THE ADDITION COMPOUNDS OF OLEFINS WITH MERCURIC SALTS

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I. INTRODUCTION

The first addition compound of a metallic salt with an olefin appears to have been isolated by Zeise about 1830 (71, 72, 73). He isolated a hydrated salt which in the anhydrous condition analyzed as $KCl \cdot PtCl_2 \cdot C_2H_4$. Many similar complexes, particularly of platinum, are now known but less stable complexes of palladium, copper, and silver have been discovered and are regarded as true coördination complexes of the olefin with the metallic salt. The olefin molecule

occupies one place in the coördination sphere, thus behaving as if it had a lone pair of electrons and, except that the combination of the metal is much looser than in the ammines, these olefin complexes differ in no marked manner from better known, characteristic coördination compounds.

The properties of these coördination compounds were extensively reviewed by R. N. Keller (32) in 1941, and advances since then have been summarized by the author (15). Of metallic salts, mercuric salts form the greatest variety and most stable addition compounds with unsaturated substances, but just as the organic chemistry of mercury is unique in the chemistry of organometallic compounds, so olefin–mercuric salt addition compounds are unique amongst olefin–metallic salt complexes. It is for this reason that they have not been reviewed together with the typical complexes of the other metals, for although there can be no doubt that the mercuric salt has added across the double bond of the olefin, in many ways they behave as coördination, as well as addition, compounds of the olefins, and have on this account recently been styled "quasi-complex" compounds by Nesmeyanov (38).

The discovery and characterization of these compounds can be attributed to Hofmann and Sand, whose work in the period 1900–1908 established the salient points in the reaction of olefins with mercuric salts in aqueous solution. It is easy to understand why the addition compounds of olefins with mercuric salts, in spite of their variety, were not recognized earlier. In general, if organic compounds react with mercuric salts, substitution, oxidation, or addition may take place; with olefins it seems that all these reactions can occur, so that the products isolated by the direct action of the olefin on an aqueous solution of a mercuric salt are often rather intractable, somewhat indefinite precipitates. Although Denigès (17, 18, 19) tackled this problem earlier, it was not until 1900, when Hofmann and Sand (26, 27) established the conditions for the formation and isolation of the simple addition products of olefins with basic mercuric salts, and characterized them, that some sort of order was established in this field.

Hofmann and Sand considered that addition had occurred across the double bond of the olefin and recognized addition compounds of two series (typified by formulas I and II) derived from ethylene, as well as a number of substitution products and polymerized substances.

$$HOCH_2CH_2HgCl \qquad O(CH_2CH_2HgCl)_2 \qquad C_2H_4\cdot Hg(OH)Cl \qquad (C_2H_4)_2\cdot HgO\cdot HgCl_2$$
$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III} \qquad\qquad\qquad \text{IV}$$
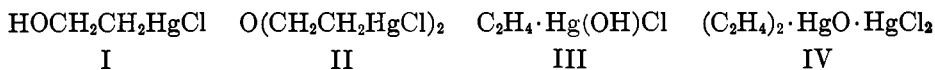
The reactions of these compounds present an enigma; by reaction with substances such as potassium cyanide, which form stable mercuric complexes, they evolve ethylene as if they were simple coördination compounds (III and IV, respectively), whereas towards other reagents, such as benzoyl chloride and iodine, they behave as the β-substituted chloromercury alkyls (I and II). Sand (47) finally concluded that there was a tautomeric equilibrium between the coördination complexes III and IV and the addition products I and II, respectively.

These mercurated olefins are soluble without decomposition in caustic potash. Thus Biilmann (8, 10), who had earlier prepared some mercury salts of unsaturated acids, was surprised to find that they were soluble in caustic alkalis but did not realize the significance of this fact until after Hofmann and Sand's first paper.

After Hofmann and Sand's work the subject entered a phase of rapid expansion. Many unsaturated compounds were added to mercuric salts, amongst which unsaturated alcohols and esters were the most fruitful subjects of research. In 1914 Schoeller, Schrauth, and Essers (54) showed that in general the solvent played an essential part in the addition and that mercuric salts in alcoholic solution reacted with olefins to produce the corresponding alkyl ethers of the compounds of series I. More recently (1929 and 1945) it has been found that in glacial acetic acid, mercuric acetate yields the acetyl derivatives (30),

$$\text{CH}_3\text{COOC}\!-\!\text{CHgOCOCH}_3$$
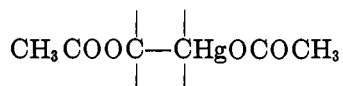
and in piperidine solution mercuric chloride gives, with ethylene, N-(β-(chloromercuri)ethyl)piperidine (23). Generally, all these compounds show the same dual character in their reactions as the simple ethylene derivatives of Hofmann and Sand.

About 1920 Manchot and Klüg (34, 35) started a controversy regarding the nature of these compounds, as to whether they were in fact coördination complexes or not. This theme was taken up by American workers (1, 36, 37), who concluded that they were saturated addition compounds of types I and II. This conclusion, which is now accepted, was reached by the study of only one series of uniquely stable and very similar compounds, and further work in 1936 by Nesmeyanov's school (24, 39) produced two new reactions which served only to emphasize the enigma.

In 1907 Sand (48) made the first kinetic study of the formation of mercuric complexes, showing that the reaction is not simple, a result confirmed by later American workers (33, 66). The addition appears to be reversible; yet attempts to approach the equilibrium by decomposition of the methoxymercurials in methyl alcohol by acetic acid indicate very little, if any, reversal (14, 43); also, stable optical isomers having as asymmetric centers the two carbon atoms originally joined by the double bond have been isolated (25, 43, 53). The solution may lie in the discovery of Lucas, Hepner, and Winstein (33) that there may be other less stable, reversibly formed coördination complexes present as intermediates of long life in the formation of the addition products isolated. The reaction seems more complex than is represented by simple addition across the double bond or simple formation of a molecular coördination complex, but appears to involve both types of reaction.

The structure of the coördination complex also presents a problem because ethylene does not have a lone pair of electrons in the same sense as ammonia; however, an addition compound of the mercuric ion with an olefin can be written

in a number of canonical forms (V to VIII) and resonance may account for the stability of the complex (33).
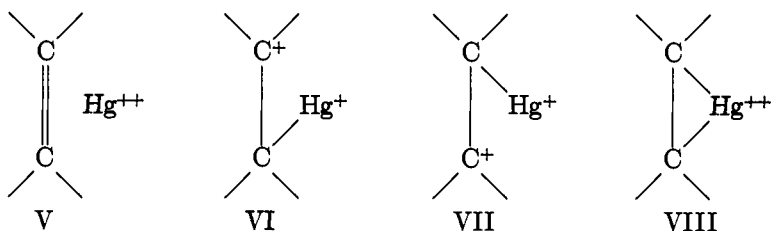

Thus we reach the present stage of the subject. There appear to be four series of simple mercuric complexes with olefins, two of which are true addition compounds (I and II) and are the quasi-complex compounds isolated and examined by all workers other than Lucas, Hepner, and Winstein, who found evidence for the two coördination complexes of types IX and X. If we assume that ethylene forms all these types, their formulas as the ionized forms would be:

$$[HOCH_2CH_2Hg]^+X^-$$
$$I$$
$$[O(CH_2CH_2Hg)_2]^{++}X_2^-$$
$$II$$
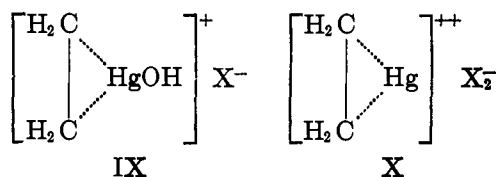
A very large number of compounds of series I are known, and they are obviously very useful intermediates in organic syntheses. No proved mechanism for their formation has yet been put forward, but we are getting close to a solution of this problem, as will be shown at the end of the following discussion.

II. PREPARATION

In the following discussion the addition compounds will be represented and named as true saturated addition compounds. They are all prepared by the direct action of the olefin on a solution of a mercuric salt, but the actual product obtained and its purity are very sensitive to the experimental conditions.

Normal mercuric salts of mineral acids do not add to olefins, nor do the mixed salts (30), e.g., IHgOCOCH₃. On the other hand, basic salts, alkoxy salts, and the normal salts of organic acids react more or less readily. Thus, ethylene is rapidly absorbed by a solution of mercuric acetate in glacial acetic acid as follows:

$$Hg(OCOCH_3)_2 + C_2H_4 \rightarrow CH_3COOC_2H_4HgOCOCH_3$$
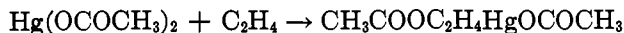
and the higher olefins behave in the same way (30).

In the preparation of complexes of the mercuric salts of the higher fatty acids with olefins it is sufficient to use the olefin, if it is liquid, as solvent for the mer-
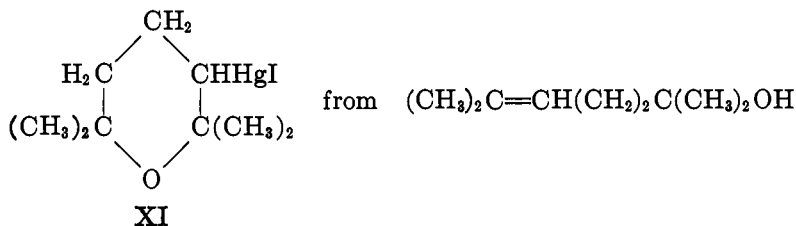
curic salt. The compounds of 1-hexadecene with mercuric palmitate and stearate have been prepared in this way (30), although attempts to combine mercuric acetate with liquid olefins alone or in dioxane as solvent were not very successful (66). However, it is usual to carry out the additions in aqueous or alcoholic solutions.

A. PREPARATION IN AQUEOUS SOLUTION

The reaction in aqueous solution is by no means simple. The actual product isolated, which may not even be an addition compound, depends on (1) the structure of the olefin, (2) the acidity of the solution, (3) the acid of the mercuric salt, (4) the temperature, and (5) the concentration of the solution.

The various products which may be isolated are as follows:

(a) The simple addition product (type I) of the olefin and a basic mercuric salt, $Hg(OH)X$ (X = acid radical); e.g., HOC_2H_4HgX from ethylene (26).

(b) The simple addition product (type II) of the olefin and the anhydride of the above basic salt, OHg_2X_2; e.g., $O(C_2H_4HgX)_2$ from ethylene (26).

(c) If the unsaturated substances contain a hydroxyl group then an internal ether (type XI) may be formed, e.g. (52):

$$\underset{\textbf{XI}}{\underset{O}{\overset{CH_2}{\underset{(CH_3)_2C \quad\quad C(CH_3)_2}{H_2C \quad\quad CHHgI}}}} \quad\quad \text{from} \quad (CH_3)_2C{=}CH(CH_2)_2C(CH_3)_2OH$$

(d) A substitution product of the olefin may be formed, e.g., $(CHCl{=}CCl)_2Hg$ from trans-dichloroethylene (22).

(e) The glycol corresponding to the olefin may be produced by reduction of the mercuric salt. This occurs (3, 4, 5, 6, 7) particularly with certain aromatic ethers containing the propenyl group $—CH{=}C(CH_3)—$ and has been suggested as a method of distinguishing and even of separating (2) isomeric substances which contain either the propenyl or the allyl grouping; e.g., with mercuric acetate safrole yields $CH_2O_2C_6H_3$-$CH_2CHOHCH_2HgOCOCH_3$ and isosafrole yields $CH_2O_2C_6H_3CHOHCH$-$OHCH_3$. Aldehydes and ketones may also be produced by the mercuric acetate oxidation.

(f) Addition compounds, which are most probably lattice compounds because they dissociate completely in solution (21, 63), are obtained from mercuric chloride and α,β-unsaturated ketones:

$$HgCl_2 + (CH_3)_2C{=}CHCOCH_3 \rightarrow (CH_3)_2C{=}CHCOCH_3 \cdot HgCl_2$$
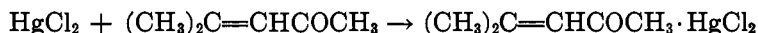
Mercuric acetate in methyl alcohol reacts with an unsaturated ketone to produce the normal simple addition product (36).

(g) Indefinite precipitates, polymerized and oxidized substances, are frequently the product, particularly from mercuric sulfate solutions or with most mercuric salts at elevated temperatures, and it is no wonder that the earliest investigations in this field did not make much progress.

(h) In addition it seems quite definite that the mercuric ion forms two true coördination complexes (IX and X) with olefins, and these may be intermediates in the formation of the above products (33).
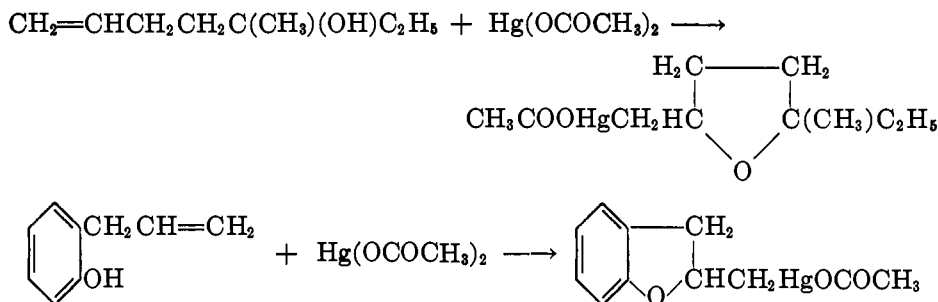
In describing a preparative method which is so sensitive to change in conditions and can yield so complex a range of products, only generalities can be discussed.

The usual test for completion of the reaction is when the solution of the reactants no longer gives a precipitate of mercuric oxide with caustic alkali, although this test does not appear to be entirely reliable (66).

1. Effect of the structure of the olefin

As would be expected, the structure of the olefin has a marked effect on the rate of reaction. In general, *trans*-olefins react more sluggishly than their *cis*-isomers (13, 14, 66), and this property has been used to determine the configuration of the two isomeric 2-butenes (61) and even for the determination of isomer composition of mixtures (14, 16, 20). Also, the presence of negative groups hinders and may even prevent the reaction. Thus fumaric, mesaconic, and cinnamic acids (11) do not form addition compounds in aqueous solution, whereas maleic, citraconic, and allocinnamic acids do. Heavily substituted ethylenes and conjugated dienes also react less readily than the simpler olefins; thus, tetramethylethylene (30) is unreactive, although unsymmetrical diphenylethylene (40) reacts slowly to yield the normal addition product. The difference in the rate of reaction of mercuric acetate with different olefins has been suggested as a method of analysis of the unsaturated substances from the cracking of oil. The determination of 2,4,4-trimethyl-1-pentene in the presence of 2,4,4-trimethyl-2-pentene can be accomplished in this way (58). Butadiene (40) forms 1,4-bis(acetomercuri)-2,3-dihydroxybutane with aqueous mercuric acetate, and isoprene (40) reacts similarly, yet tetramethylbutadiene, $(CH_3)_2C{=}CHC(CH_3){=}CHCH_3$, is unreactive (47). It is to be noted that 1,4-addition neither to conjugated dienes nor to α,β-unsaturated ketones (36) has been observed and that with unsymmetrical olefins the mercury atom invariably attaches itself to the carbon atom richer in hydrogen atoms. Addition in both senses probably occurs to the ethyl esters of oleic and elaidic esters, where the double bond is far removed from the substituent group (16). *trans*-Stilbene even in methyl alcohol solution could not be mercurated, except in the presence of a high concentration of added peroxide (13).

The reaction is most easy, the yields even in aqueous solution are quantitative, and the addition product is most stable if the olefin is substituted so that it can form an internal ether of type XI, especially if the final ring system is five-membered (1, 37, 52), e.g.:

$$CH_2{=}CHCH_2CH_2C(CH_3)(OH)C_2H_5 + Hg(OCOCH_3)_2 \longrightarrow$$

$$\begin{array}{ccc} & H_2C\text{------}CH_2 & \\ CH_3COOHgCH_2HC & & C(CH_3)C_2H_5 \\ & \diagdown O \diagup & \end{array}$$


## 2. Effect of the acidity of the solution

This is the most important factor in these preparations because all the olefinic complexes readily regenerate the olefin quantitatively in the presence of halides and mineral acid; even 5 per cent hydrochloric acid is sufficient to decompose most compounds. The ether type (II) is more stable than the simpler type (I), but even the exceptionally stable benzofuran ring types are decomposed in a few minutes by concentrated hydrochloric acid to regenerate the olefin (1).

It was Hofmann and Sand's realization of the part played by excess acid which led to their success in this field of research. Although acid prevents the addition of olefins to mercuric salts, addition does not occur in alkaline solutions such as Nessler's reagent or a suspension of mercuric oxide in caustic soda (26).

The reaction is best effected by carefully neutralizing the solution of mercuric salt until a precipitate of the basic salt starts to appear. This is then dissolved by careful addition of the olefinic substance and followed by further treatment with caustic alkali until the basic salt appears again. The alternate addition of olefin and caustic alkali is continued until alkali causes no further precipitation of basic salt (26). The reaction is carried out at or under room temperature and neutralization of the acid in this manner favors the production of the simple complexes of type I.

$$C_2H_4 + Hg(NO_3)_2 + NaOH \rightarrow HOC_2H_4HgNO_3 + NaNO_3$$
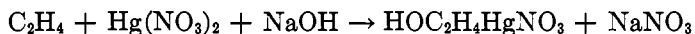
The product, generally quite soluble in caustic alkali, is best isolated by conversion to the less soluble haloid salt by addition of the theoretical quantity of alkali halide to the alkaline solution, after which passage of carbon dioxide causes the halide to precipitate.

$$HOC_2H_4HgNO_3 + KI \rightarrow HOC_2H_4HgI + KNO_3$$
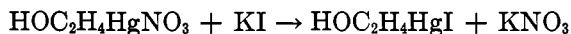
This was the general method evolved by Hofmann and Sand.

The formation of the ether type of complex (II) is favored by more acid conditions, and if an internal ether is formed considerable acid can be tolerated (1). The proportion of ether salt, which is a by-product from the above preparation, is also increased by allowing the alkaline solution to age for some days before conversion into the halide (26); also, the simple alcohol type of product is par-

tially converted into the ether salt by standing in mineral acid solution, in which it does not decompose to re-form the olefin in complete absence of halide ions (47).

3. Effect of the acid radical of the mercuric salt

The actual mercuric salt used for the preparation has a considerable influence on the rate and course of the reaction. Mercuric nitrate and acetate are the best salts for general use, because by neutralization of the acid as described above, both react rapidly and yield simple addition products. The neutralization of acid from the mercuric acetate is not so necessary as from the nitrate, because acetic acid is not sufficiently strong to make the reverse reaction in the preparation significant, yet neutralization of the acid does speed the reaction.

Mercuric sulfate in a solution as concentrated and as neutral as possible also reacts readily, but generally the product is a precipitate of complex and unknown structure (18, 26, 27, 28). Hofmann and Sand (27) describe the precipitate given by 1-butene as an intensely yellow powder insoluble in 10 per cent sulfuric acid; after conversion to the chloride it analyzed as $C_4H_6Hg_4Cl_4O_6 \cdot H_2O$ mixed with 7.4 per cent Hg_2Cl_2. This precipitate is not even partly soluble in alkali, so probably it is not related to the mercuric salt addition complexes in which we are interested.

Ethylene also gives a complex precipitate having the composition $C_6H_{10}Hg_4$-$(SO_4)_2O_4$, but this is soluble in 10 per cent caustic alkali (26) and from its alkaline solution, by treatment with alkali halide and carbon dioxide, the ether salt, bis(β-(halogenomercuri)ethyl) ether, $O(CH_2CH_2HgX)_2$, is obtained. In fact, this is the best way to prepare this salt (26, 44), which is much less soluble than the corresponding alcohol salt. In the case of propene, where this alternative route is not available because the complex sulfate precipitate is not of the right type, bis(α-methyl-β-(halogenomercuri)ethyl) ether (49), $[CH_3CH(CH_2HgX)]_2O$, can be obtained only as a by-product in the preparation of α-chloromercuri-β-hydroxypropane, e.g., $CH_3CHOHCH_2HgX$.

Mercuric chloride (26) reacts very slowly, and derivatives of both β-(chloromercuri)ethyl alcohol and bis(β-(chloromercuri)ethyl) ether are precipitated together after many hours' passage of ethylene.

Mercuric cyanide and thiocyanate do not add onto the double bonds of olefins (30).

4. Effect of temperature

Temperature affects the purity of the products; temperatures above room temperature tend to cause reduction of the mercuric salt and formation of undesirable by-products; e.g., see Biilmann (9) and also Hofmann and Sand (28) on the reaction of allyl alcohol with mercuric salt solutions.

5. Effect of concentration

The concentration of the solution does not have as marked an effect on the actual preparation as the other items above, except in so far as heat evolved in the reaction raises the temperature of a concentrated solution higher than that of a dilute solution (28).

B. PREPARATION IN NONAQUEOUS SOLUTION

The solvent influences the reaction in two ways: it can alter the rate of reaction and it also may take part in the reaction. Mercuric acetate is the salt usually used in nonaqueous solvents.

The reaction occurs most readily in methyl alcohol solution and even olefins of *trans* configuration with negative groups attached, e.g., methylcoumaric acid (12) and cinnamic acid esters (53, 57), react, as does also 1-phenylbutadiene (66). The alcohol takes part in the reaction which, except in the case of olefins difficult to mercurate, is comparatively free from side reactions so that very good yields can be obtained.

$$C_2H_4 + CH_3OH + Hg(OCOCH_3)_2 \rightarrow CH_3OC_2H_4HgOCOCH_3$$

This reaction gives a 97 per cent yield of crude product and an 85 per cent yield of pure material (54). The higher alcohols behave similarly but the reaction is slower (29, 54).

Methyl alcohol is the only solvent in which the reaction has been recently studied at all quantitatively (13, 14, 43, 66). The reaction is strongly catalyzed by peroxide, nitric acid, or boron fluoride etherate, although a catalyst is not, as a rule, essential for reaction. It is consumed during the reaction and is most conveniently provided by the addition of a little concentrated nitric acid. A typical example of the effect of nitric acid is seen in the reaction of mercuric acetate with methyl cinnamate, where the addition of one-fortieth of the ester's weight of concentrated nitric acid reduces the reaction time from 36 hr. to 75 min. Reactions which are normally rapid are not much affected by nitric acid, whereas its presence is essential for the mercuration of *cis*- and *trans*-styryl cyanides, which have an inappreciable reaction rate in its absence, and if the nitric acid is consumed before the reaction is complete the reaction stops (14). *trans*-Stilbene normally reacts so slowly that the addition product is destroyed by subsequent reactions as quickly as it is produced; even nitric acid does not speed this reaction sufficiently and the addition of one-tenth of an equivalent of benzoyl peroxide is necessary to make it possible to isolate the normal addition product (13).

The addition of sodium methoxide towards the end of a methoxymercuration generally brings the reaction rapidly to completion (66).

Substances which form a weak complex with mercury, such as nitriles or pyridine, slow down the rate of reaction, although this slowing down can be counteracted by the addition of peroxides (13).

The product from reactions in organic solvents is easily isolated by complete evaporation of the solvent under reduced pressure; this usually leaves an oil which solidifies and can be crystallized from suitable solvents.

Earlier we noted that glacial acetic acid was a suitable solvent, mercuric acetate and an olefin yielding a diacetate, and this reaction is probably general for other easily liquefied fatty acids (30). Also, liquid olefins are suitable solvents for the mercury salts of the higher fatty acids (30), but the use of inert solvents has not been investigated. It is interesting, however, that the half-life of cyclohexene and mercuric acetate in methyl alcohol solution is 30 min., whereas in

1:1 methyl alcohol–dioxane it is 4000 min. and with their equivalent of methyl alcohol in pure dioxane 6000 min. (43).

Recently the addition of ethylene to mercuric chloride has been carried out in piperidine solution (23). The piperidine takes part in the reaction in the same way as water or alcohols, so that the product is $C_5H_{10}NCH_2CH_2HgCl$, which is produced together with piperidine hydrochloride. In all respects this substance behaves as the more familiar olefin–mercuric salt compounds. It is reduced to N-ethylpiperidine by sodium amalgam and evolves ethylene with potassium cyanide or thiocyanate solution. It yields a hydrochloride with dry hydrogen chloride in ether and neither caustic soda nor hydrogen sulfide precipitates mercuric oxide or sulfide.
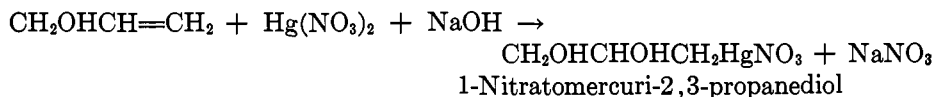
Only one attempt to prepare mercuric complexes in which both acid radicals are halogen atoms has been described. Hugel and Hibou (30) treated an ether or chloroform solution of the hexadecene–mercuric acetate compound with concentrated aqueous potassium iodide:

$$CH_3COOC_{16}H_{32}HgOCOCH_3 + 2KI \rightarrow IC_{16}H_{32}HgI + 2CH_3COOK$$
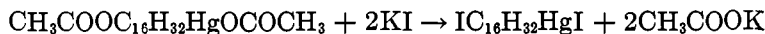
The organic solution after evaporation deposited an oil which formed white crystals, but these were so unstable that upon being touched with a glass rod they decomposed to yellow, and later red, mercuric iodide and free hexadecene.

In passing it should be mentioned that the acid radical represented as attached to the mercury atom in all the mercuric complexes ionizes, and is very readily replaced by double decomposition with other salts, although that represented as attached to the olefin requires much more drastic treatment.

One of the most surprising facts is the ease with which cyclization of unsaturated alcohols occurs. Thus, allyl alcohol carefully added to mercuric nitrate solution at under 10°C. with successive neutralization of acid, as described above, gives the simple addition compound, which is best isolated as the iodide (28):

$$CH_2OHCH{=}CH_2 + Hg(NO_3)_2 + NaOH \rightarrow$$
$$CH_2OHCHOHCH_2HgNO_3 + NaNO_3$$
1-Nitratomercuri-2,3-propanediol

However, if the reaction is carried out under similar conditions but in the presence of 40 g. of concentrated nitric acid per liter of solution and the precipitated product is dissolved in caustic alkali, then worked up in the usual way as iodide, an internal ether is produced (9, 28, 45, 50).

$$2CH_2OHCH{=}CH_2 + 2HgOHNO_3 \longrightarrow$$
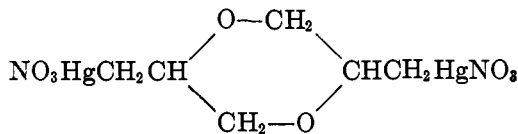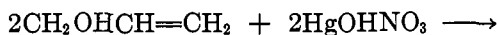
3,6-Bis(nitratomercurimethyl)dioxane

Although this appears to be the only internal ether with two oxygen atoms yet

obtained in this manner, many of type XI with one atom of oxygen (1, 37, 51, 52) are known. In a similar manner 1,5-hexadiene is mercurated in aqueous solution to produce 2,5-bis(chloromercurimethyl)tetrahydrofuran, allyl ether yields 2,6-bis(chloromercurimethyl)dioxane, and diallylamine the corresponding substituted morpholine (41); even compounds containing isoxazole rings have been isolated from the reaction of mercuric salts with unsaturated oximes, albeit in poor yield (52).

$$(CH_3)_2C\!\!=\!\!CHCH_2CH_2C(\!\!=\!\!NOH)CH_3 \longrightarrow \underset{O\text{------------}N}{(CH_3)_2\overset{\overset{\displaystyle HgI}{|}}{C}CHCH_2CH_2\overset{\|}{C}CH_3}$$
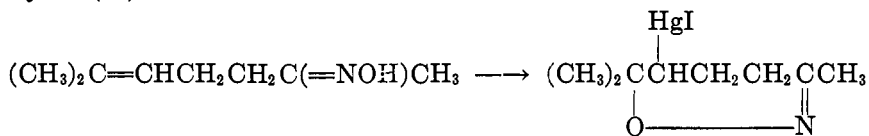
Although these reactions have been treated solely from the preparative point of view, studies of the mechanism of the reaction have been made, particularly of the reaction in aqueous and methyl alcoholic solution, and will be considered later.

III. PROPERTIES AND REACTIONS

The mercuric salt–olefin addition compounds are crystalline substances and as a rule quite stable thermally. Thus both *cis*- and *trans*-1-methoxy-2-(chloromercuri)cyclohexanes prepared from cyclohexene can be distilled under reduced pressure without change (43). Except for their greater density they are typical organic compounds. The oxyacid salts are quite soluble in water and even the haloid salts of the lower simple members are fairly soluble. The iodide is usually slightly soluble or insoluble. The acetate $CH_3OC_2H_4HgOCOCH_3$ dissolves in all the common organic solvents, including ligroin, and also in water. The ether type $O(C_2H_4HgX)_2$ have, as might be expected, higher melting points and much lower solubility in water, whilst some of the iodides of the ring types are very insoluble.

The most characteristic reaction of all the olefin–mercuric salt addition compounds is the ease with which they regenerate the olefin in the presence of halogen acids, often of only 5 per cent concentration.

$$HOC_2H_4HgCl + HCl \rightarrow C_2H_4 + HgCl_2 + H_2O$$
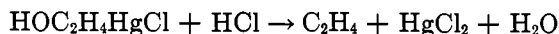
This instability is in marked contrast to the stability of alkylmercuric halides; thus, methylmercuric chloride can be prepared by the reaction of concentrated hydrochloric acid with mercury dimethyl and can even be distilled with concentrated hydrochloric acid without decomposition.

$$(CH_3)_2Hg + HCl \rightarrow CH_4 + CH_3HgCl$$
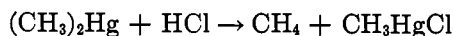
If the β-(chloromercuri)ethyl alcohol behaved as an alkylmercuric chloride, one would expect reaction between it and hydrochloric acid only with difficulty, and if reaction did occur ethyl alcohol ought to be the product, not ethylene.

Many similar reactions could be cited where ethylene is evolved when it would not be expected if the compounds behaved as substituted mercury alkyls of the

type $HOCH_2CH_2HgX$ (I), and it would appear obvious that we are dealing with the true coördination complexes of the Werner type, $C_2H_4 \cdot Hg(OH)Cl$ (III), were it not for the fact that there is equa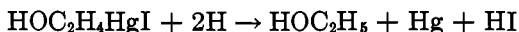lly convincing proof that the compound has the saturated structure (type I). Thus a solution of iodine in potassium iodide reacts to yield iodohydrin,

$$HOC_2H_4HgI + I_2 \rightarrow HOC_2H_4I + HgI_2$$
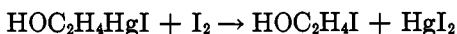
and sodium amalgam produces ethyl alcohol.

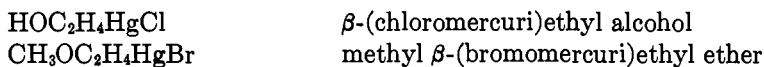$$HOC_2H_4HgI + 2H \rightarrow HOC_2H_5 + Hg + HI$$

On the basis of chemical reactions it is thus difficult to decide whether the addition compounds of ethylene with mercuric salts are saturated compounds (I) or molecular complexes (III), and the original (1903) suggestion of Sand that there is present an equilibrium labilized by acid, between the saturated form (I) and the coördination complex (III) or some equivalent mechanism, still seems the best explanation independently of what may be the electronic structure of III.

$$HOCH_2CH_2HgCl \qquad C_2H_4Hg(OH)Cl$$
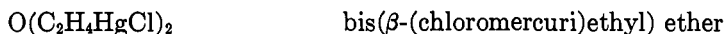$$I \qquad\qquad\qquad III$$
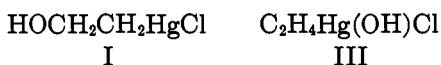
Nesmeyanov (38) has recently applied the term "quasi-complex" to such compounds, a term which aptly describes their behavior. For the purpose of discussion the compounds will be classified as follows:

    (a) Simple addition compounds:

        HOC_2H_4HgCl β-(chloromercuri)ethyl alcohol

        $CH_3OC_2H_4HgBr$ methyl β-(bromomercuri)ethyl ether

    (b) Ether compounds:

        $O(C_2H_4HgCl)_2$ bis(β-(chloromercuri)ethyl) ether

    (c) Ring types:

$$\begin{array}{c} H_2C\!-\!\!-\!\!-\!CH_2 \\ | \qquad\qquad | \\ (CH_3)_2C \qquad CHCH_2HgI \\ \diagdown \quad\; \diagup \\ O \end{array}$$
    α-(iodomercuri)methyl-α',α'-dimethyl-tetrahydrofuran from
    $(CH_3)_2C(OH)CH_2CH_2CH\!=\!CH_2$
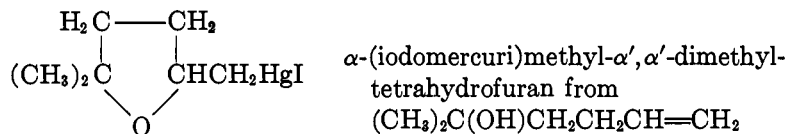
A. ACTION WITH ACIDS

The reaction with halogen acids has been mentioned. The ease with which all the olefinic complexes, even the ring types, break down and regenerate the olefin has been noted by all the workers in this field. The simple addition compounds break down immediately in cold 5 per cent hydrochloric acid. The ether types are more stable but even the ring types immediately regenerate the olefin in cold concentrated hydrochloric acid. Hydrochloric acid (20 per cent) causes immediate breakdown even of 3,6-bis(chloromercurimethyl)dioxane prepared from allyl alcohol.

It has also been noted that the methoxymercuric acetate addition product of *cis*-stilbene regenerates at least 90 per cent *cis*-stilbene and not the equilibrium mixture of *cis*- and *trans*-stilbenes with hydrochloric acid (20).

Benzoylation of the simple hydroxy compounds has a marked effect on their stability towards acid. Thus $CH_2OHCHOHCH_2HgI$ (45) is one of the least stable compounds and regenerates allyl alcohol even by action of acetic acid, with complete solution in 2 min., but its dibenzoyl derivative is so stable that even concentrated hydrochloric acid decomposes it only slowly. Similarly, $C_6H_5COOC_2H_4HgBr$ evolves ethylene only slowly in concentrated hydrochloric acid at room temperature (45), whereas the acetyl derivative shows no marked stability. From $O(C_2H_4HgCl)_2$ can be prepared the compound $O(CH_2CH_2)_2Hg$ (mercury diethylene oxide), which shows very great stability towards boiling caustic potash, potassium iodide, and potassium cyanide, yet yields its ethylene quantitatively by treatment with concentrated hydrochloric acid (46).

This enormous range in stability towards hydrochloric acid is most probably determined by the relative solubilities of the mercurials in the acid. It might be thought that instability in hydrochloric acid depends on the mercury atom being able to come within combining range of the oxygen atom and that the most stable compounds are those in which this is hindered sterically, but this is not in harmony with the observation (43) that, although there is a considerable difference in the rate of decomposition of *cis*- and *trans*-1-(chloromercuri)-2-methoxycyclohexanes by dilute hydrochloric acid, neither is exceptionally stable, yet isomerization does not occur readily and the oxygen and mercury atom of the *trans* form could not come into close proximity without isomerization.

In acid solution in the absence of halide ions these olefinic compounds are apparently labile but do not split off the olefin. Thus Sand (47) found that a solution of pure $HOC_2H_4HgNO_3$ to which was added an excess of 5 per cent sulfuric acid was 20 per cent converted to the corresponding ether compound by standing for 1 week.

$$2HOC_2H_4HgNO_3 \xrightarrow{5\% \ H_2SO_4} O(C_2H_4HgNO_3)_2 + H_2O$$
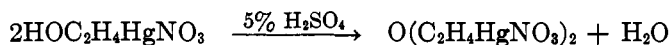
B. ACTION WITH ALKALI

Generally the olefin–mercuric salt compounds are completely soluble in 10 per cent caustic alkali, and one molecule of base is required for each mercury atom (50). The reaction is of the type:

$$HOC_2H_4HgBr + NaOH \rightarrow HOC_2H_4HgOH + NaBr$$
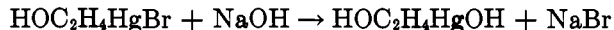
The free base HOC_2H_4HgOH, prepared by the reaction of β-(bromomercuri)-ethyl alcohol with silver oxide (35), is well known to be quite soluble and alkaline, but if the above explanation of the solubility is correct must also be largely unionized in solution. The salts most insoluble in water, e.g., iodides, cyanides, and sulfides when these are sufficiently stable, are also most difficult to dissolve in caustic alkali. $O(CH_2CH_2HgI)_2$ is insoluble in cold alkali but dissolves in hot alkali and crystallizes on cooling. The iodide of the dioxane derivative from allyl

alcohol behaves similarly, whereas the corresponding cyanide is almost insoluble even in boiling alkali. Compounds without an acid radical, e.g., $O(CH_2CH_2)_2Hg$ obtained from the ether compound $O(CH_2CH_2HgI)_2$, are completely insoluble in and unaffected by alkali (46).

As in halide-free acid solution, lability also seems to occur in alkaline solution because the ratio of ether salt to simple alcohol salt is considerably increased by aging the alkaline reaction mixture of olefin and mercuric salt for a week before working it up (26).

Aqueous ammonia also seems to increase the solubility of the more soluble olefinic compounds. Although the ammonia is lost on boiling the solution, nevertheless crystalline addition compounds of 3,6-bis(nitratomercurimethyl)dioxane and the corresponding sulfate have been isolated from ammoniacal aqueous solution, but when these are treated with potassium bromide solution they split off their ammonia and precipitate the free bromide (9, 50).

$$C_6H_{10}O_2Hg_2(NH_3)_2(NO_3)_2 + 2KBr \rightarrow C_6H_{10}O_2Hg_2Br_2 + 2NH_3 + 2KNO_3$$
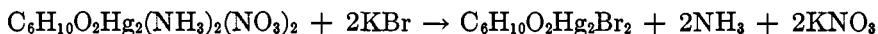
The simple addition compounds of ethylene and 1-butene in alcoholic solution precipitate a crystalline addition compound when dry ammonia (26, 27) is passed in.

$$HOC_2H_4HgBr + NH_3 \rightarrow HOC_2H_4Hg(NH_3)Br$$
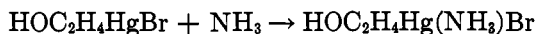
C. ACTION WITH CYANIDES AND THIOCYANATES

In general, aqueous solutions of cyanides and thiocyanates, both of which form very stable complexes with mercuric salts, cause the olefins to be evolved when they are mixed with olefin–mercuric salt addition compounds, e.g. (26):

$$HOC_2H_4HgBr + 4KCN \rightarrow C_2H_4 + K_2Hg(CN)_4 + KOH + KBr$$
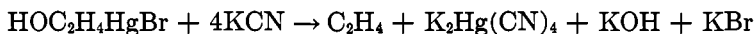
Manchot and Klüg (35) describe the action of thiocyanates with HOC_2H_4Hg-$OCOCH_3$ in some detail. The addition of one molecule of potassium thiocyanate to an aqueous solution causes the precipitation of the thiocyanate, which slowly evolves ethylene.

$$HOC_2H_4HgOCOCH_3 + KCNS \rightarrow HOC_2H_4HgCNS + CH_3COOK$$
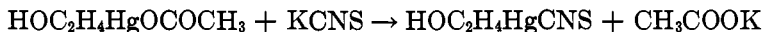
The thiocyanate can be recrystallized from methyl alcohol but tends to decompose into the double compound $HOC_2H_4HgCNS \cdot Hg(CNS)_2$. The addition of two molecules of potassium thiocyanate causes more rapid evolution of ethylene and partial solution of the precipitate first formed. Further addition of potassium thiocyanate causes rapid evolution of ethylene.

The stability towards potassium cyanide and thiocyanate seems to place the olefin compounds in the same order as stability towards hydrochloric acid. Thus, whilst the simple addition compounds and ether salts are decomposed readily, the ring compounds yield stable cyanides, even more stable than many alkyl mercuric cyanides which decompose to yield mercury dialkyls.

$$2RHgCN \rightarrow R_2Hg + Hg(CN)_2$$

D. ACTION WITH SULFIDES AND THIOSULFATES

The reaction of alkaline solutions of olefin–mercuric salt compounds with sulfides is particularly interesting. The simple compounds yield an insoluble white sulfide, easily hydrated to the more soluble hydrosulfide (26, 27).

$$2HOC_2H_4HgCl + H_2S \rightarrow (HOC_2H_4Hg)_2S + 2HCl$$

$$(HOC_2H_4Hg)_2S + H_2O \rightarrow HOC_2H_4HgSH + HOC_2H_4HgOH$$
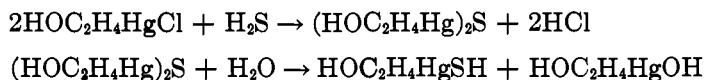
In general, the sulfides and thiosulfates are unstable. Although the earlier workers noted that mercuric sulfide is a decomposition product, they did not identify the organic residue. It appears that either the olefins may be liberated or the mercury atom may be replaced by a hydrogen atom (66). This latter reduction reaction occurs very easily with, and may be limited to, the mercurials derived from unsaturated acids and esters. In the case of these two classes of compounds, the sulfide is not precipitated as an intermediate but mercuric sulfide appears at once on passing hydrogen sulfide into the alkaline solution of the mercurial and the saturated organic residue remains. Thus the addition product of methyl cinnamate to mercuric acetate in methyl alcohol solution is converted smoothly into methyl β-methoxyhydrocinnamate.

$$C_6H_5CH(OCH_3)CH(HgOCOCH_3)COOCH_3 + H_2S + NaOH$$
$$\rightarrow C_6H_5CH(OCH_3)CH_2COOCH_3$$
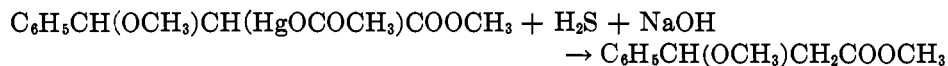
Many similar examples are known (11, 12, 55, 57). Hydrogen sulfide in alcoholic ammonia or pyridine and aqueous sodium thiosulfate are equally effective in carrying out this reduction (66).

Attempts to apply this method to remove mercury from other olefin–mercuric salt compounds, even those from α,β-unsaturated ketones and mercuric acetate, have all led to the liberation of the olefin (66). This is also true of the o-allyl-phenol compounds.

Although the first of these decompositions is a strong argument in favor of the saturated structure (I) and the second, the molecular structure type (III), neither is analogous to the reactions of alkylmercuric sulfides, which decompose as follows:

$$(RHg)_2S \rightarrow R_2Hg + HgS$$
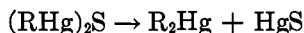
E. ACTION WITH POTASSIUM IODIDE

Potassium iodide usually yields a stable, sparingly soluble iodide with the soluble salts of olefin–mercuric salt addition compounds.

$$HOC_2H_4HgNO_3 + KI \rightarrow HOC_2H_4HgI + KNO_3$$
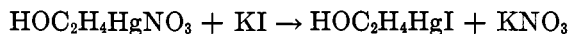
An excess of boiling potassium iodide solution may, however, cause the olefin to be liberated. Thus, upon steam distilling the mercurial from cis-stilbene with potassium iodide the equilibrium mixture of cis- and trans-stilbenes results (66). Methyl β-(iodomercuri)ethyl ether, $CH_3OC_2H_4HgI$, is so unstable that it tends to undergo slow spontaneous decomposition with deposition of mercuric iodide.

Again, under similar circumstances the alkylmercuric iodides tend to undergo a different decomposition to produce dialkyls.

$$2RHgI + 2KI \rightarrow R_2Hg + K_2HgI_4$$
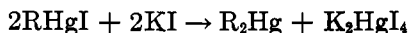
F. ACTION WITH ALKYL HALIDES

Methyl iodide, the only alkyl halide which has been tried, gives a most unexpected result when it reacts with olefin–mercuric salt compounds. When Sand (45) first tried this reaction, he expected to obtain n-propyl alcohol according to the scheme:

$$CH_3I + HOC_2H_4HgI \rightarrow n\text{-}C_3H_7OH + HgI_2$$

Instead, however, he obtained ethylene, methyl alcohol, and mercuric iodide.

$$CH_3I + HOC_2H_4HgI \rightarrow CH_3OH + C_2H_4 + HgI_2$$

The reaction appears to be general, and Manchot and Klüg (35) considered it one of the main pieces of evidence that the olefin–mercuric salt compounds are true coördination compounds. They also carried out the similar reaction with the corresponding ether salt and methyl iodide at 110°C. in a sealed tube.

$$O(C_2H_4HgI)_2 + 2CH_3I \rightarrow (CH_3)_2O + 2C_2H_4 + 2HgI_2$$
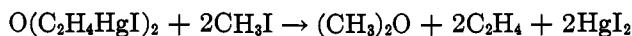
The ring compounds from o-allylphenol, however, do not react with methyl iodide (37).
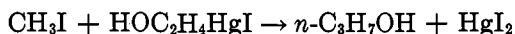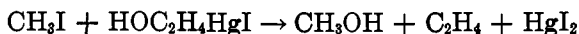
G. ACTION WITH GRIGNARD REAGENTS

Few examples of this reaction appear to be known. In the case of the simple styrene (66) and cis-stilbene (20) mercurials the unsaturated substances were liberated, but in contrast to decomposition by hydrochloric acid, complete isomerization to $trans$-stilbene had occurred in the latter case.

$$C_6H_5CH(OCH_3)CH_2HgOCOCH_3 \xrightarrow{CH_3MgBr} C_6H_5CH{=}CH_2$$

In a further example where the mercurial was derived from an unsaturated ketone, the reaction product was that which would be expected from the unsaturated ketone alone and which may have been liberated at an intermediate stage. Three molecular proportions of Grignard reagent were used (36).

$$C_6H_5COCH{=}CHC_6H_5 + CH_3OH + Hg(OCOCH_3)_2$$
$$\rightarrow C_6H_5COCH(OCH_3)CHC_6H_5(HgOCOCH_3)$$
$$\xrightarrow{C_2H_5MgBr} C_6H_5COCH_2CH_2CH(C_6H_5)C_2H_5$$
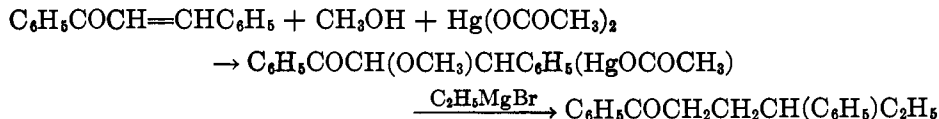
H. ACTION WITH TIN ARYLS

Although Grignard reagents liberate the unsaturated organic substance, Nesmeyanov (39) has found that tin aryls always react as if the mercury compounds were substituted alkylmercuric halides, and no sign of the production of diarylmercury was found.

$$2HOC_2H_4HgX + Ar_2SnCl_2 \rightarrow 2HOC_2H_4HgAr + SnX_2Cl_2$$
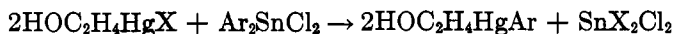
Mercurials prepared from o-allylphenol and cyclohexene behaved in exactly the same way, and the products could be repeatedly recrystallized without rearrangement into mercury diaryls and substituted dialkyls. Even these products, however, regenerated the olefin quantitatively on treatment with hydrochloric acid, cyanides, or thiocyanates, or on fusion.

I. ACTION WITH BENZOYL CHLORIDE, ACETYL CHLORIDE, AND ACETIC ANHYDRIDE

Benzoylation of the simple alcohol type of addition compound by benzoyl chloride occurs very easily in alkaline solution (45).

$$HOC_2H_4HgI + C_6H_5COCl \rightarrow C_6H_5COOC_2H_4HgI + HCl$$
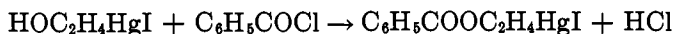
Acetylation is not so easy and only one example appears to be known. This was effected by the direct action of warm acetic anhydride (45, 52).

$$HOC_2H_4HgBr + (CH_3CO)_2O \rightarrow CH_3COOC_2H_4HgBr + CH_3COOH$$
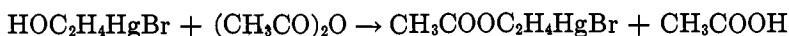
Compounds which do not contain a hydroxyl group are unaffected by attempts at benzoylation (51) but react with acetic anhydride or acetyl chloride, leading to eviction of the unsaturated substance (66). The reaction with the methoxyacetomercurials occurs in two stages. Thus, methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate, prepared by the addition of methyl cinnamate to mercuric acetate in methyl alcohol, reacts as follows:

$C_6H_5CH(OCH_3)CH(COOCH_3)HgOCOCH_3$
$$\xrightarrow{\text{1 mole CH}_3\text{COCl}} C_6H_5CH(OCH_3)CH(COOCH_3)HgCl$$

$$C_6H_5CH(OCH_3)CH(COOCH_3)HgCl \xrightarrow{\text{excess CH}_3\text{COCl}} C_6H_5CH{=\!=}CHCOOCH_3$$
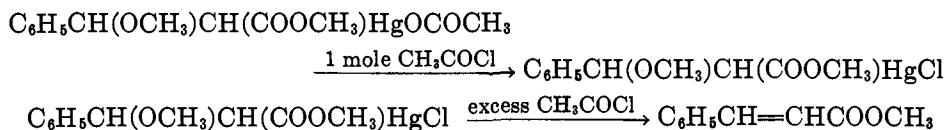
The ring benzofuran derivatives prepared from o-allylphenol are not affected by acetic anhydride (37).

J. ACTION WITH PHENYL ISOTHIOCYANATE

The hydroxyl group in $HOCH_2CH_2HgBr$ reacts with phenyl isothiocyanate (39) in the usual manner of an alcohol to give the phenyl carbamate, m.p. 124–126°C.

K. ACTION WITH DIAZOMETHANE

The reaction of diazomethane with β-(bromomercuri)ethyl alcohol gave a most unexpected result (24). Ethylene was evolved quantitatively, the other products being $BrCH_2HgBr$, formaldehyde, and mercury. The reaction obviously occurred in two stages. The first involved the evolution of nitrogen, and not until all the nitrogen had been evolved and the solvent ether removed, did evolution of ethylene begin; because this evolution was quantitative, the formaldehyde must have been produced from the diazomethane. The reaction appears to be:

$$HOC_2H_4HgBr + CH_2N_2 \rightarrow N_2 + HOC_2H_4HgCH_2Br$$
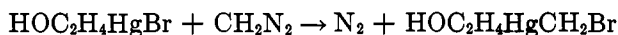
The product was stable in ether solution but decomposed when attempts were made to isolate it:

$$HOC_2H_4HgCH_2Br \rightarrow C_2H_4 + HOHgCH_2Br$$

$$2HOHgCH_2Br \rightarrow BrHgCH_2Br + H_2O + HCHO + Hg$$
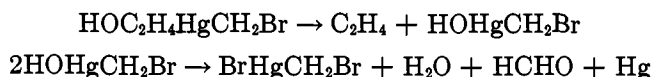
In confirmation of this latter decomposition it was noted that $BrHgCH_2Br$ deposited mercury quantitatively and produced formaldehyde on treatment with caustic soda.

In most of the reactions so far considered the free unsaturated substance has been regenerated by treating the mercurials with a wide variety of reagents, and on the basis of these reactions alone we could justifiably conclude that the olefin–mercuric salt compounds are coördination compounds. Polarographic studies by Sullam (59) also indicate that the ethylene mercurials behave as molecular complexes, e.g., $C_2H_4 \cdot Hg(OCOCH_3)_2$ and not $CH_3COOC_2H_4HgOCOCH_3$. However, the following reactions are quite different and in each case the addition compound behaves as if it were a substituted alkylmercuric halide.

L. ACTION WITH HALOGENS

The reaction with iodine was the first method evolved for finding the position of the mercury atoms and carbon skeleton of the addition compound. The reaction can be carried out either in organic solvents or in aqueous potassium iodide solution and the yields are almost quantitative (1, 45).

$$HOC_2H_4HgI + I_2 \rightarrow HOCH_2CH_2I + HgI_2$$
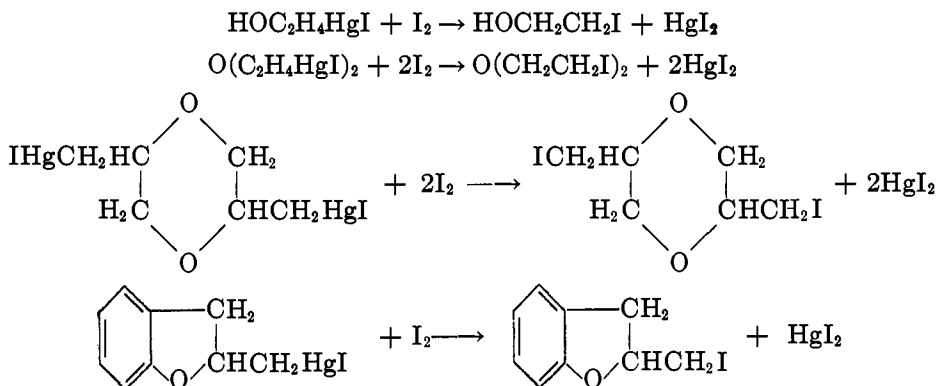
$$O(C_2H_4HgI)_2 + 2I_2 \rightarrow O(CH_2CH_2I)_2 + 2HgI_2$$

These reactions, of which there are many other examples in the literature, occur as if the olefinic complex were simply a substituted alkylmercuric iodide, and the iodine derivatives have none of the sensitivity towards hydrochloric acid possessed by the parent mercurials.

The analogous reaction with bromine has had similar application by later workers and occurs in two steps with salts other than haloid salts. The first molecule of bromine replaces the acid radical by bromine, then a second molecule splits the C—Hg bond, e.g., α-acetomercuri-β-phenyl-β-methoxyethane derived from styrene reacts in methyl alcohol solution at 0°C. as follows (66):

$$C_6H_5CH(OCH_3)CH_2HgOCOCH_3 + Br_2$$
$$\rightarrow C_6H_5CH(OCH_3)CH_2HgBr + CH_3COOBr$$

$$C_6H_5CH(OCH_3)CH_2HgBr + Br_2 \rightarrow C_6H_5CH(OCH_3)CH_2Br + HgBr_2$$
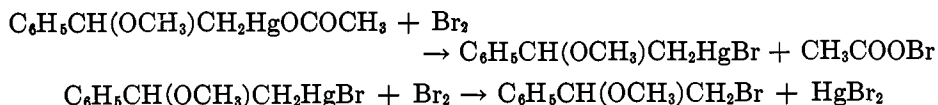
In aqueous solution hypobromous acid has been observed (9).

$$C_6H_{10}O_2Hg_2SO_4 + 2Br_2 + 2H_2O \rightarrow C_6H_{10}O_2Hg_2Br_2 + 2HOBr + H_2SO_4$$

3,6-Bis(sulfato-
mercurimethyl)-
dioxane
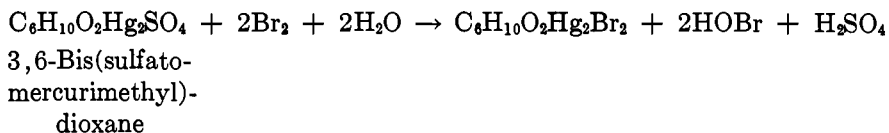
In a similar way bromocyanogen (2 moles) in methyl alcohol solution gave a 50 per cent yield of α-(bromomercuri)-β-methoxy-β-phenylethane but in excess it is not capable of breaking the mercury–carbon bond.

It seems fairly certain that replacement of —HgBr by —Br involves racemization at the carbon atom to which the mercury is attached (14, 62) in spite of an earlier report (56) to the contrary. Thus, both diastereoisomers of α-acetoxy-mercuri-β-methoxy-β-phenylpropionitrile on bromination and hydrolysis produced the same mixture of diastereoisomeric α-bromo-β-methoxy-β-phenylpropionic acids.

In alkaline solution bromine oxidizes β-(bromomercuri)ethyl alcohol to α-(bromomercuri)acetic acid without difficulty (26).

$$BrHgCH_2CH_2OH \rightarrow BrHgCH_2COOH$$
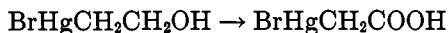
M. ACTION WITH REDUCING AGENTS

The reduction of olefin–mercuric salt compounds in alkaline solution by sodium amalgam, or electrolytically, replaces the mercury atom by hydrogen, and this reaction was found particularly useful for determining the parent carbon compound from which the ring type of mercurials was derived (51). The general reaction is typified by the equation:

$$HOC_2H_4HgI + 2H \rightarrow C_2H_5OH + Hg + HI$$
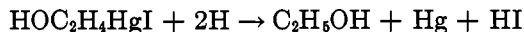
An example of its usefulness is in determining the carbon skeleton of the products from the reaction of mercuric salts with terpineol. Three products are obtained: XII, which on reduction produces cineole, and XIII and XIV, both of which are reduced to *trans*-terpin. No *cis*-terpin is obtained; hence their relationship is:
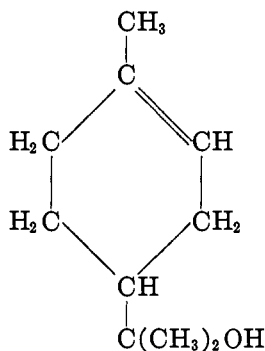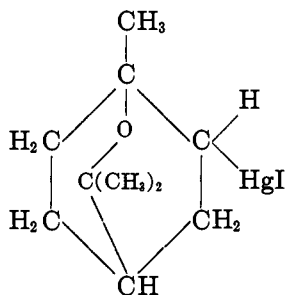
| Terpineol | XII
(An internal ether type of compound) | XIII and XIV
(Isomeric forms of the alcohol type of compound derived from *trans*-terpin) |
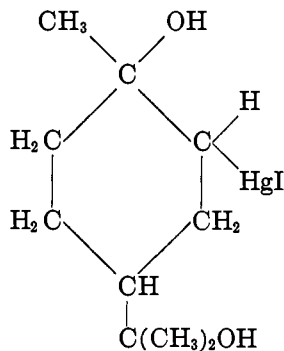
It is interesting that although derivatives corresponding to XIII and XIV, derived from *cis*-terpin, should also be possible, none were found. The potential *cis*-terpin derivatives had immediately undergone ring closure in the manner characteristic of the unsaturated alcohols with suitably placed hydroxyl groups and ethylenic bonds.

The *o*-allylphenol derivatives behave in an exceptional manner (1, 37).
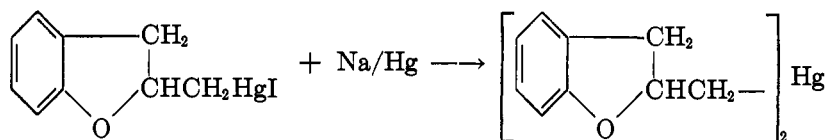
Alkaline stannite does not reduce the mercurials so completely as sodium amalgam, but again the *o*-allylphenol derivatives are exceptional for they react to regenerate the olefin (37).

The general reaction with alkaline stannite occurs in two stages. The simple addition compounds are reduced immediately to reddish violet insoluble mercurous compounds, which quickly decompose into poisonous volatile substituted dialkyls with deposition of mercury. This reaction has been investigated only very sketchily (45, 46).

$$HOC_2H_4HgBr \rightarrow [(HOC_2H_4Hg)_2] \rightarrow (HOC_2H_4)_2Hg + Hg$$

The ether salts behave in exactly the same way except that the intermediate compound is sufficiently stable to be isolated in almost quantitative yield:
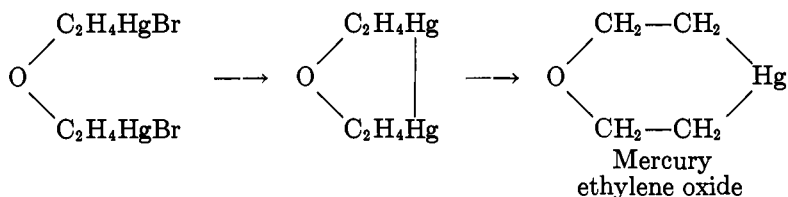
The intermediate is insoluble in water, caustic soda, and organic solvents but evolves ethylene and produces mercurous chloride in concentrated hydrochloric acid. When heated in a sealed tube with benzene to 140°C. it is decomposed to mercury ethylene oxide in 60 per cent yield. This last substance is easily soluble in most organic solvents but not in caustic potash or aqueous solvents. It also
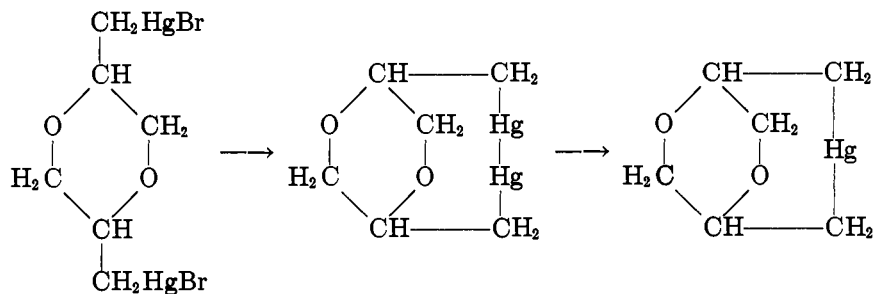
evolves ethylene with concentrated hydrochloric acid but otherwise is exceptionally stable (46). 3,6-Bis(bromomercurimethyl)dioxane is reduced in exactly the same way, except that the mercurous intermediate is even more stable but is decomposed by strong sunlight (46).

Hydrazine sulfate does not reduce the olefin–mercuric salt compounds (52).

IV. ISOMERISM

With this brief résumé of the reactions of the mercurials derived from unsaturated substances it is now possible to consider the types of isomerism which occur amongst them, also the mechanism of their formation, and their structure. These three aspects are interrelated, and first we shall consider the occurrence of optical isomers.

A. OPTICAL ISOMERISM

The only compounds examined for optical isomerism have been methoxy derivatives obtained by reaction of the unsaturated substance with mercuric acetate in methyl alcohol.

When an olefin, RHC=CHR′, reacts with a mercuric salt, the two carbon atoms originally involved in double bond formation become asymmetric and the product of the reaction is capable of existing in four optically active forms, *dd*, *dl*, *ld*, and *ll*. Actually, Marvel and coworkers (25, 53) obtained only two when they attempted to separate the four optical isomers from the products of the mercuration of the cinnamic esters of optically active alcohols. They were as follows:

	MELTING POINT	$[\alpha]_D^{25°}$	MELTING POINT	$[\alpha]_D^{25°}$
	°C.		°C.	
l-Menthyl-β-methoxy-α-bromomercuri-hydrocinnamate	146	−48.6	135	+61.9
l-Menthyl-β-methoxy-α-(iodomercuri)hydrocinnamate	99	−24.27	128	+65.89
d-Bornyl-β-methoxy-α-(bromomercuri)hydrocinnamate	132	+17.3	148	+14.9

The levorotatory menthyl bromo derivative was converted into the levorotatory iodo derivative by the action of potassium iodide but the quantity of the dextrorotatory salt was too small to attempt this conversion. All attempts to find the other two isomers failed, although a considerable gummy residue was obtained from the mother liquors and it could have contained them.

It seems that *l*-menthyl allocinnamate would produce the two missing optically active isomers, because Wright (66) has obtained two different pure methyl α-(chloromercuri)-β-methoxy-β-phenylpropionates by the methoxymercuration of *cis*- and *trans*-methyl cinnamates. Both were reduced to yield the same β-methoxy-β-phenylpropionic acid by alkaline sulfide and thus must be mixtures whose constituents bear a diastereoisomeric relationship to each other. The mercurial derived from methyl allocinnamate showed no tendency to isomerize

upon 8 hr. boiling in ethyl acetate but both mercurials decompose thermally at 25 mm. pressure to produce, in about 50 per cent yield, methyl *trans*-cinnamate at 157°C. and 170°C., respectively. Similarly the isomeric styryl cyanides (14), Δ^2-butenes (61), and stilbenes (13) produce pure diastereoisomeric pairs, one only from each isomer.

The methoxymercuration of cyclohexene is exactly analogous (43). Romeyn and Wright obtained only the *trans* isomer by the reaction of cyclohexene with mercuric acetate in methyl alcohol. The product, isolated as the chloride, can theoretically exist in four optically active forms, i.e., two racemic mixtures. Viewed along the plane of the ring they can be represented as follows:

```
H——OCH₃      CH₃O——H        H——OCH₃      CH₃O——H

H——HgCl      ClHg——H        ClHg——H           H——HgCl

   dd             ll            dl                ld
          cis                         trans
```
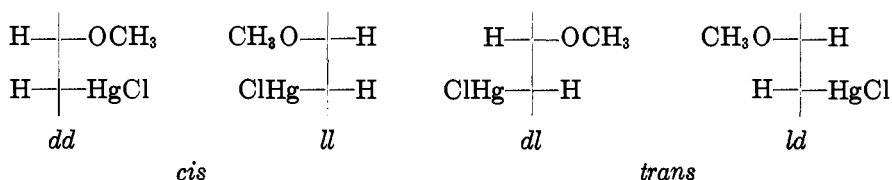
(The configuration designation of the asymmetric centers is entirely arbitrary.)

The *trans* isomer obtained in the preparative reaction, designated the α-isomer, m.p. 116°C., can be converted into a mixture, m.p. 86°C., by boiling its alcoholic solution in the presence of a suitable catalyst such as benzoyl peroxide. From this mixture the β- or *cis* isomer, m.p. 114°C., was isolated. The two isomers have very similar properties and both can be distilled unchanged under reduced pressure, but generally the α-isomer is more soluble and reactive than the β-isomer. Particularly, it is more soluble in alkali and decomposes more quickly in the presence of dilute hydrochloric acid. It was on the basis of these reactions and because a single geometric isomer is always produced in such preparations that it was originally given a *cis* configuration, but the *trans* configuration has now been established by an x-ray crystal structure determination of both isomers (67).

By means of an asymmetric synthesis using *l*-mercuric lactate instead of the acetate in the preparation, a pure levorotatory enantiomer, m.p. 63°C. ($[\alpha]_D = -40.00$ in 5 per cent ethyl alcohol), was isolated together with the α-isomer, which must thus be a racemic compound. Isomerization of this enantiomer produced a mixture from which the pure diastereoisomer, m.p. 66.2°C. ($[\alpha]_D = +12.82°$ in 6 per cent ethyl alcohol), was isolated.

The catalysts for this isomerization are benzoyl peroxide, diphenylmercury, and hydrazine hydrate, which have in common the property of converting RHgCl into R₂Hg, so equilibrium is probably set up as follows:

```
H——OCH₃                                    H——OCH₃
            ⇌   (C₇H₁₃O)₂Hg   ⇌
H——HgCl              +                      ClHg——H
                   HgCl₂

  β-Isomer                                    -Isomer
```
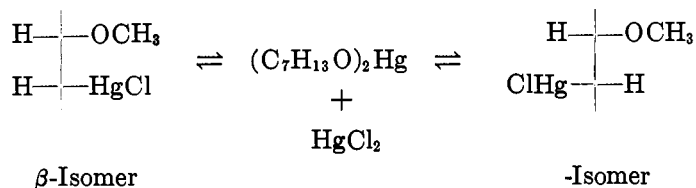
The equilibrium seems to lie largely to the side of the β-isomer because no conversion of the β- to the α-isomer could be detected; however, as considerable decomposition occurs during the isomerization, and this would be expected if it occurs by the above mechanism, rigorous proof that no conversion of β- into α-isomer occurs was not possible.

The mercuration of 1,3-butadiene in ethyl alcohol solution produces two identical asymmetric carbon atoms and the product, $[CH_3COOHgCH_2CH(OC_2H_5)—]_2$, has been isolated in meso and racemic forms (31).

B. OTHER TYPES OF ISOMERISM

A second type of isomerism, observed particularly amongst the reaction products of hydroxyolefins, has received no satisfactory explanation. An oily "intermediate" has frequently been observed in the preparation of olefin–mercuric salt compounds, but always the oil was converted more or less rapidly to the solid mercurial on dissolving it in warm organic solvents. However, in the few cases where analysis of the oil was carried out, it has proved to be isomeric with the solid product. Hugel and Hibou (30) noted these oils particularly in the mercuration of the higher olefins; also Balbiano and Paolini (4) obtained the addition product of allyl-substituted aromatic ethers in stable isomeric forms which may be a manifestation of the same phenomenon. The isomerism seems also to be characteristic of the preparations from unsaturated alcohols which yield cyclic ethers, and the more stable the ring the more fleeting the existence of the oil.

No recent study of these oils has been made, the only definite information being that of Sand and Singer (51, 52), who observed them first in the addition of mercuric nitrate to α-terpineol by successive neutralization of the liberated acid. Three products were obtained: (1) a derivative of cineole (i.e., the usual cyclic ether salt); (2) two isomers derived from trans-terpin.

α-isomer, m.p. 123–125°C., stable
β-isomer, m.p. 38°C., labile
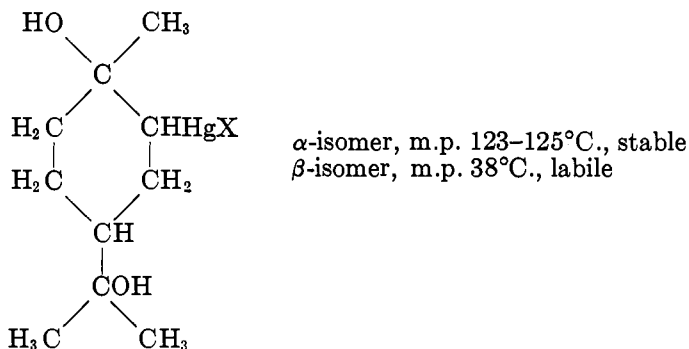
The α-isomer is stable both in alkaline solution and in organic solvents, but the β-isomer is readily converted to the α-isomer in hot organic solvents, so that attempts at recrystallization from these media always produce an oil. Nevertheless, its conversion to the α-isomer in aqueous alkaline solution is very slow and it was purified by causing it to crystallize from aqueous alkali by passing in carbon dioxide. No conversion of the α- into the β-isomer was ever obtained.

Reduction of their alkaline solutions by sodium amalgam yielded, from both isomers, *trans*-terpin and no *cis*-terpin, nor was *cis*-terpin converted to *trans*-terpin under the conditions of the reduction; thus the isomers are both derived from *trans*-terpin and must have the structure given above. Surprisingly, the labile isomer is the more stable towards acid. Thus, if the α-iodide is covered with dilute nitric acid it immediately reddens, owing to liberation of mercuric iodide, but the labile isomer under the same treatment remains colorless for half an hour.

In this case Sand and Singer interpreted the isomerism as geometric isomerism, so that looking along the plane of the ring we have:

$$CH_3 \qquad C_3H_7O \qquad\qquad CH_3 \quad HgI \quad C_3H_7O$$

$$OH \quad HgI \qquad\qquad\qquad OH$$

Stable α-isomer   Labile β-isomer

This explanation cannot be correct, because this type of isomerism appears to be fairly general and some general explanation to cover all cases is required.

The best examples are given by the derivatives of 2,6-dimethyl-5-hepten-2-ol, $(CH_3)_2C{=}CHCH_2CH_2C(OH)(CH_3)_2$ (52). Mercuration of this yields two pairs of isomers and these cannot be interpreted as *cis* and *trans* isomers. They are:

(*1*) A pair of isomeric glycols analyzing as:

$$(CH_3)_2C{-}CHCH_2CH_2C(CH_3)_2 \qquad \alpha\text{-isomer, m.p. }125°C\text{., stable}$$
$$OH\;HgI \qquad\qquad OH \qquad\qquad \beta\text{-isomer, oil, labile}$$
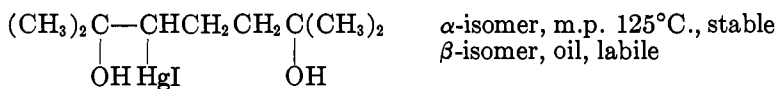
(*2*) A pair of isomeric internal ether salts:

$$CH_2$$
$$IHgHC \qquad CH_2 \qquad\qquad \alpha\text{-isomer, m.p. }108\text{--}110°C\text{., stable}$$
$$(CH_3)_2C \qquad C(CH_3)_2 \qquad \beta\text{-isomer, oil, labile}$$
$$O$$
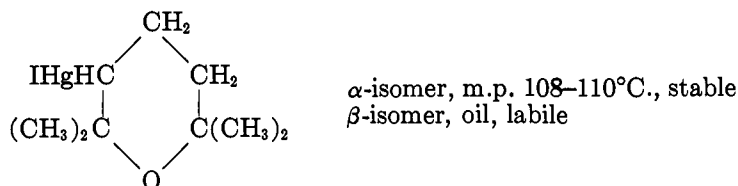
Qualitatively the properties of the isomeric glycols above correspond to those of the isomeric glycols derived from terpineol, and the cyclic ethers are similar. Unfortunately, Sand and Singer did not reduce these compounds nor replace the mercury by iodine, so that there is no definite evidence that the isomers have the same oxygen–carbon skeleton and one can only assume it is so by analogy with the terpineol derivatives.

When the cyclic ether is five-membered, ring production is especially favored and the corresponding glycol has never been observed. Thus 5-methyl-1-hepten-5-ol (52), $C_2H_5C(CH_3)(OH)CH_2CH_2CH{=}CH_2$, and *o*-allylphenol (1) yield exclusively internal ethers:

$$\begin{array}{c}
\text{H}_2\text{C} \!-\!\!-\!\!-\! \text{CH}_2 \\
\text{C}_2\text{H}_5 \diagdown \quad | \qquad\quad | \\
\diagdown \text{C} \quad\quad \text{CHCH}_2\text{HgI} \\
\diagup \quad \diagup \\
\text{CH}_3 \quad \text{O}
\end{array}
\quad \text{and} \quad
\begin{array}{c}
\diagup\!\!\!\diagdown \!-\!\!-\!\!-\! \text{CH}_2 \\
| \quad\quad\quad | \\
\diagdown\!\!\!\diagup \quad \text{CHCH}_2\text{HgI} \\
\diagup \\
\text{O}
\end{array}$$
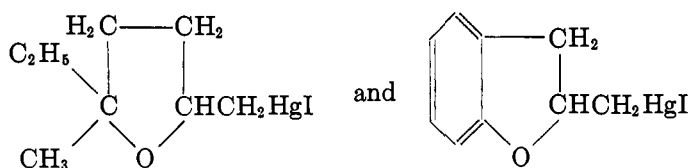
Again an oil appeared but its existence, although quite definite, was too fleeting to allow of isolation and analysis. In the latter case Adams, Roman, and Sperry (1) assumed that it was an intermediate of different composition from their final product but made no analysis.

Whether the explanation of these low-melting labile substances is the same in every case and whether they are all really intermediates of the same composition as the final product cannot be judged from the present evidence, but Sand (47) considered them to be true coördination complexes of type XVII which tautomerized into the saturated addition compound of type XVI (equation II). This does not fit his own observation that the labile form, which should thus be the coördination complex, is the more stable towards acid; however, with the small amount of evidence available, any views on the nature of these oils would be highly speculative.

V. MECHANISM OF THE ADDITION OF MERCURIC SALTS TO OLEFINS

Before 1935 most workers in this field assumed that the mercuric salt and olefin combined molecularly and then the product reacted with the solvent (e.g., 26, 66).
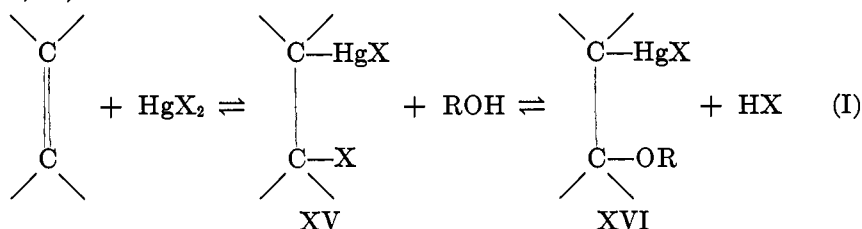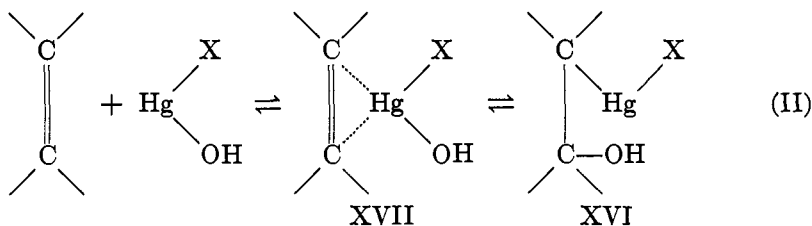
$$\begin{array}{c}
\diagdown \quad \diagup \\
\text{C} \\
\| \qquad\qquad + \text{HgX}_2 \rightleftarrows \\
\text{C} \\
\diagup \quad \diagdown
\end{array}
\quad
\begin{array}{c}
\diagdown \quad \diagup \\
\text{C}\!-\!\text{HgX} \\
| \qquad\qquad + \text{ROH} \rightleftarrows \\
\text{C}\!-\!\text{X} \\
\diagup \quad \diagdown \\
\text{XV}
\end{array}
\quad
\begin{array}{c}
\diagdown \quad \diagup \\
\text{C}\!-\!\text{HgX} \\
| \qquad\qquad + \text{HX} \qquad (\text{I}) \\
\text{C}\!-\!\text{OR} \\
\diagup \quad \diagdown \\
\text{XVI}
\end{array}$$

Sand (47), however, in 1903 did put forward another view which bears a superficial resemblance to those current at present. He considered that the double bond by its partial valencies combined directly with the metal in the basic salt, the latter being bound by its auxiliary valencies to yield the coördination complex (XVII), which then rearranged to form the final addition product (XVI):

$$\begin{array}{c}
\diagdown \quad \diagup \\
\text{C} \\
\| \qquad + \text{Hg} \\
\text{C} \\
\diagup \quad \diagdown
\end{array}
\begin{array}{c}
\diagup \text{X} \\
\diagdown \\
\text{OH}
\end{array}
\rightleftarrows
\begin{array}{c}
\diagdown \quad \diagup \\
\text{C} \\
\| \qquad \text{Hg} \\
\text{C} \\
\diagup \quad \diagdown
\end{array}
\begin{array}{c}
\diagup \text{X} \\
\diagdown \\
\text{OH} \\
\text{XVII}
\end{array}
\rightleftarrows
\begin{array}{c}
\diagdown \quad \diagup \\
\text{C} \\
| \qquad \text{Hg} \\
\text{C}\!-\!\text{OH} \\
\diagup \quad \diagdown \\
\text{XVI}
\end{array}
\begin{array}{c}
\diagup \text{X} \\
\diagdown \\
\end{array}
\qquad (\text{II})$$

In the regeneration of the olefin by hydrochloric acid it was assumed that

the alkoxyl or hydroxyl group was replaced by chlorine, followed by the decomposition of the unstable chloride. However, these earlier views are now of historic interest rather than of practical value.

There seems to be no doubt that the reaction is reversible, because in aqueous solutions of low pH and the presence of substances with a strong affinity for the mercuric ion, a condition which exists in a hydrochloric acid solution, the olefin is rapidly liberated, yet in neutral organic solvents there can be no lability because the optical isomers with asymmetric centers at the carbon atoms of the original double bond show no tendency to spontaneous racemization. Wright and coworkers have also attempted on two occasions (14, 43) to approach the equilibrium from the side of the organic addition compound in methyl alcohol solution in the presence of one equivalent of acetic acid and showed that the reaction of formation under these conditions is almost, if not entirely, complete.

A. MEASUREMENT OF THE EQUILIBRIUM CONSTANT

The first attempt to measure the equilibrium constant for the reaction was made in 1907 by Sand and Breest (48).

$$HgCl_2 + H_2O + C_2H_4 \rightleftharpoons HOC_2H_4HgCl + H^+ + Cl^-$$
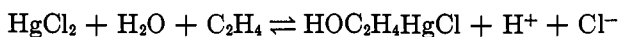
They reacted ethylene at atmospheric pressure with a solution of mercuric chloride in conductivity water and measured the conductivity of the solution after various intervals of time until equilibrium was established. This usually required 2–3 hr. They then estimated the acid produced in the establishment of the equilibrium from the final value of the conductivity. They took into account the formation of the complex ion $[HgCl_3]^-$ from the hydrochloric acid liberated in the reaction and obtained the value

$$K = \frac{[H^+][Cl^-][C_2H_5OHgCl]}{[HgCl_2][C_2H_4]} = 2.81\alpha^{-1} \times 10^{-7} \text{ at } 25°C.$$

where α = the solubility of ethylene at 25°C. and 1 mm. pressure. This value was the mean of ten concordant results.

When they attempted to find the equilibrium constant by decomposing β-(chloromercuri)ethyl alcohol with hydrochloric acid of different concentrations and measuring the equilibrium pressure of ethylene they obtained a rather different result. Using 1 g. of the chloride in 18 ml. of 0.1 N hydrochloric acid, $K = 1.21\alpha^{-1} \times 10^{-7}$; using 12.0 ml. of 0.2 N hydrochloric acid, $K = 1.34\alpha^{-1} \times 10^{-7}$.

They now attempted to determine the velocity constant for the reaction of formation from the initial rate of change of the conductivity of the solution during the reaction but could not obtain a constant on the assumption of either reaction I or reaction II above, and concluded that the liberated acid probably catalyzed the reaction or the rearrangement of XVII in reaction II. At any rate their results did not accord with any simple mechanism.
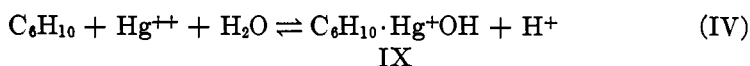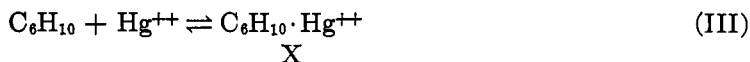
The most recent attempts to elucidate the mechanism of the addition are the work of American chemists. Lucas, Hepner, and Winstein (33) investigated the equilibrium between cyclohexene and aqueous mercuric nitrate in the presence of varying quantities of nitric acid and produced the only substantial evidence

for the existence of coördination complexes of olefins with mercuric salts. Unfortunately they did not link up their results with the results of previous workers who, so far as we know, have always isolated addition products, but suggested that mercuration is analogous to bromination and proceeds through the mercurinium ion, a result contested by Wright *et al.* (13, 14, 43, 66, 70), who have studied the kinetics of the addition of various olefins, including cyclohexene, to mercuric acetate in methyl alcohol solution.

First we shall consider the evidence of Lucas *et al.* (33) that cyclohexene forms coördination complexes with the mercuric ion.

The equilibrium was investigated by measuring the partition coefficient of cyclohexene between mercuric nitrate solution and carbon tetrachloride at various acidities with precautions to prevent the formation of peroxides, as these catalyzed the precipitation of solid by-products. Potassium nitrate was also present in such quantity that all the mercuric salt solutions had an initial ionic strength of unity. The cyclohexene in each layer was estimated by a bromination method and the mercury in the aqueous layer by thiocyanate titration.

Their results could be interpreted very well on the basis that two equilibria are rapidly established.

$$C_6H_{10} + Hg^{++} \rightleftharpoons C_6H_{10} \cdot Hg^{++} \qquad (III)$$
$$X$$

$$C_6H_{10} + Hg^{++} + H_2O \rightleftharpoons C_6H_{10} \cdot Hg^+OH + H^+ \qquad (IV)$$
$$IX$$

The latter is by far the more important. The mercury of both these complexes can be titrated with thiocyanate as if it were free mercuric ion. On the other hand, the mercury content of the ions of type $HOC_2H_4Hg^+$, which are derived from compounds of type I by ionization and which have been the subject of this review, react with only one molecule of thiocyanate (66). It seems, therefore, that there are two species of $Un(OH)Hg^+$ ion[1] (IX and I) as well as a $UnHg^{++}$ ion, but the existence of these two new types of ions, $UnHg^{++}$ and $UnHg^+OH$, is based only on this one series of results by Lucas, Hepner, and Winstein.

The equilibrium constants found for the reactions were:

$$K_{III} = 2.2 \times 10^4; K_{IV} = 5.0 \times 10^4$$

The equilibria at low acidities tended to drift with time with slow production of acid, decrease of titratable mercury content, and increase of unsaturation as shown by bromine titration. Thus in their solution of lowest acidity, 0.0981 mole of nitric acid per liter, the content of titratable mercury in the aqueous solution fell some 27 per cent in 13 hr., and the unsaturation rose 3 per cent in 3 hr. and 40 per cent after 17 hr. The reactions producing these effects have been investigated by Brook and Wright (68), who found the decrease in mercuric mercury content of the solution and apparent increase in unsaturation to be caused by the reduction of the mercuric to mercurous salt, which is then titratable with bromine as if it were cyclohexene. Formylcyclopentane and its trimer were also produced in quantity over a period of 16 hr.

[1] Un = unsaturated substances.

These side reactions do not appear to invalidate the results of Lucas, Hepner, and Winstein, because they are all much slower than the reaction between mercuric nitrate solution and cyclohexene and their effects were satisfactorily eliminated by extrapolation of the values of the equilibrium constant, found by analysis of the mixture after $\frac{1}{2}$, 1, and $1\frac{1}{2}$ hr., to zero time. There can be no doubt that cyclohexene reacts rapidly with acid mercuric nitrate solution, because it dissolves in a few minutes and the production of acid is immediate when they are mixed. The total mercury found by thiocyanate titration is initially theoretical and the odor of cyclohexene returns during the titration.

The good agreement between the various values of the equilibrium constant found at different acid and mercury concentrations could hardly be fortuitous and leaves little doubt that cyclohexene combines with the mercuric ion to produce two 1:1 compounds, viz., $C_6H_{10}Hg^{++}$ and $C_6H_{10}HgOH^+$, the latter being the more important. However, if the cyclohexene addition compound $HOC_6H_{10}HgX$ is so unstable that the mercury can be titrated in acid solution with thiocyanate as if it were present as the free salt, then the ions of types IX and I could be identical. Evidence thus points to the possibility that mercuration of olefins is a parallel reaction to bromination and takes place through a mercurinium ion. The mercurinium ion may well be cyclic, which would explain the *trans* addition and the production of only pure diastereoisomeric pairs from each geometric isomer of suitably substituted olefins.

$$
\underset{}{\overset{\diagdown C \diagup}{\underset{\diagup C \diagdown}{\parallel}}} + Hg^{++} \rightleftharpoons \underset{\diagup C \diagdown}{\overset{\diagdown C \diagup}{Hg^{++}}} + HO^- \rightleftharpoons \overset{HO\dot{C}-}{\underset{-\dot{C}-Hg^+}{}} \qquad \text{(V)}
$$

XVIII
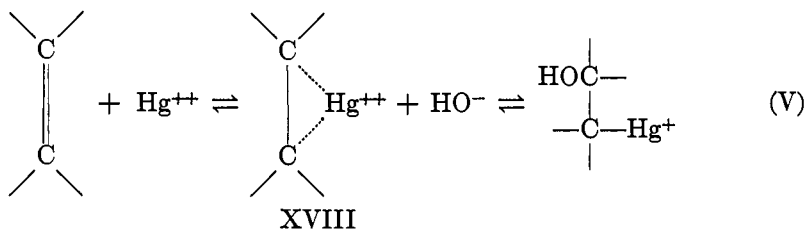
B. MEASUREMENT OF THE RATE OF REACTION

All recent kinetic studies (13, 14, 43, 61, 66) have been carried out in methyl alcohol solution, where the reaction is usually rapid. Wright and coworkers followed the reaction by taking samples after different intervals of time and titrating the mercury against thiocyanate, after the sample had been diluted with water and the olefin–mercury compound extracted with chloroform. When the chloroform extraction was omitted, the olefin–mercury compound decomposed slightly in the thiocyanate to give a false end point. This analytical technique labels all the water-soluble mercury as free mercuric salt but water-soluble mercury-containing by-products are formed, a result which gives the false impression that the reaction proceeds to an appreciable equilibrium whereas, in fact, this equilibrium cannot be approached from the other direction (14, 43).

The methoxymercuration of cyclohexene seems to be a typical fast reaction and has been extensively studied (43). In order to slow down the reaction to a measurable rate the mercuric acetate was used at a concentration of 10^{-3} mole per liter and the mercury determined by dithizone. Using pure reagents a good

second-order constant was obtained, whereas in the peroxide-catalyzed reaction the "rate constant," initially very high, decreased rapidly as the catalyst was consumed (table 1). The mercuric lactate, in spite of attempts at purification, still contained enough peroxide to give a positive reaction with titanous chloride.

Besides the peroxide catalysis, interfering side reactions occur. However, in all the reactions examined, whether catalyst was present or not, the reaction started as a second-order reaction. Then usually at about one-third to three-quarters life, the reaction rate, as measured by the above technique, fell off.

Generally, when the reaction is rapid, whether catalyzed or not, the yields of methoxymercurial are high. If, on the other hand, the reaction is slow, what are normally by-products become main products and the yield falls. Thus *trans*-stilbene after a period of 15 days in methyl alcohol solution with 1 equivalent of mercuric acetate yields all the mercury as mercurous acetate and no mercurial

TABLE 1

Rate constants of the methoxymercuration of cyclohexene

PURE REAGENTS: 10^{-3} MOLE PER LITER		PURE REAGENTS: 2×10^{-3} MOLE PER LITER PLUS 2×10^{-4} MOLE PER LITER OF PERACETIC ACID		PURE REAGENTS: 1.6×10^{-3} MOLE PER LITER OF MERCURIC LACTATE INSTEAD OF ACETATE	
Time	$k \times 10^{-2}$	Time	$k \times 10^{-2}$	Time	$k \times 10^{-2}$
min.		*min.*		*min.*	
3.0	27	1.2	356	4.2	141
7.0	44	4.4	134	12.3	166
16.0	37	10.6	68	29.8	112
33.1	32	24.6	45	65.2	86
52.5	35	128.2	34		
82.0	32				
110.7	35				
183.7	32				

can be isolated; by heating the solution for 4 days with a further equivalent of mercuric acetate a 20 per cent yield of $(C_6H_5CHOCH_3)_2$ is obtained. As heating the mercurial from *cis*-stilbene in methyl alcohol solution with mercuric acetate gives the same product, it seems probable that the reaction with *trans*-stilbene is so slow that the mercurial is removed by oxidation to 1,2-dimethoxy-1,2-diphenylethane as fast as it is formed (13). The addition of 0.1 equivalent of benzoyl peroxide to the reaction mixture causes the mercuration of *trans*-stilbene to take place in the course of 1 day to produce a 24 per cent yield of the normal addition product, $C_6H_5CH(HgOCOCH_3)CH(OCH_3)C_6H_5$, isolated as the chloride (13).
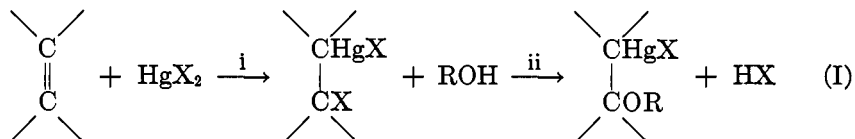
Substances such as nitriles and pyridine, which form complex compounds with mercuric salts, slow down the addition but their effect, unlike that of peroxide catalysts, increases with concentration until they are present in quantities equivalent to the reactants. Now, the addition of peroxide even in small quantities of, say, 0.1 equivalent, counterbalances the inhibition of the above substances (13).

The catalyst appears to function as an electron acceptor, and boron trifluoride

etherate, but not boron acetate, is an effective catalyst. The catalysts do not affect all mercurations equally; mercurations which are normally rapid are less affected by peroxides than those which are sluggish. The etherate, on the other hand, catalyzes both types of reaction and is also consumed during the reaction, as are the peroxide catalysts (13).
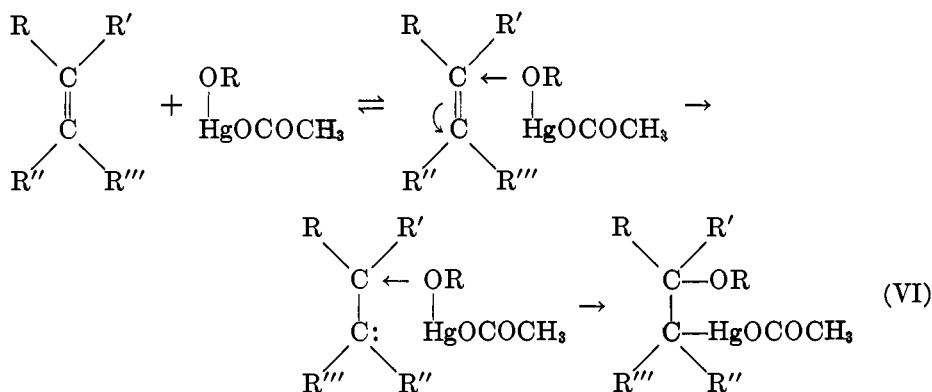
C. MECHANISM OF REACTION

No satisfactory mechanism for the reaction has been advanced. Wright's work (43, 66, 69) leaves no doubt that the addition of olefins to mercuric salts does not occur by reaction I, assumed by most workers before 1935.

$$
\begin{array}{c}
\diagdown\diagup \\
C \\
\parallel \\
C \\
\diagup\diagdown
\end{array}
+ \ HgX_2 \ \xrightarrow{\text{i}} \
\begin{array}{c}
\diagdown\diagup \\
CHgX \\
\vert \\
CX \\
\diagup\diagdown
\end{array}
+ \ ROH \ \xrightarrow{\text{ii}} \
\begin{array}{c}
\diagdown\diagup \\
CHgX \\
\vert \\
COR \\
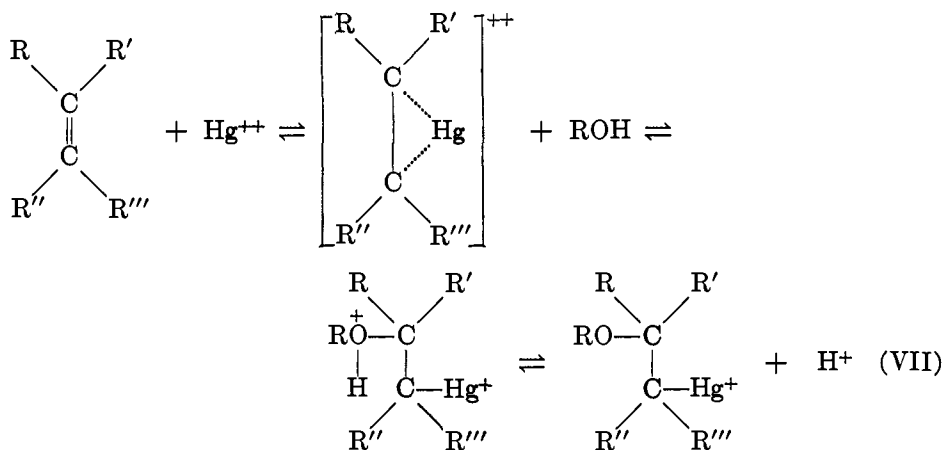\diagup\diagdown
\end{array}
+ \ HX \qquad (I)
$$

If this mechanism were correct and (ii) were the rate-controlling step, the reaction would be pseudo-unimolecular but actually it is of second order. If (i) were the rate-controlling step, the influence of the solvent should not be so marked as it is. Wright (69) has finally settled this point by preparing the addition product of cyclohexene with mercuric acetate and then reacting this with methyl alcohol. Both the rate of addition of mercuric acetate to cyclohexene and its subsequent conversion to the methoxymercurial in methyl alcohol were so slow as to preclude all possibility of these being intermediate steps in the methoxymercuration of cyclohexene by mercuric acetate in methyl alcohol solution.

Two mechanisms for the addition, both having points in their favor but neither completely satisfactory, now hold the field. In particular, neither explains the catalysis by peroxides. A free-radical mechanism seems to be excluded by the fact that isomeric olefins retain their configuration during the addition and their subsequent liberation by hydrochloric acid, an argument which is also against any mechanism involving a carbonium ion. Neither do peroxides cause any change in the orientation of the addition to the double bond.

The suggested mechanisms are as follows:

$$
\begin{array}{c}
R \diagdown \ \diagup R' \\
C \\
\parallel \\
C \\
R'' \diagup \ \diagdown R'''
\end{array}
+
\begin{array}{c}
OR \\
\vert \\
HgOCOCH_3
\end{array}
\ \rightleftharpoons \
\begin{array}{cc}
R\diagdown \ \diagup R' & \\
C \leftarrow OR & \\
\parallel & \vert \\
C & HgOCOCH_3 \\
R''\diagup \ \diagdown R''' &
\end{array}
\ \rightarrow
$$

$$
\begin{array}{cc}
R\diagdown \ \diagup R' & \\
C \leftarrow OR & \\
\vert & \vert \\
C: & HgOCOCH_3 \\
R'''\diagup \ \diagdown R'' &
\end{array}
\ \rightarrow \
\begin{array}{c}
R\diagdown \ \diagup R' \\
C - OR \\
\vert \\
C - HgOCOCH_3 \\
R'''\diagup \ \diagdown R''
\end{array}
\qquad (VI)
$$

$$R_2C=CR''R''' + Hg^{++} \rightleftharpoons \left[\text{cyclic } Hg \right]^{++} + ROH \rightleftharpoons$$

$$\overset{+}{RO}-CRR' \quad HC(Hg^+)R''R''' \rightleftharpoons RO-CRR' \quad C(Hg^+)R''R''' + H^+ \quad (VII)$$

Mechanism VI, favored by Wright (70), involves the molecular addition of the alkoxy or basic mercuric salt to the olefin. The presence of methoxymercuric acetate in a methyl alcohol solution of mercuric acetate has never been demonstrated, but it is assumed that it would be present in the equilibrium and formed rapidly. Mechanism VII is essentially ionic, with the mercurinium ion (33) as an intermediate, although $^+HgOCOCH_3$ rather than Hg^{++} is probably the reactive ion. The configuration of the olefin during the reaction is retained in the first case by the intermediate carbanion, and in the second by the cyclic mercurinium ion.

Mechanism VII leads naturally to a *trans* addition, as has already been postulated in the analogous mechanism for bromination; mechanism VI leads naturally to *cis* addition or a mixture of *cis* and *trans*. Wright overcomes this difficulty by supposing that the electrons liberated from the double bond by the attack of the alkoxyl oxygen at the face yRH of the lower tetrahedron must necessarily lead to the lone pair of the carbanion occupying the *trans* apex (x) of the second tetrahedron, because of the configurational inversion which would thus occur at the lower tetrahedron.
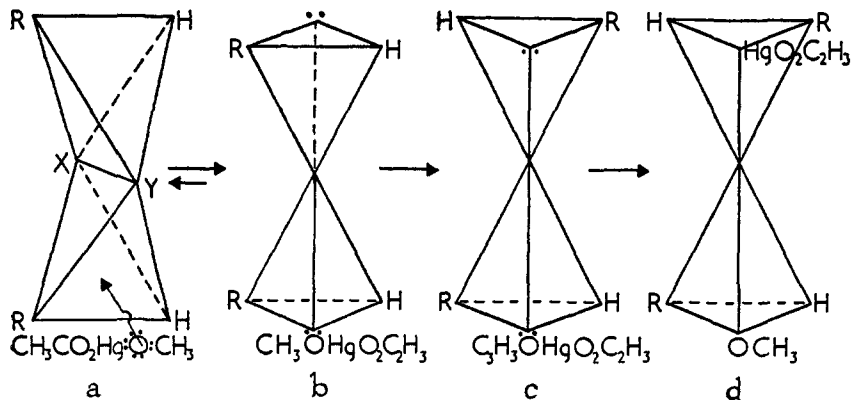
The use of tetrahedra with edges in common is perhaps not the best representation of a double bond which is really a σ bond with nonlocalized electrons in π orbitals symmetrically above and below the RCH—RCH plane. It is thus difficult to see why the addition by this mechanism would occur exclusively in a *trans* sense; also in the case of addition to cyclohexene, the free rotation converting (b) to (c) would be prevented by the cyclohexane ring. For a detailed discussion of the molecular addition mechanism the reader is referred to Wright's "Oxymercuration of Alkenes" (70).

The mercurinium-ion mechanism seems to have much in its favor; the reactions may be formulated as follows:
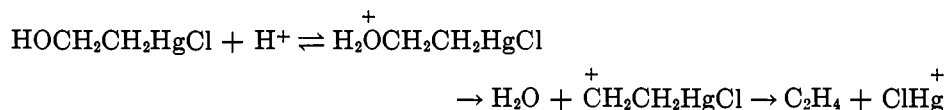
$$HgX_2 \rightleftharpoons {}^+HgX + X^- \qquad (i)$$

 (ii)

 (iii)

 (iv)
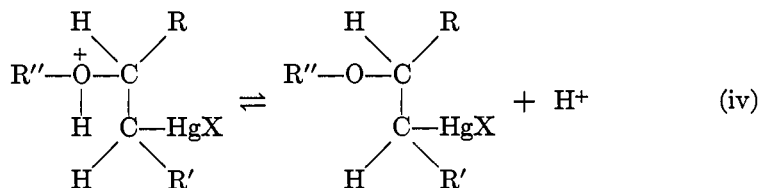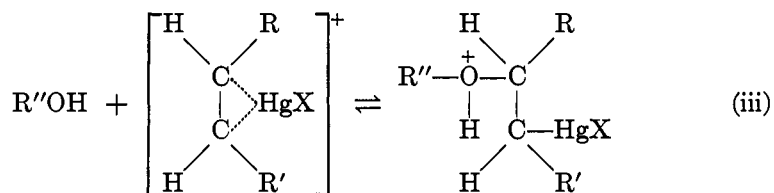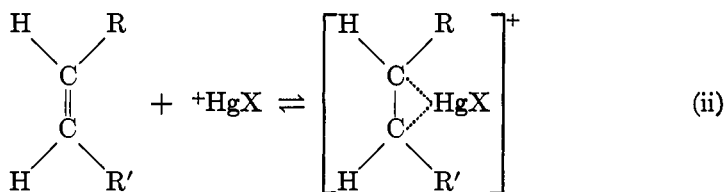
Provided the equilibrium represented by the combination of (i), (ii), (iii), and (iv) lies in favor of R″OCHR—CHR′(HgX) in neutral solution, the main features of the addition and liberation of olefins are explained:

(1) The addition occurs only in a *trans* sense.

(2) The solvent (H_2O, ROH, R_2NH, etc.) appears in the product.

(3) The reaction occurs most rapidly with the most ionic mercuric salts, e.g., when X = NO_3^-, CH_3COO^-, but is very slow when X = Cl and does not occur for X = CN or CNS.

(4) The simultaneous necessity for hydrogen ion and halide ion for the decomposition arises from the fact that reaction (i) can only be shifted in favor of HgX_2 if X^- has a high affinity for ^+HgX, as it has when X = Cl^-, Br^-, I^-, CN^-, CNS^-, etc. but not when X = NO_3^-, HSO_4^-, etc.

The decomposition by acid, of oxymercurials derived from olefins, has been

discussed by Whitmore (64), who suggested that the first stage is the addition of a proton to the oxygen atom, followed by the decomposition of the oxonium salt to a carbonium ion. This by an electron shift splits into a stable chloromercury ion and the olefin:

$$HOCH_2CH_2HgCl + H^+ \rightleftharpoons H_2\overset{+}{O}CH_2CH_2HgCl$$

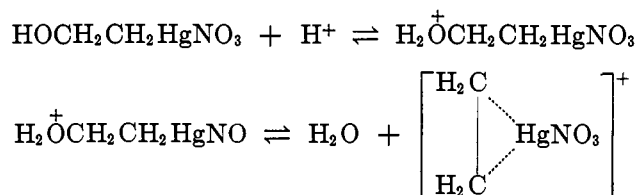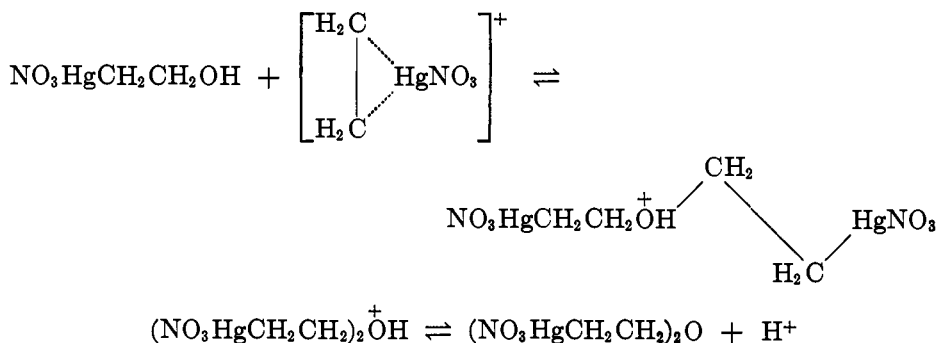$$\rightarrow H_2O + \overset{+}{C}H_2CH_2HgCl \rightarrow C_2H_4 + ClHg\overset{+}{}$$

This cannot be the whole story, because any strong acid should cause decomposition whereas, in fact, neither sulfuric nor nitric acid does so in the absence of halide or such ions. The postulate of the relatively stable mercurinium ion instead of the unstable carbonium ion as the intermediate overcomes this difficulty by introducing the equilibria (ii) and (i), the latter being shifted sufficiently to the left only by the halide type of ion.

(5) Wright (70) holds against the ionic mechanism the fact that mrecuration of olefins occurs most readily in methyl alcohol solution and not in the more ionizing solvent, water. Two factors come into play here: (a) The reaction in aqueous solution is usually heterogeneous and even if both the aqueous and methanolic solution reactions are heterogeneous, as when gaseous olefins are used, the olefin has greater solubility in methyl alcohol. (b) The final product of hydroxymercuration is an alcohol, e.g., $HOCH_2CH_2HgX$, and that of alkoxymercuration is an ether, e.g., $CH_3OCH_2CH_2HgX$. Alcohol oxygen atoms are much more basic than ether oxygen atoms; hence equilibrium (iv) will lie farther to the left in hydroxymercuration than in alkoxymercuration. It is thus the final reaction (reaction (iv)) which holds up hydroxymercuration and not the ionization reaction (reaction (i)).

(6) The preferential formation of ether salts in acid media is explained.

In aqueous acid media the reversal of equilibrium (iv) becomes important, particularly in the case of hydroxy salts, with consequent increase in concentration of the mercurinium ion, which is fairly stable in the absence of halide or such ions. Thus if the reaction is presented with two courses, one leading to a hydroxy salt and the other to an ether salt, the formation of the less basic ether salt will be favored by the presence of acid for the reason given under (5b) above. Good examples are the reaction of mercuric nitrate with allyl alcohol (page 16) and the conversion of $HOCH_2CH_2HgNO_3$ to $O(CH_2CH_2HgNO_3)_2$ by keeping it in acid solution until equilibrium is established. This reaction may be represented as follows:

$$HOCH_2CH_2HgNO_3 + H^+ \rightleftharpoons H_2\overset{+}{O}CH_2CH_2HgNO_3$$

$$H_2\overset{+}{O}CH_2CH_2HgNO \rightleftharpoons H_2O + \begin{bmatrix} H_2C \\ \\ H_2C \end{bmatrix}^+ HgNO_3$$

$$NO_3HgCH_2CH_2OH + \left[\begin{array}{c} H_2C \\ | \quad \searrow HgNO_3 \\ H_2C \end{array}\right]^+ \rightleftharpoons$$

$$NO_3HgCH_2CH_2\overset{+}{O}H \diagup\overset{CH_2}{\diagdown}\diagup HgNO_3$$

$$(NO_3HgCH_2CH_2)_2\overset{+}{O}H \rightleftharpoons (NO_3HgCH_2CH_2)_2O + H^+$$
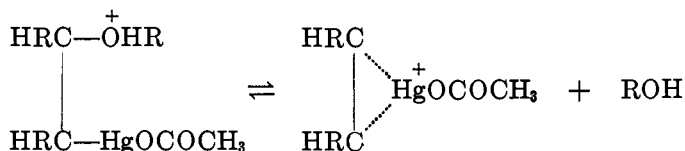
(7) The formation of cyclic products is simply explained, e.g.:
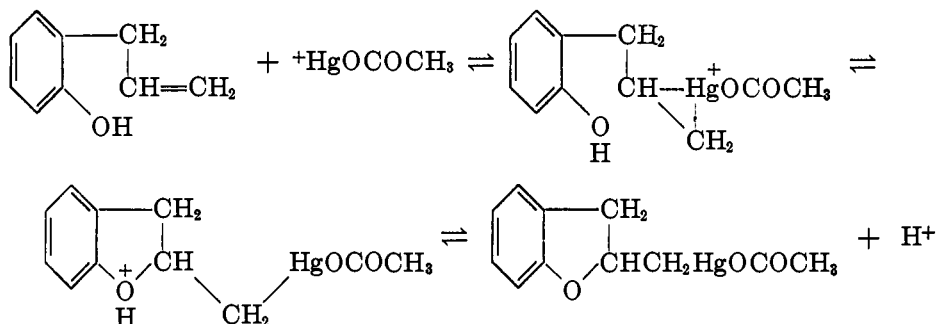
The greater stability of the ring types is explained by the fact that the oxygen atom is an ether oxygen atom and the extreme stability of the benzofuran types, as in the example above, is explained by the fact that the oxygen atom is attached to an aromatic system and has an even smaller tendency towards oxonium salt formation than has an aliphatic ether.

(8) The liberation of the olefin by hydrochloric acid, almost entirely in the same isomeric form as it was originally, is explained.

If reaction (iii) were to be reversed when the alkoxonium group occupies a position *cis* to the acetomercuri group, thus leading to a change of configuration of the olefin, the mercury atom would have to overcome the steric and electrical repulsion of the alkoxonium ion before the mercurinium ion could be formed.

$$\begin{array}{c} HR\overset{+}{C}-\overset{+}{O}HR \\ | \\ | \\ HR\overset{.}{C}-HgOCOCH_3 \end{array} \rightleftharpoons \begin{array}{c} HRC \\ | \quad \searrow \overset{+}{HgOCOCH_3} + ROH \\ HRC \end{array}$$

Hence the reaction occurs almost entirely with the —OHR and —HgOCOCH$_3$ groups in the *trans* position.

When it is impossible for the —$\overset{+}{OHR}$ group to occupy the *trans* position, as in *cis*-1-methoxy-2-(acetomercuri)cyclohexane, because of the restraint exercised by

the cyclohexane ring, the rate of decomposition by acid is found to be about one-fifth of that of the *trans* isomer (43).

(*9*) When decomposition with isomerization of the olefin occurs, then the attack probably occurs at the mercury atom. Reagents with a specially high affinity for mercury and in neutral or nonionizing solution might be expected to do this.

$$\text{ROCHRCHR'HgBr} + \text{X}^- \rightarrow \text{ROCHRCHR'}^- + \text{XHgBr}$$
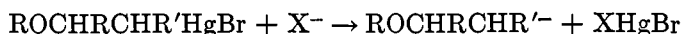
The carbanion would then decompose to the olefin and a stable alkoxyl ion, so isomerization of the olefin to the thermodynamically stable form would be expected. Grignard reagents, R''MgBr, may react in this manner by behaving as a source of the carbanion R''$^-$, which acts as the group X$^-$.

The salient facts of the uncatalyzed reaction are thus explained by the mercurinium-ion mechanism but the mechanism of the catalysis, particularly by peroxides, has not yet received any explanation.

The electronic structure of the mercurinium ion cannot be regarded as settled but is probably related to that of the silver-ion complexes, which have been investigated more thoroughly (60, 65). A study of the Raman spectra of a number of unsaturated compounds dissolved in solutions of silver salts shows a lowering of the strong double-bond frequency consistent with the view that the complex is stabilized by resonance of the forms XIX, XX, and XXI, which should be compared with V, VI, VII, and VIII (page 10) and Pitzer's structure for diborane (42).
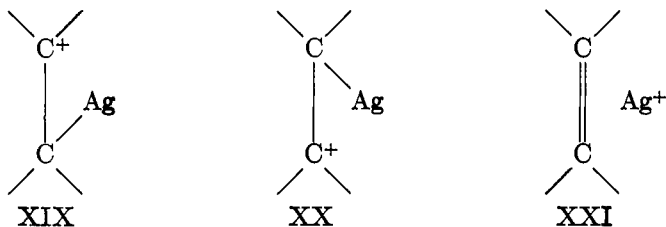
These silver-ion complexes are often compared with the platinous, palladous, and cuprous chloride olefin complexes, but this comparison does not appear to be valid. In the former case the silver ion appears to be essential and the more ionized silver salts, such as the perchlorate, form the greater variety of olefinic compounds. In the case of the platinous olefinic coördination compounds the metal is certainly not present as an ion but in a covalent state, and the oxy salts form less stable olefinic complexes than does the chloride. The presence of filled *d* orbitals on the metal atom seems to be essential for the formation of the platinous complexes (15). Thus Pitzer's structure may be correct for the silver-ion complexes and for the mercurinium ion but not for the platinous and similar covalent complexes with olefins.

We thus have an outline of what happens in the mercuration of an olefin: the reaction seems to be analogous to bromination, except that the intermediate three-membered cyclic cation (XVIII, page 34) possesses much greater stability

and longer life than its bromine analog. Many details remain to be filled in, however, before the exact mechanism of formation and decomposition of these quasi-complex compounds can be stated with certainty.

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