury salts of various aliphatic carboxylic acids which do not lose carbon dioxide when heated has been studied. In cases where there is a replaceable hydrogen on the α carbon atom, the mercury usually takes that position, giving an inner anhydride.

2. The abnormal behavior of the mercury salt of trichloro-acetic acid has been pointed out.

3. In the case of the mercury salts of phenylated acetic acids the velocity of mercuration in the benzene nucleus was found to be greater than that of the α carbon atom—so that in working with 15- or 20g. lots, no side chain substitution products could be isolated.

4. In the case of mercury salts of substituted aliphatic acids which split off carbon dioxide readily, the mercury usually takes the place previously occupied by the carboxyl groups, thus linking the two molecules. (See the behavior of benzoylacetic acid for the possibilities of side reactions.)

5. The substituted mercury acetone derivatives, the bridged as well as unbridged, do not react with sodium hydroxide, but give an immediate precipitate of mercuric sulfide when treated with ammonium sulfide. Their behavior is similar to that of mercuric cyanide.

6. It is pointed out that the evidence is more in favor of a nitrile structure for mercuric cyanide than an isocyanide structure.

7. The linking of carbon to carbon through the intermediate mercuri-*bis* compounds is discussed, and the formation of dihydrophthalide from mercuric-phthalide-carboxylate is considered in the light that it is merely a case of intramolecular oxidation-reduction in which the mercury acts as the oxidizing agent.

8. The oxidation of a γ lactone to a ketonic acid by the use of mercuric oxide in alkaline solution has been observed.

9. The preparation of the following new compounds is described: mercury-*bis*-benzoylmethane; anhydro-α-hydroxymercuri-benzoyl-acetic acid; mercuric phthalide-carboxylate; mercurous benzoylformate; mercuric benzoylformate; mercuric α,α-diethyl-aceto-acetate; mercury-*bis*-acetodiethylmethane; aceto-diethyl-methyl-mercuric chloride; mercuric α,α-

dimethyl-aceto-acetate;   mercury-*bis*-aceto-dimethylmethane;   aceto-di-
methyl-methyl-mercuric chloride; mercuric trimethylacetate.

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NEW METHODS OF SPLITTING PYRIMIDINES. II. THE DECOMPOSITION OF PYRIMIDINES BY MEANS OF FERROUS SALTS

BY MIMOSA HORTENSE PFALTZ[1] AND OSKAR BAUDISCH

The reactions which we have used in splitting pyrimidines take place under conditions resembling as closely as possible natural conditions in the metabolism of plants and animals.   Two methods have been studied inten-sively, namely, the system, ferrous sulfate plus sodium bicarbonate plus air, and the system, sodium pentacyano-aquo-ferroate,[2] $[Fe^{II}(CN)_5OH_2]Na_3$, plus oxygen or air.   In both cases the reactions were carried out at room temperature (primary process), while the complete hydrolysis of the in-termediate products (secondary process) was brought about at blood-temperature or at the temperature of the water-bath.

These methods, which were introduced by Baudisch,[3] will be applied to other types of compounds.   The use of the system, ferrous sulfate plus sodium bicarbonate plus air, in a very sensitive test for thymine has al-ready been described.[4]

Ferrous salts, which have been used previously only as reducing agents, under suitable conditions exert a strong hydrolyzing and oxidizing action on certain types of compounds.   The reactions in the cases which have already been studied are quite similar to the hydrolytic changes brought about by life processes or by light energy.   Under mild conditions it is possible to cause a partial hydrolysis of the stable pyrimidine ring with the formation of substances which are completely hydrolyzed by sodium bi-carbonate at temperatures between 37° and 80°.

The Action of Ferrous Sulfate Plus Sodium Bicarbonate Plus Air on Pyrimidines

When ferrous sulfate is added to an aqueous solution of uracil containing an excess of sodium bicarbonate, a green ferrous carbonate peroxide is precipitated.   When the reaction mixture is shaken with air, the ferrous compound is oxidized gradually to ferric hydroxide, while the pyrimidine

¹ This paper is constructed from a dissertation presented by Mimosa Hortense Pfaltz to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.   (O. B.)

² Hofmann, *Ann.*, **312**, 1 (1900).

³ Baudisch, *Ber.*, **54**, 406 (1921).

⁴ Johnson and Baudisch, THIS JOURNAL, **43**, 2670 (1921); *Ber.*, **55**, 18 (1922).