[Contribution from the Chemical Department, Birkbeck College, University of London]

UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS.

III. THE CONSTITUTION OF SOME MERCURY DERIVATIVES

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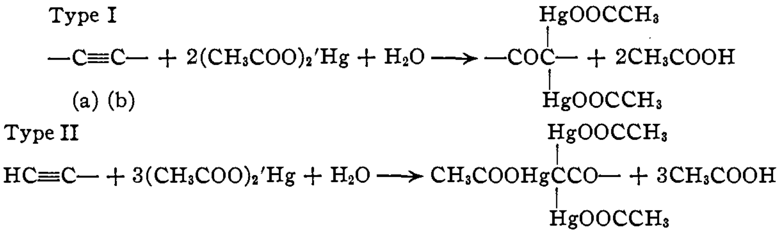
Earlier communications published from these Laboratories[1] described the isolation of mercury derivatives formed by the action of mercuric acetate upon various acetylenic acids and esters in acetic acid solution. The acetylenic compounds employed were of two types: I, $CH_3(CH_2)'_mC\equiv C(CH_2)'_nCOOR$, where R is alkyl or hydrogen and where the values of m and n were

$m = 0, n = 7$ in 9–10 undecinoic acid
$m = 7, n = 7$ in stearolic acid
$m = 7, n = 11$ in behenolic acid

and II, $HC\equiv C(CH_2)'_nCOOR$, where $n = 8$ in 10,11-undecinoic acid.

The mode of formation and the composition of the mercury compounds as well as the nature of the products derived from them by decomposition with hydrochloric acid were in accord with the following interpretation of the action of mercuric acetate upon the acetylenic linkage.



Type I

$$\underset{\text{(a) (b)}}{-C\equiv C-} + 2(CH_3COO)_2'Hg + H_2O \longrightarrow -CO\overset{HgOOCCH_3}{\underset{HgOOCCH_3}{C}}- + 2CH_3COOH$$

Type II

$$HC\equiv C- + 3(CH_3COO)_2'Hg + H_2O \longrightarrow CH_3COOHg\overset{HgOOCCH_3}{\underset{HgOOCCH_3}{C}}CO- + 3CH_3COOH$$

In Type II the acetylenic hydrogen atom is substituted while the usual addition takes place at the triple bond.

During decomposition of the mercury compounds with hydrochloric acid, each acetoxymercuri group was assumed to be replaced by hydrogen with formation of a ketonic compound free from mercury. In the case of 9,10-undecinoic acid (Type I) and its ethyl ester, two isomeric ketonic derivatives were isolated, thus establishing an alternative reaction in which the acetoxymercuri groups were added to the carbon atom (a) and the oxygen atom to (b) in the equation given above.

The present communication describes further investigations upon the constitution of the mercury compounds.

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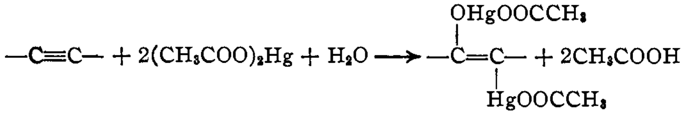
[1] (a) Myddleton and Barrett, This Journal, 49, 2258 (1927); (b) Myddleton, Berchem and Barrett, *ibid.*, 49, 2264 (1927).

Mercuration of Acetylenic Compounds of Type I

In the mercury derivatives from esters of Type I there appeared to be a difference in reactivity of the two mercury atoms toward caustic alkalies and hydrogen sulfide but this could not be established by the isolation of pure products from these reactions. An alternative constitution was therefore tentatively assigned to the mercury derivatives to account for a difference in reactivity of the mercury groups and evidence of this constitution was sought and discovered in other directions. The alternative constitution was derived from the following interpretation of the action of mercuric acetate upon the acetylenic bond.



$$-C\equiv C- + 2(CH_3COO)_2Hg + H_2O \longrightarrow -\overset{OHgOOCCH_3}{\overset{|}{C}}=\underset{\underset{HgOOCCH_3}{|}}{C}- + 2CH_3COOH$$

The resulting mercury derivative is unsaturated and the first action of hydrochloric acid in causing the replacement of acetoxymercuri groups by hydrogen would be to yield an enolic product containing the group —C(OH)=CH—. Rapid transformation to the ketonic form might be anticipated under the influence of the mineral acid. Indeed no signs of an enolic form were discovered during the decomposition of the mercury derivatives already described. The most favorable conditions for observing the intermediate formation of an enolic derivative were sought by choosing an acetylenic ester with a shorter carbon chain and with the acetylenic bond near to the ester group. Methyl octine-1-carboxylate $CH_3(CH_2)_5C\equiv C\text{-}COOMe$ when acted upon with mercuric acetate in the manner previously described gave a mercury derivative analyzing in accordance with the composition $CH_3(CH_2)_5C(OHgOOCCH_3)=C(HgOOCCH_3)COOMe$.

The decomposition of this compound with concentrated hydrochloric acid gave an ester which, as soon as liberated, gave a deep violet coloration with ferric chloride in alcoholic solution, indicating the presence of an enolic form. Analysis of the ester by the method of Kurt Meyer[2] indicated the presence of 13.5% of the enolic form.

The mercury derivative was very slightly soluble in hot alcohol and when the cooled solution was mixed with two drops of a neutral aqueous solution of ferric chloride it gave in about one minute a faint reddish-violet coloration indicating an enolic structure. In this reaction there is a direct replacement of an acetoxymercuri group by iron to give the colored ferric salt of an enolic compound. To facilitate this reaction a mercury derivative more soluble in alcohol was sought by introducing a phenyl group into the acetylene. Ethyl phenylpropiolate $C_6H_5C\equiv CCOOEt$ gave a mercury derivative melting with decomposition at 192° and analyzing in agreement with the composition $C_6H_5C(OHgOOCCH_3)=C(HgOOCCH_3)COOEt$. It was

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[2] K. Meyer, *Ber.*, **44**, 2718 (1911).

readily soluble in hot alcohol and moderately soluble in cold. The cold alcoholic solution gave in a few seconds a deep reddish-violet coloration with two drops of aqueous ferric chloride. The ester liberated from the mercury derivative by the action of hydrochloric acid gave a similar coloration and was shown by Kurt Meyer's method to contain 20% of the enolic form an hour after isolation.

The Action of Halogens on the Mercury Derivatives.—As a means of further distinguishing between the two structures $—COC(HgOOCCH_3)_2—$ and $—C(OHgOOCCH_3){=}C(HgOOCCH_3)—$ the action of halogens was investigated. In the first case chlorine would be expected to produce a dichloro ketone by causing the replacement of each acetoxymercuri group by a chlorine atom; in the second case a monochloro ketone would result through the intermediate formation of $—C(OCl){=}CCl—$ which after hydrolysis in the aqueous acid used in the isolation would lead to $—C(OH){=}CCl—$ and finally the ketonic form $—COCHCl—$.

The mercury derivatives prepared from stearolic acid and behenolic acid were made to react with chlorine and with bromine in refined petroleum ether, in chloroform and in glacial acetic acid. Mono-halogen ketonic acids were formed quantitatively. The mercury derivatives from methyl octine-1-carboxylate and from ethyl phenylpropiolate gave dibromo ketonic esters when decomposed with bromine. As in the last two instances the mercury derivatives developed a violet coloration in contact with alcoholic ferric chloride, it cannot be assumed that the formation of a dibromo ketonic ester is evidence that two mercury atoms are attached to one carbon atom. To reconcile the two reactions it is necessary to assume that during treatment with bromine the following changes take place.

$$—C(OHgOOCCH_3){=}C(HgOOCCH_3)— \xrightarrow{+Br_2} —C(OBr){=}CBr— \xrightarrow{+Br_2}$$
$$—C(OBr)BrCBr_2— \xrightarrow{-Br_2} —COCBr_2—$$

The dibromo ketonic ester prepared in this way from ethyl phenylpropiolate gives the theoretical yield of benzoic acid after hydrolysis with a seminormal alcoholic solution of potassium hydroxide, thus proving that when mercuric acetate acts upon ethyl phenylpropiolate under the stated conditions the mercury groups enter the side chain exclusively. Phenylpropiolic acid is also mercurated exclusively in the side chain and the derivative formed yields with bromine benzoyl dibromo-acetic acid, which is recovered as ω-dibromo-acetophenone after loss of carbon dioxide.

Mercuration of Acetylenic Compounds of Type II

The following acetylenic compounds containing the group $HC{\equiv}C—$ were converted into mercury derivatives by the action of mercuric acetate in acetic acid solution.

$HC\equiv C(CH_2)_2COOH$	10.11-undecinoic acid
$CH_3(CH_2)_4C\equiv CH$	Heptine-1
$CH_3(CH_2)_5C\equiv CH$	Octine-1
$C_6H_5C\equiv CH$	Phenylacetylene

The analysis of the products indicates the presence of three acetoxymercuri groups, and methyl ketones are formed by decomposition with hydrochloric acid.

The mercury derivative from phenylacetylene cannot be decomposed with bromine at a temperature sufficiently low to yield a simple product, but the other derivatives examined gave tribromo ketones with bromine in the form of non-crystallizable oils. Since they give bromoform when they are decomposed with caustic alkalies, it is necessary to assume that during mercuration the acetylenic hydrogen is replaced by an acetoxymercuri group.

It is possible to formulate the behavior of these mercury derivatives on the assumption that they possess a constitution similar to those derived from acetylenic compounds of Type I, namely, $—C(OHgOOCCH_3)=C(HgOOCCH_3)_2$, although no evidence has been obtained of unsaturation or of the formation of enolic compounds during decomposition with acids. They do not for example develop any coloration with ferric chloride in alcohol, but this of course may be due to their insolubility.

The decompositions of these derivatives with hydrochloric acid and with bromine may be accounted for as follows

$$—C(OHgOOCCH_3)=C(HgOOCCH_3)_2 \xrightarrow{HCl} —C(OH)=CH_2 \longrightarrow —COCH_3$$

$$—C(OHgOOCCH_3)=C(HgOOCCH_3)_2 \xrightarrow{Br_2} —C(OBr)=CBr_2 \xrightarrow{Br_2}$$

$$—C(OBr)BrCBr_3 \xrightarrow{-Br_2} —COCBr_3$$

Experimental Part

The Action of Mercuric Acetate on Acetylenic Compounds.—The preparation of mercury derivatives of acetylenic compounds by the action of mercuric acetate was carried out under the conditions described in a previous communication.[1b]

When the acetylenic compound contains the group $HC\equiv C—$, it was found desirable to moderate the reaction by dissolving the mercuric oxide in hot acetic acid and then cooling to crystallize some mercuric acetate before adding the acetylene slowly. Under other conditions the heat evolved was sufficient to cause the formation of much mercurous acetate and even free mercury by reduction. Further experience in the preparation of these mercury derivatives has shown that they sometimes separate as viscous oils when the acetic acid solution is diluted with water. Such oily products may be converted into a microcrystalline powder by triturating with alcohol and then with ether.

Analysis of the Mercury Derivatives.—Mercury was determined by the destructive hydrogenation method of H. ter Meulen.[3] Other analyses were carried out as described in the earlier communication.[1a] The following results were obtained.

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[3] H. ter Meulen, *Rec. trav. chim.*, **45**, 368 (1926).

	Analysis of Hg derivative		
Acetylenic compd.	Hg, %	CH_3COO, %	Yield of ketonic compd. after decomp. with HCl, %
Methyloctine carboxylate	56.1	16.75	24.0
Calcd. for $C_{14}H_{22}O_7Hg_2$	57.0	16.78	26.45
Ethyl phenylpropiolate	56.46		26.6
Calcd. for $C_{15}H_{16}O_7Hg_2$	56.56		27.07
Heptine-1	67.8	20.1	13.0
Calcd. for $C_{13}H_{20}H_7Hg_3$	67.6	19.93	12.84
Octine-1	66.5	19.5	14.0
Calcd. for $C_{14}H_{22}O_7Hg_3$	66.6	19.6	14.13
Phenylacetylene	66.9	19.1	
Calcd. for $C_{14}H_{14}O_7Hg_3$	67.17	19.8	
Phenylpropiolic acid	64.5	15.0	
Calcd. for $C_{13}H_{11}O_7Hg_{2.5}$	64.24	15.12	

Decomposition of the Mercury Derivatives with Hydrochloric Acid.—The mercury derivative of methyl octine carboxylate was suspended in water and decomposed by adding concd. hydrochloric acid. The oily ester liberated was extracted with light petroleum, the extract washed, dried and evaporated. From 50 g. of material was obtained 12 g. of methyl β-keto-nonoate, b. p. 137.5° (28 mm.). By dissolving in alcohol and adding cupric acetate, the green copper salt was obtained, melting after recrystallization from benzene at 99°. The ester gave a deep violet coloration with ferric chloride in alcohol and a determination by the method of Kurt Meyer[2] showed the presence of 13.5% of the enolic form one hour after isolation.

A quantity of the ester was allowed to stand in contact with concd. hydrochloric acid for two days at room temperature. A mass of crystalline lamellae formed. After washing with water and recrystallization from light petroleum, these crystals of β-keto-nonoic acid melted at 70.5° and decomposed just above this temperature, losing carbon dioxide and forming methyl hexyl ketone, b. p. 171° (760 mm.); semicarbazone, m. p. 123°. The semicarbazone mixed with the semicarbazone of authentic methyl hexyl ketone melted at 123°. The mercury derivative of heptine-1 gave with hydrochloric acid almost theoretical yields of methyl *n*-amyl ketone, b. p. 150° (760 mm.); semicarbazone, m. p. 123°, unchanged by admixture with semicarbazone of authentic methyl *n*-amyl ketone. It will be noted that this semicarbazone melts at the same temperature as that of methyl *n*-hexyl ketone.

The mercury derivative of octine gave methyl *n*-hexyl ketone, identified by the characteristics described above.

The mercury derivatives from phenylacetylene and phenylpropiolic acid gave with hydrochloric acid acetophenone, b. p. 200° (760 mm.). The semicarbazone melted when slowly heated between 188–190°, and when heated rapidly at 201°. The semicarbazone of authentic acetophenone behaved similarly. The oxime melted at 59°.

Decomposition of the Mercury Derivatives with Halogens.—The reaction between the mercury derivatives and halogens was found to proceed best in chloroform. In carbon tetrachloride the reaction was slower and in acetic acid was complicated by contamination of the halogen derivative with halogen-free ketonic compounds. By varying the water content of the acetic acid this complication was found to be due to the hydrolysis of the halogen followed by the action of the halogen hydracid thus formed on the mercury compound. Refined light petroleum was also an effective medium.

The mercury derivatives were suspended in the solvent and the halogen added slowly. In most cases it was necessary to warm the mixture in a water-bath at 40° during addition of the halogen. When excess was present the mixture was allowed to stand for several hours. The precipitate was filtered off and the solution washed repeatedly with water acidified with hydrochloric acid, and finally with distilled water. It was then dried over anhydrous sodium sulfate and evaporated. In some cases it was found possible to distil the halogen derivative under diminished pressure without decomposition and in these cases the boiling point is recorded in the table below.

Mercury derivative from	Halogen derivative analyzed	B. p., °C.	Halogen, %	
			Calcd.	Found
Stearolic acid	Chloroketostearic acid	Dec.	Cl 10.66	10.68
	Bromoketostearic acid	Dec.	Br 21.20	21.07
Behenolic acid	Chloroketobehenic acid	Dec.	Cl 9.12	9.02
	Bromoketobehenic acid	Dec.	Br 18.46	18.36
Methyl octine carboxylate	Methyl dibromoketononoate	169 (14 mm.)	Br 46.49	46.31
Ethyl phenylpropiolate	Ethyl benzoyldibromoacetate	194 (15 mm.)	Br 45.72	45.92
Heptine-1	Tribromomethyl *n*-amyl ketone	120 (0.5 mm.)	Br 68.36	68.4
Octine-1	Tribromomethyl *n*-hexyl ketone	137 (0.5 mm.)	Br 65.74	65.8
Phenylacetylene	Very slight action at low temperatures			
Phenylpropiolic acid	ω-Tribromo-acetophenone	174 (14 mm.)	Br 67.22	67.0
10,11-Undecinoic acid	Trichloroketo-undecoic acid	Dec.	Cl 35.06	34.8

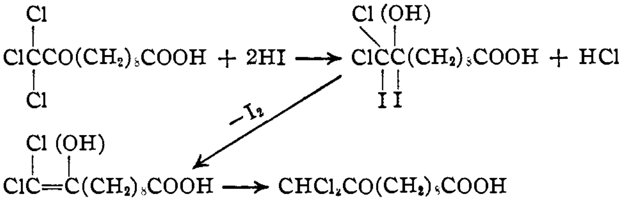
Characteristics of the Halogen Derivatives.—9-Chloro-10-ketostearic acid and the corresponding bromo acid were obtained as viscous oils which were converted into non-crystalline resinous masses by cooling with a mixture of solid carbon dioxide and ether. The sodium, potassium and lithium salts were soft and soapy. The calcium, barium and lead salts were cheese-like solids. The ethyl and methyl esters were oils which could not be distilled under a pressure of 2 mm. Both the chloro and the bromo acids were reduced to 10-ketostearic acid melting at 76° by refluxing on a water-bath with aqueous alcoholic hydriodic acid under the following conditions: 2 g. of the halogen acid was dissolved in 50 cc. of absolute alcohol and to the solution were added 5 g. of potassium iodide in 50 cc. of water and 5 cc. of concd. hydrochloric acid. The mixture was heated on a boiling water-bath under reflux for fifteen minutes and a titration made with *N*/10 thiosulfate until only a faint yellow coloration remained. The flask was again heated, thiosulfate being added at intervals of five minutes to remove free iodine. The heating was continued until only a faint coloration appeared during ten minutes. Water was added and the precipitate filtered off and recrystallized from light petroleum. The ketonic acid thus obtained was identified after establishing absence of halogen by its melting point and its unchanged melting point when mixed with the ketonic acid derived from the corresponding mercury compound by decomposition with hydrochloric acid.

13-Chloro-14-ketobehenic acid and the corresponding bromo acid were also obtained as viscous oils showing the same general characteristics as the stearic derivatives. Reduction with hydriodic acid gave 14-ketobehenic acid melting at 83–84°.

The mercury derivative of 10,11-undecinoic acid gave with chlorine the trichloro ketonic acid $Cl_3CCO(CH_2)_8COOH$ in quantitative yield. The acid and its methyl and ethyl esters were viscous oils which could not be distilled under a pressure of 2 mm.

They showed no tendency to hydrate. The acid decomposed when warmed with a 20% solution of caustic soda to yield chloroform and sodium sebacate. After one hour's reduction with aqueous alcoholic hydriodic acid under the conditions already described the acid gave an iodine-free oil containing 30.8% of chlorine. After twenty-two hours, during which liberated iodine was removed by addition of thiosulfate at intervals, an oil containing 24.2% of chlorine was obtained. Iodine was absent. Dichloro-keto-undecoic acid contains 26.26% of chlorine.

The removal of chlorine during this reaction can be accounted for by the simultaneous replacement of chlorine by iodine and the addition of hydrogen iodide to the carbonyl group.



$$CCl_3CO(CH_2)_8COOH + 2HI \longrightarrow ClC(Cl)(I)C(OH)(I)(CH_2)_8COOH + HCl$$

$$\xrightarrow{-I_2} ClC(Cl){=}C(OH)(CH_2)_8COOH \longrightarrow CHCl_2CO(CH_2)_8COOH$$

The analyses recorded in this communication were effected by the methods of H. ter Meulen.

Summary

1. Mercury derivatives prepared by the action of mercuric acetate upon acetylenic compounds have been utilized for the synthesis of halogenated ketones, ketonic acids and esters.

2. Where the acetylenic compounds contain no labile acetylenic hydrogen atom, the mercury derivatives have been shown to be unsaturated and to contain the grouping $—C(OHgOOCCH_3){=}C(HgOOCCH_3)—$.

3. Where the acetylenic compound contains labile acetylenic hydrogen, substitution of this hydrogen atom takes place and, while no evidence of unsaturation has been obtained, the properties of the mercury compounds can be accounted for by assuming the presence of the unsaturated grouping $—C(OHgOOCCH_3){=}C(HgOOCCH_3)_2$.

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