

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STRUCTURE OF THE COMPOUNDS PRODUCED FROM OLEFINS AND MERCURY SALTS: MERCURATED DIHYDROBENZOFURANS

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Received May 25, 1922

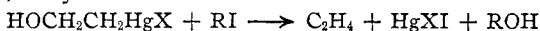
From the time it was first discovered that mercury salts would react with olefins, there has been a controversy as to the structure of the products.

Hofmann and Sand showed that ethylene and mercuric or basic mercuric salts react in aqueous solutions to give two compounds to which they at first assigned the formulas $\text{HOCH}_2\text{CH}_2\text{HgX}$ and $\text{XHgCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{HgX}$;¹ when the reaction takes place in an alcohol solution a single substance is produced which corresponds to the formula $\text{ROCH}_2\text{CH}_2\text{HgX}$. The first two substances react with iodine to give, respectively, ethylene iodohydrin, $\text{HOCH}_2\text{CH}_2\text{I}$, and β, β' -di-iodo-diethyl ether, $\text{ICH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{I}$, the structures of which are unquestioned; moreover, the first of the above-mentioned mercury compounds reacts with benzoyl chloride to give a benzoyl derivative with the formula $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_2\text{HgI}$.²

On the other hand, all of the mercury compounds, even the benzoyl derivative just mentioned, are decomposed most readily by the action of mineral acids, especially hydrochloric acid even when very dilute, to give a mercuric salt, ethylene and a residual product, water, an alcohol or benzoic acid, depending upon the nature of the substance treated.



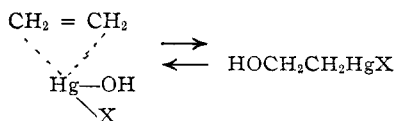
The compound $\text{HOCH}_2\text{CH}_2\text{HgX}$ also reacts with alkyl iodides to give a mercuric salt, ethylene and an alcohol.



Both of these last reactions are decidedly different from those of simple alkyl mercuric halides which are unchanged by dil. acids but by heating with conc. acid are converted into a hydrocarbon and a mercuric halide.³



and are unaffected by boiling with alkyl halides. These facts lead Sand to modify his original views and to assume that the addition compounds were tautomeric;⁴ thus, the structure of the simple compound between ethylene and mercuric chloride would be formulated as follows.



¹ Hofmann and Sand, *Ber.*, **33**, 2694 (1900). Sand, **34**, 1388, 2906 (1901).

² Sand, *ibid.*, **34**, 1390 (1901). Manchot, *ibid.*, **53**, 984 (1920).

³ Buckton, *Ann.*, **108**, 105 (1858).

⁴ Sand, *ibid.*, **329**, 151 (1903).

The first formula would explain the reaction with acids and with alkyl halides, while the second would represent the reaction with iodine.

Manchot also believes that the products from olefins and mercuric salts are not normal double-bond addition compounds, but prefers to formulate the various substances in a slightly different way from Sand, merely as of the double salt or molecular type:⁵ $C_2H_4 \cdot Hg(OH)X$; $2C_2H_4 \cdot HgO \cdot HgX_2$; $C_2H_4 \cdot Hg(OR)X$; $C_2H_4 \cdot Hg(OCOR)X$. In a recent publication he has given a detailed account of the previous work in this field and points out in detail his reasons for adopting the molecular formulas just mentioned. Such formulas explain well the reactivity of the compounds with acids or alkyl halides but on the other hand certain other reactions are not so simply explained.

It is apparent from reading the publications of others interested in mercuric compounds formed by the addition of mercuric salts to olefins, that the formulas representing true addition to the double bond are generally accepted. The action of acid or of alkyl halides is explained merely by the peculiar reactivity of the particular grouping $-OCH_2CH_2HgX$. The present authors hold this same view. Manchot cannot reconcile himself to believing that compounds of this type could have such peculiar activity when alkyl mercuric halides react so differently and when ordinary alcohols are usually so stable. There are, however, innumerable examples in organic chemistry where a combination of groups, especially when attached to adjacent carbons, causes a new type of activity. As examples might be mentioned that the carboxyl group in the compound RCO_2H is stable, but in the compound $RCOCH_2CO_2H$ exceedingly unstable; that the hydroxyl in the substance $RCHOHCH_2CO_2H$ has a much greater tendency to be eliminated with the formation of a double bond than in the substance $RCHOHCH_3$; that the compound $C_6H_5OCH_2CH_2Br$ reacts with sodium ethylate,⁶ or sodium malonic ester⁷ or sodium cyanide to give not the expected derivative, but in every instance almost exclusively the substance $C_6H_5OCH_2CH_2OC_6H_5$; that the addition compound between acetylene and arsenic chloride,⁸ having the formula $ClCH=CHAsCl_2$, reacts with cold sodium hydroxide solution to give not the expected product, $ClCH=CHAsO$, but instantly complete decomposition with the quantitative regeneration of acetylene; that the compound $R_2NaC \cdot CNaR_2$ reacts with $R'I$ to give not $R_2R'C - CR'R_2$ but $R_2C=CR_2$, sodium iodide and the hydrocarbon $R'R'$.

In discussing the mercury addition compounds, Manchot neglected to

⁵ Manchot, *Ann.*, **420**, 174 (1920), in which references are given to previous articles in same field; *ibid.*, **421**, 316, 331 (1921).

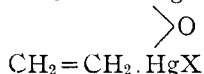
⁶ Perkin, *J. Chem. Soc.*, **69**, 1503 (1896).

⁷ Perkin, *ibid.*, **69**, 171 (1896).

⁸ Green and Price, *ibid.*, **119**, 448 (1921).

⁹ Schlenck, *Ber.*, **47**, 473 (1914).

point out certain known facts which are extremely difficult to explain provided molecular formulas are assumed. In order to show how ethylene iodohydrin and β, β' -di-iodo-diethyl ether can be produced by the action of iodine on the addition compounds of mercuric iodide and ethylene, $\text{CH}_2=\text{CH}_2 \cdot \text{Hg}(\text{OH})\text{X}$ and $\text{CH}_2=\text{CH}_2 \cdot \text{HgX}$, Manchot assumes that



because the mercury has a greater affinity for iodine than it does for oxygen the oxygen is forced out and immediately attaches itself to one of the carbons in the ethylene. This produces a disturbance in the molecule which then allows an atom of iodine to be taken up by the other carbon, forming the substances which are actually obtained. This explanation in itself is rather an extraordinary one and does not have any analogs in organic chemistry. By the true addition formulas, no complex assumptions have to be made. Even though the explanation by Manchot is perhaps possible for the simple mercury derivatives, it seems very unlikely that analogous reactions with iodine would take place in such compounds as would be formulated by Manchot as follows: $\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OR})\text{I}$ or $\text{C}_2\text{H}_4 \cdot \text{Hg}(\text{OCOR})\text{I}$ to give $\text{ROCH}_2\text{CH}_2\text{I}$ or $\text{RCO}_2\text{CH}_2\text{CH}_2\text{I}$.

Manchot has neglected to explain by means of molecular formulas the formation of certain secondary products from various addition compounds. There are numerous cases mentioned in the literature where the HgX group in the addition compound may be replaced by hydrogen by means of alkaline reagents without disturbing the hydroxyl or substituted hydroxyl group. The following transformations take place with the greatest readiness. In each case the formulas are written as true addition products. By means of alcoholic ammonia and hydrogen sulfide, the substances represented by the formula, $\text{C}_6\text{H}_5\text{CH}(\text{OR})\text{CH}(\text{HgOAc})\text{CO}_2\text{CH}_3$, are converted very smoothly into methyl β -alkoxy hydrocinnamates, $\text{C}_6\text{H}_5\text{CH}(\text{OR})\text{CH}_2\text{CO}_2\text{CH}_3$,¹⁰ by means of sodium hydroxide and hydrogen sulfide, the substance $\text{C}_6\text{H}_5\text{CHOHCH}(\text{HgOAc})\text{CO}_2\text{H}$ gives an 80% yield of phenyl



hydracrylic acid, $\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CO}_2\text{H}$,¹¹ the compound $\text{C}_6\text{H}_5\text{CH}(\text{OR})\text{CH}(\text{HgOAc})\text{CO}_2\text{H}$ gives a practically quantitative yield of β -ethoxy-hydrocinnamic



acid, $\text{C}_6\text{H}_5\text{CHORCHCO}_2\text{H}$,¹² the compound $\text{CH}_3\text{CHOHCH}(\text{HgOAc})\text{CO}_2\text{H}$ gives β -hydroxy-butyric acid.¹³ In none of the replacement

¹⁰ Schoeller, Schrauth, Struensee, Ref. 12; *Ber.*, **44**, 1048, 1432 (1911); *Ger. pat.*, 228,877.

¹¹ Biilmann, *Ber.*, **35**, 2571 (1902); **43**, 575 (1910).

¹² Schoeller, Schrauth, Struensee, *ibid.*, **43**, 697 (1910).

¹³ Ley, *ibid.*, **33**, 1014 (1900); *Bull. soc. chim.*, [3] **33**, 1320 (1905). Ref. 11, p. 2572; p. 579.

reactions which have just been noted will the reagents used convert the initial products, to which the mercuric salt has originally been added, into the final products which are obtained by the action of the same reagents on the mercuric salt addition compounds. Consequently, it is most improbable that the mercuric salt addition compound first decomposes into the original products, before the formation of the final product takes place.

Another reaction difficult to explain by molecular formulas is the reduction of $\text{HOCH}_2\text{CH}_2\text{HgX}$ or $\text{CH}_3\text{CHOHCH}_2\text{HgX}$ in alkaline solution either electrolytically or by sodium amalgam and water to give ethyl or isopropyl alcohol, respectively.¹⁴

An interesting fact in regard to various organic mercury compounds should not be overlooked. Mercury salts form in a great many instances double salts with various types of organic compounds. In practically every instance where one molecule of mercuric salt is involved, the resulting substance consists either of one molecule of organic compound and one molecule of mercuric oxide, or one molecule of organic compound and one molecule of mercuric salt. The present authors have been unable to find, however, any such compounds with the exception of the olefins where the basic mercury salt and not the normal salt was added. If there are any, they are exceptions and not the rule. It seems probable that if the ethylene derivatives were merely molecular compounds they would have the general formula $\text{C}_2\text{H}_4\cdot\text{HgX}_2$, and not $\text{C}_2\text{H}_4\cdot\text{Hg}(\text{OH})\text{X}$.

The general instability to acid has been one of the fundamental reasons for assuming that mercury salt addition compounds are molecular in type. On the other hand, if such compounds were found which were stable to acids, doubt would be thrown on the molecular formulas. It has been pointed out by many investigators that the addition compounds show stability to acetic acid but are unstable to mineral acids, especially hydrochloric acid. It is not true that all such compounds have this property since a number have been described in the literature which are decidedly stable. The compound derived from allyl alcohol by the addition of basic mercuric salts has the formula $\text{CH}_2\text{OHCHOHCH}_2\text{HgX}$ and is unstable to hydrochloric acid;¹⁵ on the other hand, the dibenzoyl derivative is perfectly stable to conc. hydrochloric acid.

Another product which is stable to acid is of considerable interest; in fact, it is formed in acid solution¹² from allyl alcohol and mercuric salts and probably has the structural formula $\text{CH}_2\text{—O—CHCH}_2\text{HgX}$. The

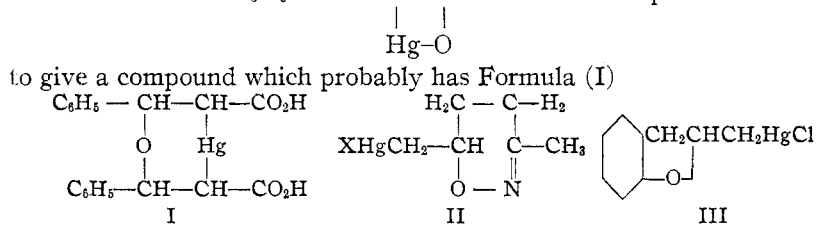


¹⁴ Sand and Singer, *Ber.*, **35**, 3180 (1902).

¹⁵ Büllmann, *ibid.*, **33**, 1642 (1900). Hofmann and Sand, *ibid.*, **33**, 2700 (1900). Sand and Hofmann, *ibid.*, **33**, 1359 (1900).

formation of such a substance may be explained by the primary addition of HgX_2 to allyl alcohol and then the condensation of two molecules of the product with the elimination of 2 molecules of halogen acid. It would be very difficult to find a reasonable molecular formula to agree with the correct empirical formula.

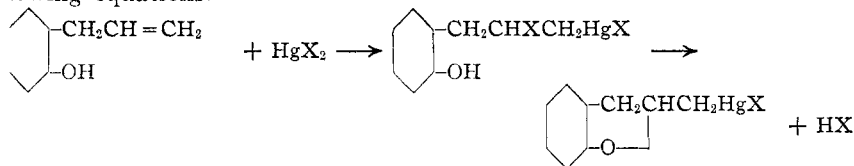
The substance $\text{C}_6\text{H}_5\text{CHORCH}-\text{CO}$ reacts with potassium iodide¹²



and which is perfectly stable to boiling conc. acid and also to ammonium sulfide. Such stability would seem absolutely inconceivable when the structure is written as a molecular formula $2\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{H} \cdot \text{HgO}$.

An interesting compound in which an intermolecular condensation has taken place is described in the literature, although the final product is unstable to acid.¹⁶ It is formed by the addition of mercuric acetate to allyl acetoxime (II). Again, to find a satisfactory molecular formula for this substance would be difficult.

The possibility of acquiring a further insight into the nature and structure of mercury addition compounds by studying those that might condense intermolecularly to give acid-stable products, and especially to give products the structures of which might readily be determined, can immediately be seen. Such compounds can be produced by the treatment of *o*-allyl-phenol with mercuric salts. There are thus formed mercurated dihydrobenzofurans the properties and reactions of which afford convincing proof that they have such structures. The reactions take place with the greatest ease and at room temperature in the manner shown by the following equations.



The primary addition product is unstable, as would be expected, but instead of hydrolyzing in the usual way with the water used as the solvent to give a product containing the side chain, $-\text{CH}_2\text{CHOHCH}_2\text{HgX}$, the acid X group attached to the carbon has a greater tendency to react with the hydrogen of the phenol group with the elimination of a molecule of HX and the production of a dihydrobenzofuran derivative. It is certain

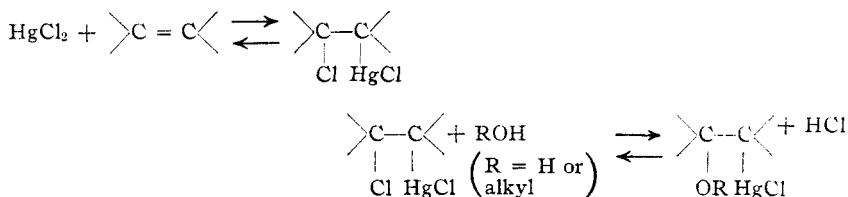
¹⁶ Ref. 4, p. 181.

that the mechanism given above is correct, since identically the same product is formed when an alcohol is used as a solvent in place of water. If the acid grouping X on the carbon atom first reacted with the water or alcohol, the intermediate products would be stable under the conditions employed and no ring structure would be formed. This is especially true if an alcohol is used as a solvent since an ether would thus be produced which would have no tendency to condense with the formation of a dihydrobenzofuran.

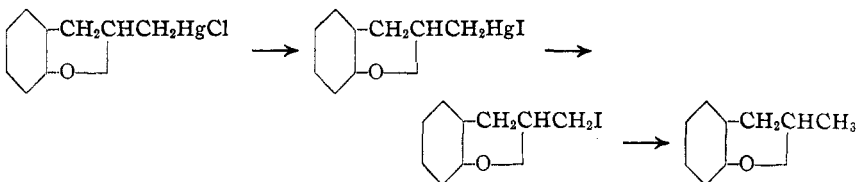
Probably the most interesting fact concerning the mercurated dihydrobenzofurans is their remarkable stability to acids in comparison with other olefin-mercuric salt addition compounds. One would predict from their structure that the former might be more stable to acids than the latter. Thus, it is found that 1-chloromercurimethyl-1,2-dihydrobenzofuran (III) is perfectly stable to boiling glacial acetic acid; it is undecomposed by 15% hydrochloric acid or 50% sulfuric acid even after standing at ordinary temperatures for several days. Conc. hydrochloric acid, however, decomposes the substance during the course of a few minutes to yield *o*-allyl-phenol and mercuric chloride, the expected products, provided the mercurated dihydrobenzofuran decomposes with acid in the same manner as other mercury salt-olefin compounds. The corresponding sulfate is even more stable to acids than the chloride.

The mercuric salt of acetic acid will add directly to olefins, but the mercuric salts of mineral acids cannot in general be added to olefins unless alkali is present. This may be interpreted as meaning that a basic mercury salt first forms and then adds to the double bond; mercuric acetate adds without alkali since a certain amount of basic mercuric acetate is always present in solution and the final addition compound is stable to acetic acid. On the other hand, an interpretation that seems more likely is that the normal mercury salt adds in each case but that the acid group attached to the carbon immediately hydrolyzes with the formation of a molecule of acid; if this is a mineral acid it immediately causes practically a complete reversion unless alkali is present for its neutralization. If the latter interpretation is correct, mercury salts of mineral acids such as mercuric chloride and sulfate should add to *o*-allyl-phenols without the addition of alkali just as readily as mercuric acetate, because the resulting dihydrobenzofurans are stable to mineral acids. This is exactly what happens—practically quantitative yields of mercurated dihydrobenzofurans are obtained merely by treating an aqueous solution of mercuric chloride or an acid solution of mercuric sulfate with *o*-allyl-phenol. Moreover, it was observed that when mercuric chloride and *o*-allyl-phenol were condensed in a hydrochloric acid solution, there always formed along with the mercurated dihydrobenzofuran, various amounts of by-product which was readily converted to the mercurated dihydrobenzofuran by

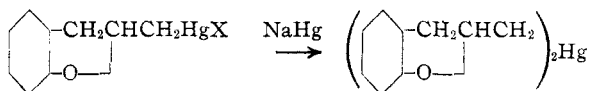
crystallizing the reaction product from water or alcohol. This by-product was not obtained pure but was undoubtedly an unstable intermediate product, the addition compound of *o*-allyl-phenol to normal mercuric chloride. This is further evidence that the mechanism of this type of reaction is represented as follows.



The mercurated dihydrobenzofurans, as for example that formed from mercuric chloride and *o*-allyl-phenol, react rapidly and quantitatively with potassium iodide to give the corresponding iodides, which on treatment with iodine yield 1-iodomethyl-1,2-dihydrobenzofuran, that can be readily reduced to a 1-methyl-1,2-dihydrobenzofuran.



Mercurated dihydrobenzofurans, upon treatment with sodium amalgam, yield compounds of the type R_2Hg ,

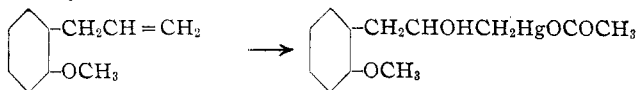


The formation of such dialkyl mercury compounds is of considerable interest because no case is reported in the literature where the mercury salt addition products to olefins can be converted into the corresponding dialkyl mercury compounds. This reaction is in general typical merely of alkyl mercuric halides. From this reaction, as well as the stability to acids, it can be seen that the mercurated dihydrobenzofurans resemble closely alkyl mercuric halides.

It is needless to discuss molecular formulas for the mercurated dihydrobenzofurans. It is impossible to write one which will explain in a reasonable way their structure or their various reactions which have just been mentioned. The simple addition formulas allow for a simple explanation of all the experimental facts.

If *o*-allyl-phenol methyl ether is treated with mercuric salts, it would be expected that only mercuric acetate would add if alkali is not present, since the formation of dihydrobenzofurans is prevented by the presence

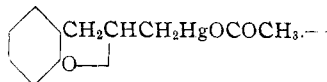
of the methyl ether. This is exactly what is found, mercuric chloride and sulfate yielding no addition product. Mercuric acetate does add and the product resembles in its reactions the mercuric acetate addition compounds of any ordinary olefin.



A further study of mercurated dihydrobenzofurans is being made.

Experimental

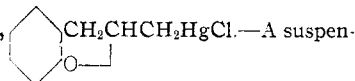
1-Acetoxymercurimethyl-1,2-dihydrobenzofuran,



A solution of 23.7 g. of mercuric acetate in 100 cc. of water was added slowly with stirring to a suspension of 10 g. of *o*-allyl-phenol in 100 cc. of water. The reaction mixture was then stirred for an additional half hour during which time a heavy, grayish oil settled out. The aqueous solution was poured off and set aside to stand overnight, during which time crystals separated from the solution. After several hours the gray oil, which remained as a residue, solidified. The crystals from the aqueous solution and the solidified gray oil were mixed and crystallized from water or alcohol, and then formed white plates melting at 80–81°. The yield was nearly quantitative.

Analysis. Subs., 0.1824: Hg, 0.0930. Calc. for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{Hg}$: Hg, 50.9. Found: 51.0.

1-Chloromercurimethyl-1,2-dihydrobenzofuran,



A suspension of 25 g. of *o*-allyl-phenol in a solution of 52.5 g. of mercuric chloride in 1000 cc. of water was stirred mechanically for 3 hours during which time a white solid separated. This was filtered off and after crystallization from alcohol weighed 66.5 g. it melted when pure at 137°.

Analyses. Subs., 0.5355, 0.6243, 0.7794: CO_2 , 344.8 cc. (30°, 743 mm.), 396.2 cc. (28°, 743 mm.), 493.8 cc. (26°, 743 mm.). Calc. for $\text{C}_9\text{H}_9\text{OClHg}$: C, 29.3. Found: 29.1, 29.0, 29.2.

Subs., 0.1819, 0.1953: Hg, 0.0984, 0.1063. Calc. for $\text{C}_9\text{H}_9\text{OClHg}$: Hg, 54.2. Found: 54.1, 54.4.

This substance can also be produced by warming a solution of sodium chloride with an aqueous solution or suspension of 1-acetoxymercurimethyl-1,2-dihydrobenzofuran.

When 13.5 g. of mercuric chloride was dissolved in 43 cc. of absolute alcohol and 6 g. of *o*-allyl-phenol added, a white precipitate began to settle as soon as stirring was started. In about 20 minutes no more solid appeared. This was filtered off and dried. It weighed 4.5 g. and was practically pure 1-chloromercurimethyl-1,2-dihydrobenzofuran. The filtrate was treated with 12 to 15 g. of mercuric chloride (adding small amounts gradually until no more dissolved). A white precipitate was produced which proved to be slightly impure product. It melted at about 134° and was pure after one crystallization; 15 g. was obtained. By repeating the same treatment with the filtrate more product was obtained but it was distinctly impure.

A similar experiment was carried out, using mercuric chloride in *n*-butyl alcohol. A white precipitate was produced which proved to be 1-chloromercurimethyl-1,2-dihydrobenzofuran. The yields, however, were not as good as when ethyl alcohol was used.

A solution of 20 g. of mercuric chloride in 250 cc. of water and 5 cc. of conc. hydrochloric acid was heated on a water-bath and mechanically stirred while 10 g. of *o*-allyl-phenol was added, drop by drop, during the course of 2 hours. A precipitate was formed which later became pinkish. After the addition was complete, stirring was continued for half an hour longer. By filtration a crude product was formed which obviously contained two different substances. Upon recrystallizing this crude product, however, from water and alcohol there appeared to be complete conversion of the impurity into the 1-chloromercurimethyl-1,2-dihydrobenzofuran. Whenever the addition of mercuric chloride to *o*-allyl-phenol was carried out in the absence of hydrochloric acid and heating, no such impurity appeared.

1-Bromomercurimethyl-1,2-dihydrobenzofuran.—This substance was formed quantitatively from a solution of 3 g. of 1-acetoxymmercurimethyl-1,2-dihydrobenzofuran in 200 cc. of water when treated with 3 g. of potassium bromide and the mixture warmed on a water-bath for about an hour to complete the reaction. After cooling and standing for some time, the precipitate was filtered and washed. The product was crystallized from alcohol, from which it formed white, shining crystals melting, when pure, at 122°. The yield was practically quantitative.

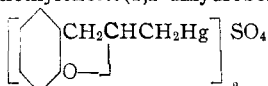
Analyses. Subs., 0.4595, 0.4040: 43.1 cc., 37.9 cc. of 0.02599 *N* NaCN. Calc. for C_9H_9OBrHg : Hg, 48.50. Found: 48.77, 48.86.

1-Iodomercurimethyl-1,2-dihydrobenzofuran.—This substance was formed by treating 1-acetoxymmercuri-1,2-dihydrobenzofuran with potassium iodide as described for the bromide. It formed white plates which upon crystallization from alcohol melted at 114–115.5°.

It was also produced by powdering 1-chloromercurimethyl-1,2-dihydrobenzofuran and heating it to boiling with stirring for 5 minutes with an aqueous solution of potassium iodide.

Analyses. Subs., 0.1953, 0.1938: Hg, 0.0858, 0.0849. Calc. for C_9H_9OIHg : Hg, 43.3. Found: 43.4, 43.8.

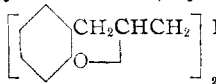
1,1-Sulfatomercuridimethylenebis(1,2-dihydrobenzofuran),



—A solution of mercuric sulfate was made by warming 7 g. of mercuric oxide with 20 cc. of conc. sulfuric acid in 180 cc. of water. The solution was then cooled, 5 g. of *o*-allyl-phenol was added very slowly from a dropping funnel, and the mixture was stirred vigorously. Particular care was taken not to add the *o*-allyl-phenol so fast that drops of liquid settled to the bottom, since the formation of a pure product depended upon having the *o*-allyl-phenol completely dissolved before precipitation of the sulfate began. After the 5 g. of *o*-allyl-phenol was added, a precipitate started to form, and practically the entire amount of condensation product which was present in solution separated. It was filtered off within a few minutes, since the sulfuric acid tended to turn it dark upon standing. The product was washed carefully with water and then dried. No good solvent was found for this product. The substance as formed, however, was quite pure as shown by analyses. It melted with decomposition at 123°.

Analysis. Subs., 0.3030: 30.5 cc. of 0.02599 *N* NaCN. Calc. for $C_{18}H_{18}O_6SHg_2$: Hg, 52.45. Found: 52.56.

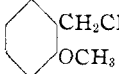
1,1-Mercuridimethylenebis(1,2-dihydrobenzofuran) by the Reduction of 1-Chloromercurimethyl-1,2-dihydrobenzofuran,



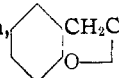
—Fifteen g. of 1-chloromercurimethyl-1,2-dihydrobenzofuran and 100 cc. of absolute alcohol were placed

in a 200cc. round-bottom flask with a reflux condenser attached. Three g. of sodium amalgam containing 1.5 g. of sodium was added, a few pieces at a time, through the condenser. The flask was then heated very gently to start the reaction and to keep it running smoothly until the amalgam was decomposed (20 min.). The mixture was finally boiled for half an hour. The crystals of 1-chloromercurimethyl-1,2-dihydrobenzofuran completely disappeared at the end of this time and a grayish precipitate had formed in the flask. After cooling, the precipitate was filtered off and was found to consist of 2.5 g. of sodium chloride with a trace of organic impurities. The alcohol solution was allowed to evaporate, whereupon white crystals appeared as nodules together with a slight amount of sticky impurity. The crystals were redissolved in ether, a large portion of the impurities remaining as a sediment in the bottom of the flask. Upon evaporation of the ether, crystals still somewhat impure were obtained. The melting point was 88–90°. These crystals were purified further by dissolving them once more in ether and crystallizing in the usual way. Pure white crystals were finally obtained, melting sharply at 93°. The yield was 6 g. of pure crystals and about 1 g. of impure product recovered from the mother liquor, equivalent to about a 50% yield of purified product.

Analyses. Subs., 0.4700, 0.4150: 38.65, 33.70 cc. of 0.02599 *N* NaCN. Calc. for $C_{18}H_{15}O_2Hg$: Hg, 42.98. Found: 42.88, 42.76.

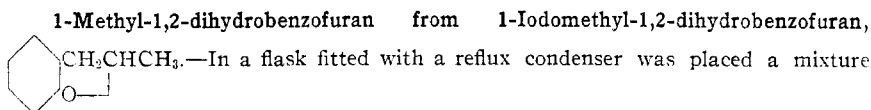
1-Acetoxymercuri-3-*o*-anisyl-2-propanol, .—To a

solution of 23.7 g. of mercuric acetate in 100 cc. of water was added slowly with stirring, 10 g. of *o*-allyl-anisol. The mixture was stirred for several hours during which time a thick grayish oil separated. The aqueous layer was removed and the oil allowed to stand. It did not solidify and no convenient way was found for purifying it. Upon treatment with hydrochloric acid it proved to be decidedly unstable, regenerating *o*-allyl-anisol. When shaken with sodium chloride it apparently was converted into the corresponding chloride compound which was also an oil. Mercuric acetate also reacted with *o*-allyl-anisol in absolute methyl alcohol to give an oily addition product. Mercuric chloride or sulfate did not react with *o*-allyl-anisol.

1-Iodomethyl-1,2-dihydrobenzofuran from 1-Iodomercrimethyl-1,2-dihydrobenzofuran, .—Twenty g. of 1-iodomercurimethyl-1,2-dihydrobenzofuran

was finely ground and suspended in a solution of 11 g. of iodine, 20 g. of potassium iodide and 250 cc. of water. The mixture was stirred mechanically and heated just to boiling. Within a very short time the black solution turned to a light red after which the flame was removed and the mixture stirred for about 10 minutes longer. A heavy black oil precipitated and was removed and washed once with potassium iodide solution. Upon distillation, it boiled at 129–130° at 4 mm. and the distillate weighed 9.4 g. The liquid was practically colorless except for the first and last drops of distillate. Upon redistillation it boiled at 150–151° at 13–15 mm. and then, on standing overnight, formed to a pink solid. This solid, when pressed on a porous plate, became practically pure white and after a crystallization from absolute alcohol melted at 36.5–37.5°. The constants for the liquid material before it solidified were as follows: d_{25}^{24} , 1.792; n_D^{23} , 1.614.

Analyses. Subs., 0.2055, 0.2456: 7.24, 8.63 cc. of 0.1096 *N* AgNO₃. Calc. for C_9H_9OI : I, 48.8. Found: 49.0, 48.9.



of 32.5 g. of 1-iodomethyl-1,2-dihydrobenzofuran, 48 g. of granulated zinc and 270 cc. of 20% hydrochloric acid. This mixture was stirred mechanically and heated on a boiling water-bath for about 3 hours. 1-Methyl-1,2-dihydrobenzofuran was produced and rose to the top as it formed. It was separated, washed with a little sodium chloride solution containing sodium bicarbonate, filtered off and dried. The boiling point was 199–202° at 744 mm. and gave the constants, d_{20}^{24} , 1.507, n_D^{22} , 1.536, indicating without doubt that it was 1-methyl-1,2-dihydrobenzofuran.

The analyses for mercury on several of the compounds described in this paper, were kindly made by E. B. Middleton of Northwestern University using the method described by F. C. Whitmore in his book "Organic Mercury Compounds," p. 365.

The analyses for mercury on the other compounds were made by a slight modification of the procedure described by Bauer.¹⁷

A weighed sample of substance, about 0.5 g., was placed in a 200cc. round-bottom flask fitted with a rubber stopper holding a small separatory funnel and an outlet tube attached to a Peligot tube filled with water. Through the funnel 5 cc. of conc. hydrochloric acid was added to the compound and the mixture warmed until decomposition took place. The mercury compound was thus decomposed completely with the formation of mercuric chloride. The water in the Peligot tube was now washed back into the reaction flask and the dilution brought up to 100 cc. Hydrogen sulfide was passed through the solution until the precipitation was complete. The mercuric sulfide was filtered and washed. The filter paper holding the mercuric sulfide was now returned to the original flask, the flask again attached to the Peligot tube, a mixture of 2 cc. of conc. nitric acid and 2 cc. of conc. hydrochloric acid added and the mixture boiled for about 3 minutes. The resulting solution was then diluted to about 100 cc., the sulfur carefully filtered off, and the filtrate made alkaline with ammonium hydroxide. This solution was then titrated for mercury in the following way. First, 5 cc. of a 10% potassium iodide solution was added together with a small amount of a standard silver nitrate solution sufficient to give a precipitate. This mixture was then titrated with a standard sodium cyanide solution which took the precipitated silver iodide into solution and formed a complex with the mercury. The excess of sodium cyanide was then titrated with the standard silver nitrate solution until cloudiness appeared.

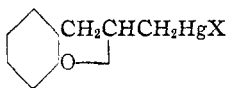
By this process very good results were obtained in all cases. The decomposition of the above mercury compounds by means of hydrogen peroxide did not give satisfactory results.

Summary

1. Experimental evidence is adduced from the literature to disprove molecular formulas, such as $\text{CH}_2=\text{CH}_2.\text{Hg}(\text{OH})\text{X}$, for the compounds from olefins and mercuric salts.

2. Not only mercuric acetate but also mercuric chloride and sulfate condense with *o*-allyl-phenol to give mercurated dihydrobenzofurans of the general structure

¹⁷ Bauer, *Ber.*, **54**, 2079 (1921).



These compounds are remarkably stable to acids in comparison with other mercury salt-olefin compounds.

3. The mercurated dihydrobenzofurans formed from mercuric acetate or mercuric chloride and *o*-allyl-phenol, upon treatment with potassium iodide, yield the corresponding iodide. This iodide, on treatment with iodine, yields 1-iodomethyl-1,2-dihydrobenzofuran which in turn is readily reduced to 1-methyl-1,2-dihydrobenzofuran.

4. The mercurated dihydrobenzofurans, by treatment with sodium amalgam, give compounds of the general type R_2Hg .

5. No reasonable molecular formula for the mercurated dihydrobenzofurans can be written which will explain the structure and the chemical reactions of these compounds. The addition formula allows for a simple explanation of all the experimental facts.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE
UNIVERSITY OF IOWA]

THE MIGRATION OF ACYL FROM NITROGEN TO OXYGEN

BY L. CHAS. RAIFORD AND JOHN R. COUTURE

Received May 29, 1922

In a previous communication from this laboratory¹ it was pointed out that when certain aminophenols were acylated in such a way as to introduce both the acetyl and the benzoyl radicals into the same molecule, the heavier of these groups was found attached to nitrogen, regardless of the order in which they were introduced. In one case acetyl must have migrated from nitrogen to oxygen, while benzoyl may have shifted in the opposite direction. It was recognized at that time, however, that the cases studied might have been isolated ones, and that much more work would be necessary to show that the behavior of these substances represented a general reaction. Attention was drawn also to the possibility that this rearrangement might be determined by factors other than that which was emphasized in the first observations, namely, the difference in weight of the acyl radicals.

To answer the question whether the behavior reported for the three bases already studied is general for the group, it seemed important, first of all, to show that aminophenols isomeric with one of those previously studied and differing from it only in the relative positions of the radicals present, with the exception that the hydroxyl and amino groups must

¹ THIS JOURNAL, 41, 2068 (1919).