acid were heated together. The product separated as an oil when the mixture was poured into water, but it solidified after standing a day. The crude product was light brown and melted at 65°. Purification by alcohol raised the melting point to 103°. It crystallizes in almost colorless needles, that are soluble in acetone, alcohol, ether, benzene or chloroform.

*Analysis.* Subs., 0.1591: AgCl, 0.1849. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.75.

## Summary

1. The three new nitrodichloro-acetanilides were prepared.

2. The *p*-compound appeared as a decomposition product when dichloro-hydroxy-ethylidene-bis-*p*-nitro-aniline was treated with hot dil. sulfuric acid. Its production established the location of the hydroxyl group on the $\alpha$-carbon. The methoxy and ethoxy derivatives gave the same anilide.

3. The *o*-nitrodichloro-acetanilide was similarly obtained.

4. The *ortho* and *para* compounds were also obtained by the action of dichloro-acetic acid on the nitro-anilines in the presence of phosphorus pentoxide.

5. The *meta* isomer could be obtained only by the direct method since the hydroxy and alkoxy derivatives of trichloro-ethylidene-bis-*m*-nitro-aniline cannot be prepared

CHAPEL HILL, NORTH CAROLINA

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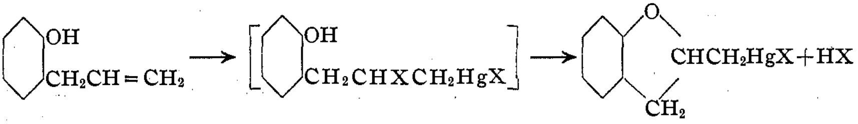
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# MERCURATED 1-METHYL-1,2-DIHYDRO-BENZOFURANS

BY LINDLEY E. MILLS WITH ROGER ADAMS[1]

Received May 24, 1923

In a recent paper by Roger Adams, F. L. Roman and W. N. Sperry,[2] involving a discussion of the structure of compounds produced from olefins and mercury salts, it was shown that mercury salts and *o*-allylphenol reacted readily to give mercurated 1-methyl-1,2-dihydro-benzofurans according to the following equation.



A study of the preparation of the corresponding compounds from mercury salts and substituted *o*-allylphenols, and a study of their chemical reactions had been made. In view of the fact that the mercurated 1-methyl-1,2-dihydro-benzofurans, in contrast to the compounds from mercuric salts

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[1] This communication is an abstract of a thesis submitted by L. E. Mills in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

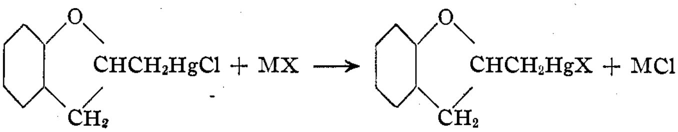
[2] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922).

and other olefins, are unusually stable toward hydrochloric acid, a comparison of the chemical reactions of these compounds with the chemical reactions of the alkyl mercuric halides and with the chemical reactions of the compounds from simple olefins and mercuric salts was of especial interest.

It has been shown that the addition of mercuric salts to *o*-allylphenols is a general one. Mercuric acetate and mercuric chloride react readily with the following compounds: 2-allyl-4-methylphenol, 2-allyl-5-methylphenol, 2-allyl-6-methylphenol, 2-allyl-4-bromophenol, 2-allyl-4-carboxyphenol, 2-allyl-6-carboxyphenol, 2-allyl-6-carbomethoxyphenol and 2-allyl-4-carboxyvinylene-phenol. The only difference noticed among any of the reactions is the speed with which they take place. The yields are almost quantitative in every reaction.

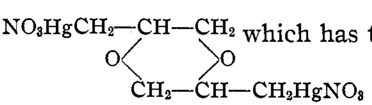
The acetoxy or chloromercurimethyl-1,2-dihydro-benzofurans show the usual reactions of various types of acetoxy and chloromercuri compounds with solutions of bromides or iodides, giving the corresponding bromo- or iodomercuri compounds. No mercuri-bis compounds or compounds free from mercury are formed by the action of iodides.[3]

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with the greatest ease with both alcoholic potassium cyanide and alcoholic potassium thiocyanate to yield the corresponding cyanomercuri or thiocyanatemercuri compounds. It is impossible by longer refluxing with excess of reagent to convert these into the corresponding mercury-bis compounds.

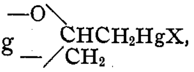


where X = Br, I, SCN, CN.

This behavior of the 1,2-dihydro-benzofurans is in contrast to that of alkyl mercuric halides which generally give mercury-bis compounds, and to that of the compounds obtained from mercuric salts and olefins which lose their mercury entirely under such treatment, giving the original unsaturated compound.[4] It is interesting to note that 2,5-dinitratemercurimethyl-dioxane



which has the grouping



in common with the mercurated dihydro-benzofurans under consideration not only is stable to acid but also yields a dicyanomercuri compound by the action of aqueous potassium cyanide.[5]

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[3] Steinkopf and Bauermeister, *Ann.*, **403**, 57 (1914). Biilmann, *Ber.*, **43**, 574 (1910).

[4] Hoffman and Sand, *Ber.*, **33**, 1344 (1900).

[5] Sand, (a) *ibid.*, **33**, 2679 (1900); **34**, (b) 1387, (c) 1394 (1901).

The 1-hydroxymethyl-1,2-dihydro-benzofurans are readily obtainable from the corresponding chlorides by the action of absolute alcoholic sodium hydroxide. The sodium chloride is filtered and the alcoholic filtrate is concentrated to obtain the hydroxymercuri compounds. These substances are crystalline solids and have the expected property of being readily neutralized by all types of organic or inorganic acids such as hydrochloric, sulfuric, tartaric, oxalic, *p*-nitrobenzoic acids, etc. The hydroxymercuri compounds precipitate insoluble metallic hydroxides such as cupric hydroxide from neutral solutions of their salts.

Most aliphatic hydroxymercuri compounds recorded in the literature have been obtained from the corresponding bromides or iodides by the action of moist silver oxide. The present experiments suggest a better method for making these compounds. The mercury dialkyls made by the method of Marvel[6] and others, when treated with mercuric chloride in alcohol, give quantitative yields of alkyl mercuric chlorides. When these are treated with sodium hydroxide in absolute alcohol, the corresponding hydroxides should be formed. This method has been tested in the case of methyl mercuric chloride with perfect success. Presumably, any of the series could be formed similarly.

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with an alkaline solution of sodium stannite to give an immediate precipitate of metallic mercury and a quantitative yield of the corresponding allylphenol. No indication of an intermediate mercury compound was noted. The reaction of alkaline sodium stannite with both alkyl mercury salts and compounds of mercuric salts and olefines is usually to give compounds of the mercuri-bis type and metallic mercury.[7] No previous example could be found in the literature in which mercury is completely removed from an organic mercury compound by means of sodium stannite.

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react instantaneously with ammonium sulfide, potassium hydrosulfide or hydrogen sulfide in dil. acid solution to give quantitative yields of the corresponding allylphenol and mercuric sulfide. No intermediate organic mercuri sulfides were isolated. This reaction is in contrast to the action of sulfides upon alkyl mercuric salts which almost invariably form organic mercuri sulfides of varying stability; these decompose to mercury-bis compounds and mercuric sulfide. The sulfide reagents react in different ways with compounds from olefins and mercuric salts; a complex organic mercuri sulfide may be formed, the mercuri grouping may be replaced by hydrogen, or the original unsaturated compound may be regenerated, this latter

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[6] Marvel and Gould, THIS JOURNAL, **44**, 153 (1922). Marvel and Calvery, *ibid.*, **45**, 820 (1923).

[7] Dimroth, *Chem. Zentr.*, **1901**, I, 451. Ref. 5c.

reaction being analogous to that observed with the 1-halogen-mercurimethyl-1,2-dihydro-benzofurans.[8]

Sodium thiosulfate is a reagent that has been used frequently for converting aromatic organic mercuric salts to the corresponding mercury-bis compounds. Very frequently an intermediate sodium thiosulfate-mercuri compound of the general formula $RHgSSO_3Na$ has been isolated. Nothing could be found in the literature, however, on the action of sodium thiosulfate upon alkyl mercuric halides or upon compounds from olefins and mercuric salts. By treating 1-chloromercurimethyl-1,2-dihydro-benzofurans with a cold saturated solution of sodium thiosulfate, a 1-sodium thiosulfate-mercurimethyl-1,2-dihydro-benzofuran is obtained. The product darkens in the air in a few minutes and decomposition is complete within a few hours; when the substance is heated the decomposition is made much more rapid. Red mercuric sulfide and the corresponding allylphenol are formed. The compounds in general are so unstable that even recrystallization from water is impossible without decomposition.

The only reagent tested which converts the 1-halogen-mercurimethyl-1,2-dihydro-benzofurans into the corresponding mercury-bis compounds is sodium amalgam and alcohol. In the preliminary paper it was mentioned that 1-chloromercurimethyl-1,2-dihydro-benzofuran was converted readily to the corresponding mercury-bis compound in this way. It has now been found that other derivatives, such as the 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran, react in a similar manner under the same conditions. Sodium amalgam-alcohol also converts alkyl mercuric halides into mercury-bis compounds.

The mercurated 1-methyl-1,2-dihydro-benzofurans are unaffected by boiling with methyl iodide or acetyl chloride. Alkyl halides do not react with these reagents, but compounds from olefins and mercuric salts react with alkyl halides to regenerate the original olefin and with acetyl chloride to yield the acetyl derivative of the hydroxyl group without affecting the substituted mercury radical.[9]

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with 2 atoms of bromine in cold chloroform suspension to yield a precipitate of mercuric salts and a solution containing 1-bromomethyl-1,2-dihydro-benzofuran. Under these conditions no hydrogen bromide is evolved, although when the proper precautions as regards temperature are not followed, hydrogen bromide is evolved and probably bromination in the benzene ring takes place.

It is obvious from the comparative reactions that have been made that

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[8] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., **1921**, pp. 50–53.

[9] Ref. 4, p. 1349. Ref. 5b, p. 1393. Kutscheroff, *Ber.*, **17**, 21 (1884).

the mercurated-methyl-1,2-dihydro-benzofurans resemble in many of their reactions the alkyl mercuric halides, and in many others the compounds from olefins and mercuric salts. In some of the reactions such as those with potassium thiocyanate, potassium cyanide, sodium thiosulfate and sodium stannite, they may be said to stand midway between the two classes.

The reactions of these mercurated-1-methyl-1,2-dihydro-benzofurans, as described above, certainly offer still further convincing evidence that the compounds are not "molecular" substances but actually true addition compounds as suggested and discussed in the preliminary paper.

## Experimental Part

The *o*-allylphenols used in this investigation were prepared according to the directions of Claisen.[10] The 2-allyl-4-carboxyvinylene-phenol was prepared according to the same general procedure, and the details are given in the latter part of the experimental section.

The method of analysis for mercury in the various compounds was similar to that described in the preliminary article. A few minor details were changed; silver nitrate was standardized against very pure mercuric chloride in the same way as it was titrated in the analyses for mercury in the organic compounds. The mercuric chloride had been resublimed several times and was analyzed gravimetrically. Another slight change was that the solution containing the precipitate of mercuric sulfide was heated almost to boiling and hydrogen sulfide passed in again for a few minutes just before filtration.

**General Method for the Preparation of Substituted 1-Mercurimethyl-1,2-dihydro-benzofurans.**—To a solution of 1 molecular equivalent of mercuric acetate or mercuric chloride in water, 10 g. of a substituted *o*-allylphenol was added slowly while the mixture was vigorously stirred. With the mercuric chloride a saturated solution was used, with the acetate about 10 g. of salt in each 100 cc. of water. When mercuric acetate was used, the time of addition was from $^1/_2$ to 1 hour and stirring was continued for several hours longer to insure completion of the reaction. When mercuric chloride was used the substituted *o*-allylphenol was added slowly and a flocculent precipitate of product was formed. In the case of *o*-allylphenol itself a rate of 4 to 5 drops per minute was found to give the best results. In the case of the substituted *o*-allylphenols it was found more convenient to add the phenol during a period of 1 hour and then to continue the stirring until the heavy oil solidified. Stirring was then discontinued and the solid material pulverized with a stirring rod and the mixture stirred again. Six to 8 hours was usually required for the complete procedure when 2-allyl-4-methylphenol, 2-allyl-5-methylphenol or

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[10] Claisen and Eisleb, *Ann.*, **401**, 21 (1913).

2-allyl-6-methylphenol was used, as compared to 3 hours for 2-allylphenol itself. The 2-allyl-4-bromophenol required 10 hours. The 2-allyl-6-carbomethoxyphenol required 15 hours' stirring and 2 days' standing. In the case of 2-allyl-4-carboxyphenol, 2-allyl-6-carboxyphenol and 2-allyl-6-carboxyvinylene-phenol the best results were obtained by adding just enough sodium hydroxide to a suspension of the carboxyphenol in water to dissolve it and then adding an aqueous solution to the theoretical amount of mercuric chloride. In each case a precipitate of the desired product began to form immediately and was complete in a few minutes.

With the exception of mercuric acetate with 2-allyl-5-methylphenol, 2-allyl-4-methylphenol and with 2-allyl-4-bromophenol, all of the compounds obtained were solids. The three just mentioned were obtained as oils and did not solidify under the conditions used. Their conversion, however, by treatment with sodium halide into the corresponding halogen mercury compounds, indicated without question that an addition had taken place.

The solid compounds were white and well crystallized. They were purified from alcohol, except 1-chloromercurimethyl-6-carbomethoxy-1,2-dihydro-benzofuran, for which methyl alcohol was used.

The 1-chloromercurimethyl-6-methyl-, 1-chloromercurimethyl-5-methyl-, 1-chloromercurimethyl-4-methyl-, and the 1-chloromercurimethyl-4-bromo-

TABLE I

MERCURATED 1,2-DIHYDRO-BENZOFURANS PREPARED BY THE ADDITION OF MERCURY SALTS TO SUBSTITUTED ORTHO-ALLYLPHENOLS

| 1,2-Dihydro-benzofurans | M. p. °C. | Subs. G. | $AgNO_3$ Cc. | Hg Calc. % | Hg Found % |
|---|---|---|---|---|---|
| 1-acetoxymercurimethyl-6-methyl- | 113 | 0.1257 | 11.80 | 49.36 | 49.57 |
| | | .1428 | 13.28 | | 49.11 |
| | | | N. F.[a] −0.0263 | | |
| 1-chloromercurimethyl-6-methyl- | 91 | .2168 | 21.38 | 52.35 | 52.06 |
| | | | N. F. −0.0263 | | |
| 1-acetoxymercurimethyl-5-methyl- | oil | ... | ..... | ... | ... |
| 1-chloromercurimethyl-5-methyl- | 127.5 | .1825 | 18.04 | 52.35 | 52.18 |
| | | | N. F. −0.0263 | | |
| 1-acetoxymercurimethyl-4-methyl- | oil | ... | ..... | ... | ... |
| 1-chloromercurimethyl-4-methyl- | 99.5 | .4508 | 44.90 | 52.35 | 51.92 |
| | | | N. F. −0.0566 | | |
| 1-acetoxymercurimethyl-4-bromo- | oil | ... | ..... | ... | ... |
| 1-chloromercurimethyl-4-bromo- | 108 | .6575 | 25.73 | 44.77 | 44.22 |
| | | .5697 | 22.30 | | 44.23 |
| | | | N. F. −0.0566 | | |
| 1-chloromercurimethyl-6-carboxy- | 200 with decomp. | .2525 | 10.85 | 48.55 | 48.55 |
| | | | N. F. −0.0566 | | |
| 1-chloromercurimethyl-6-carbomethoxy- | 107 with decomp. | .1721 | 15.22 | 46.95 | 46.70 |
| | | .1018 | 8.98 | | 46.61 |
| | | | N. F. −0.0263 | | |
| 1-chloromercurimethyl-4-carboxy- | 212–213 with decomp. | .2089 | 19.45 | 48.55 | 48.43 |
| | | | N. F. −0.0566 | | |
| 1-chloromercurimethyl-4-carboxyvinylene- | 300 with decomp. | .1429 | 12.42 | 45.68 | 45.21 |
| | | | N. F. −0.0263 | | |

[a] N. F. = normality factor.

1,2-dihydro-benzofurans described in the following table were made not only by addition of mercuric chloride to the proper *o*-allylphenol, but also by the treatment of the corresponding acetate with sodium chloride solution according to the general method described immediately after Table I.

**General Method for the Conversion of 1-Chloromercuri- or 1-Acetoxymercuri-methyl-1,2-dihydro-benzofurans into the Corresponding Bromides and Iodides.**—A solution of 5 g. of the chloromercuri- or acetoxymercurimethyl-1,2-dihydro-benzofuran in absolute alcohol was mixed with a boiling, absolute alcohol solution of 1 molecular equivalent of potassium halide. As the mixture cooled the halogen mercury compound separated. After this was washed with water to remove the potassium salts, it was necessary to make one recrystallization from alcohol in order to obtain a pure product.

The conversion of the acetoxymercuri compounds to the corresponding chlorides, bromides or iodides, took place more readily than the conversion of the chloromercuri compounds to bromides or iodides. It was often unnecessary to heat the reaction mixture in order to effect the former conversions.

The same reaction could be carried out by dissolving or suspending 5 g. of the acetoxy or chloromercuri compounds in 200 cc. of water and then heating the mixture for about an hour on a water-bath with an aqueous solution of 1 molecular equivalent of potassium halide. As the reaction mixture cooled the precipitate solidified; it was separated, washed and recrystallized from alcohol.

TABLE II

MERCURATED 1,2-DIHYDRO-BENZOFURANS

| | | | | Hg | |
|---|---|---|---|---|---|
| 1,2-Dihydro-benzofurans | M. p. °C. | Subs. G. | $AgNO_3$ Cc. | Calc. % | Found % |
| 1-iodomercurimethyl-6-methyl-.... | 88 | 0.1529 | 12.19 | 42.35 | 42.10 |
| | | .2016 | 16.00 | | 41.92 |
| | | | N. F. −0.0263 | | |
| 1-iodomercurimethyl-5-methyl-.... | 131.5 | .1840 | 15.00 | 42.35 | 42.41 |
| | | | N. F. −0.0263 | | |
| 1-iodomercurimethyl-4-methyl-.... | 94 | .2112 | 16.82 | 42.35 | 42.06 |
| | | .1687 | 13.36 | | 41.83 |
| | | | N. F. −0.0263 | | |
| 1-bromomercurimethyl-4-bromo-.. | 93 | .6536 | 23.25 | 40.73 | 40.18 |
| | | .4870 | 17.45 | | 39.57 |
| | | | N. F. −0.0566 | | |
| 1-iodomercurimethyl-4-bromo-.... | 101 | .4968 | 16.27 | 37.18 | 37.00 |
| | | .4853 | 15.86 | | 36.92 |
| | | | N. F. −0.0566 | | |

**1-Hydroxymercurimethyl-1,2-dihydro-benzofurans.**—From a solution of 10 g. of the substituted 1-chloromercurimethyl-1,2-dihydro-benzofuran in 1 molecular equivalent of sodium hydroxide in 50 cc. of warm absolute ethyl alcohol, sodium chloride immediately precipitated. The solution was filtered and evaporated to half its volume and then cooled slowly. It was finally allowed to remain in an ice-salt mixture for several hours, and the sides of the beaker were rubbed vigorously from time to time with a glass rod. Crystallization gradually took place and the crystals were separated, washed with a small amount of cold alcohol and dried. They were then recrystallized in the same manner from 95% alcohol.

The hydroxymercuri compounds were readily soluble in most organic solvents but only slightly soluble in water, giving solutions which were slightly alkaline to litmus.

All the hydroxymercuri compounds studied were very readily soluble in alcohol, tended to form supersaturated solutions and then to precipitate as oils. By following the procedure indicated above, white crystalline solids were obtained except in the case of 1-hydroxymercurimethyl-6-methyl-1,2-dihydro-benzofuran, which was obtained only as an oil. The yields of the hydroxymercuri compounds were quantitative.

1-Hydroxymercurimethyl-1,2-dihydro-benzofuran was also obtained in 80% yield by refluxing 5 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran with the calculated amount of moist, freshly precipitated silver oxide in 75 cc. of ethyl alcohol.

Table III

1-Hydroxymercurimethyl-1,2-dihydro-benzofurans

| | | | | Hg | |
|---|---|---|---|---|---|
| 1,2-Dihydro-benzofurans | M. p. °C. | Subs. G. | $AgNO_3$ Cc. | Calc. % | Found % |
| 1-hydroxymercurimethyl- | 152 | 0.1162 | 11.86<br>N. F. −0.0280 | 57.19 | 57.34 |
| 1-hydroxymercurimethyl-6-methyl- | thick oil | .1462 | 14.33<br>N. F. −0.0280 | 55.00 | 55.07 |
| 1-hydroxymercurimethyl-4-methyl- | 149 | .2749 | 27.00<br>N. F. −0.0280 | 55.00 | 55.18 |

**Mercurated 1,2-Dihydro-benzofurans by Neutralization of the Hydroxymercuri Derivatives with Acids.**—When alcoholic or aqueous solutions of 1-hydroxymercurimethyl-1,2-dihydro-benzofurans were neutralized with dil. hydrochloric acid, the corresponding chloromercuri compounds were precipitated. For the preparation of the organic acid salts the hydroxymercuri compounds were dissolved in hot alcohol and the solution was then diluted with hot water, the amount added being insufficient to cause the precipitation of any of the mercury compound. A hot alcoholic or aqueous alcoholic solution of the proper acid was then added until a faint acid reaction to litmus was obtained. The solution was allowed to cool and was filtered. The precipitated products were recrystallized from alcohol in which they were somewhat soluble when hot and practically insoluble when cold. All of the salts were well-crystallized solids.

The *p*-nitrobenzoates of the mercury compounds were yellow but all the others were white.

TABLE IV

MERCURATED 1,2-DIHYDRO-BENZOFURANS

| 1,2-Dihydro-benzofurans | M. p. °C. | Subs. G. | $AgNO_3$ Cc. | Hg Calc. % | Hg Found % |
|---|---|---|---|---|---|
| 1-tartrate-di(mercurimethyl- | 192 with decomp. | 0.3165 | 27.86<br>N. F. −0.0280 | 49.20 | 49.45 |
| 1-oxalate-di(mercurimethyl- | 175 | .2069 | 19.51<br>N. F. −0.0280 | 53.11 | 52.98 |
| 1-(p)nitrobenzoate-mercurimethyl- | 148 | .2606 | 18.61<br>N. F. −0.0280 | 40.14 | 40.12 |
| 1-(p)nitrobenzoate-mercurimethyl-6-methyl- | 162.5 | .2943 | 20.53<br>N. F. −0.0280 | 39.04 | 39.19 |
| 1-(p)nitrobenzoate-mercurimethyl-4-methyl- | 136.5 | .2386 | 16.50<br>N. F. −0.0280 | 39.04 | 38.85 |

**1-Cyanomercurimethyl and 1-Thiocyanate-mercurimethyl Derivatives of Substituted 1,2-Dihydro-benzofurans.**—Into a hot saturated solution of 1 molecular equivalent of potassium cyanide or potassium thiocyanate in absolute alcohol, was stirred 10 g. of powdered 1-chloromercurimethyl-1,2-dihydro-benzofuran. An immediate precipitation of potassium chloride occurred. After a few minutes the mixture was filtered and the filtrate allowed to cool. The cyanomercuri or thiocyanatemercuri compound crystallized. Upon filtering and concentrating the filtrate, or upon pouring it into water a further quantity of the material was obtained. These substances are readily purified from alcohol, forming white crystals. The yield in every case was almost quantitative.

TABLE V

MERCURATED 1,2-DIHYDRO-BENZOFURANS

| 1,2-Dihydro-benzofurans | M. p. °C. | Subs. G. | $AgNO_3$ Cc. | Hg Calc. % | Hg Found % |
|---|---|---|---|---|---|
| 1-thiocyanatemercurimethyl- | 112.5 | 0.2028 | 18.40<br>N. F. −0.0280 | 51.21 | 50.97 |
| 1-cyanomercurimethyl- | 162 | .1723 | 17.03<br>N. F. −0.0280 | 55.76 | 55.53 |
| 1-thiocyanatemercurimethyl-4-methyl- | 102.5 | .2761 | 24.34<br>N. F. −0.0280 | 49.43 | 49.53 |
| 1-cyanomercurimethyl-4-methyl- | 148 | .3050 | 29.02<br>N. F. −0.0280 | 53.67 | 53.45 |

**1-Sodiumthiosulfate-mercurimethyl-1,2-dihydro-benzofuran.**—Just enough water was added to 10 g. of finely ground 1-chloromercurimethyl-1,2-dihydro-benzofuran to moisten it, and the latter was then quickly and thoroughly stirred into a hot saturated solution of 3.4 g. of sodium thiosulfate in water. A large amount of the material turned black because of the formation of mercuric sulfide. The mixture was immediately filtered hot by gentle suction and the filtrate cooled. Glistening white scales of the sodium salt separated. These were separated and dried on a porous plate.

*Analysis.* Subs., 0.2184: 18.61 cc. of 0.02608 *N* $AgNO_3$. Calc. for $C_9H_9HgO_4S_2$-Na: Hg, 44.90. Found: 44.75.

This compound was also prepared by triturating together the same quantities of materials in the cold for a few minutes and then filtering and washing with a very small amount of cold water. The product weighed 11 g., which is about a 92% yield. No method for recrystallization was found.

It is very soluble in hot water, decomposing into mercuric sulfide and *o*-allylphenol. After the original reaction mixture had been warmed on the steam-bath for 2 hours the decomposition of the intermediate sodium salt was complete. The sulfide was filtered and washed well with acetone. The mixture of the washings and the filtrate was extracted with ether and dried with calcium chloride. A yield of 2.9 g. of *o*-allylphenol, or 87%, was obtained from 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran.

When heated, the salt turned dark at about 120°. At ordinary temperatures the decomposition proceeded more slowly. The crystals began to darken after a few minutes and were completely decomposed after about 12 hours. All the experiments in which the decomposition took place at room temperature gave rise to the red modification of mercuric sulfide.

**1-Sodiumthiosulfate-mercurimethyl-4-methyl-1,2-dihydro-benzofuran.**—This substance was prepared in the same way as was the preceding compound which it resembled closely in properties. The yield by the hot method was low, by the cold method almost quantitative. The properties of the product were identical with those of the previous compound.

*Analysis.* Subs., 0.2491: 20.52 cc. of 0.02618 *N* $AgNO_3$. Calc. for $C_{10}H_{11}HgO_4S_2Na$: Hg, 43.53. Found: 43.25.

When the reaction mixture was warmed for 2 hours and the 2-allyl-4-methylphenol recovered as in the previous case of *o*-allylphenol, an 85% yield was obtained.

**Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofurans with Alkaline Sodium Stannite Solution.**—An alkaline solution of sodium stannite was prepared by dissolving 3 g. of stannous chloride crystals in 50 cc. of water and then adding 50% more of 10% sodium hydroxide solution than was sufficient just to dissolve the precipitate. A thin paste of 5 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran and water was then slowly stirred in. A gray precipitate of mercury was formed immediately. After the liquid had been warmed on the steam-bath for a few minutes it was decanted, made acid with dil. hydrochloric acid and extracted with ether. The ether solution was dried over calcium chloride and the ether distilled. There was obtained 1.4 g. or an 83% yield of *o*-allylphenol.

A yield of 85% of 2-allyl-4-methylphenol was obtained from 5 g. of 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran by the same procedure.

**Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofurans with Sulfides.** WITH HYDROGEN SULFIDE.—A suspension of 5 g. of finely ground 1-chloromercurimethyl-1,2-dihydro-benzofuran was made in 100 cc. of water containing 2 cc. of concd. hydrochloric acid and the solution shaken frequently while being saturated with hydrogen sulfide. The precipitate of mercuric sulfide was allowed to settle and the liquid decanted. The mercuric sulfide was washed thrice with acetone by decantation and the washings were added to the liquid first decanted. After extraction with ether there was obtained 1.3 g. or a 77% yield of *o*-allylphenol. Similar treatment of 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran gave an 85% yield of 2-allyl-4-methylphenol.

WITH AMMONIUM SULFIDE.—Ten g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran was suspended in 100 cc. of water containing 5 cc. of concd. ammonium hydroxide (d., 0.90) and saturated for 1 hour with hydrogen sulfide while it was shaken frequently. The mercuric sulfide was separated and the *o*-allylphenol recovered as in the preceding case; yield, 3.2 g., or 90%. A similar result was obtained with the 4-methyl derivative.

WITH POTASSIUM HYDROSULFIDE.—To 5 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran suspended in 100 cc. of water was added slowly with stirring a solution containing 2 g. of potassium hydrosulfide in 50 cc. of water. The precipitated mercuric sulfide was filtered and the *o*-allylphenol recovered as in the preceding case. The yield was 1.5 g., or 89%. This reaction was also carried out in absolute alcohol with similar results.

In no case was any intermediate organic mercuric sulfide isolated. The initial precipitate in each instance was black. It was noted that upon first forming, the precipitate was somewhat bulky and flocculent, indicating the possible formation of a very unstable organic mercuri sulfide. This precipitate became granular after it had stood for a few minutes.

**1,1-Mercuridimethylenebis-(4-methyl-1,2-dihydro-benzofuran).**—A mixture of 15 g. of 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran and 100 cc. of absolute alcohol was placed in a 200 cc. round-bottom flask and refluxed with 1.5 g. of sodium in the form of a 3% amalgam in exactly the same manner as directed for 1-chloromercurimethyl-1,2-dihydro-benzofuran in the preceding paper.[2] The product was purified by crystallization from ether. The yield was 5.5 g. of pure white crystals, or 35%; m. p., 89.5°.

*Analysis.* Subs., 0.2174: 15.07 cc. of 0.02618 *N* $AgNO_3$. Calc. for $C_{20}H_{22}O_2Hg$: Hg, 40.53. Found: 40.37.

**Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofuran with Methyl Iodide and Acetyl Chloride.**—A mixture of 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran and 10 g. of methyl iodide in 75 cc. of absolute alcohol was refluxed for 4 hours. As the mixture cooled, 93% of the unchanged chloromercurimethyl compound crystallized.

A mixture of 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran and 2.2 g. of redistilled acetyl chloride in chloroform was refluxed. After the solution had cooled, the precipitate that formed was found to consist of 9.6 g. of the unchanged chloromercurimethyl compound.

**Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofuran with Bromine.**—A suspension of 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran in 50 cc. of carbon tetrachloride was made, and 4.5 g. of bromine in carbon tetrachloride solution was added slowly at 0° to 5°. The bromine was decolorized immediately, and no evolution of hydrobromic acid was noted. The mixture was filtered and the precipitate washed with a little carbon tetrachloride and dried. The weight of the precipitate was 7.8 g. corresponding to a 91% yield based on the amount of mixed chloride and bromide of mercury. The carbon tetrachloride solution was evaporated on the water-bath, when there was obtained 5.7 g. or 96% of the calculated amount of light brown, viscous oil, which boiled at 140–143° (20 mm.), showing it to be 1-bromomethyl-1,2-dihydro-benzofuran.[11]

When more than 4.5 g. of bromine was added, hydrogen bromide was evolved, and a total of 4 atoms of bromine was absorbed before immediate decolorization ceased, indicating bromination in one position in the ring. No attempt was made to identify the bromination product.

**Solution of 1-Chloromercurimethyl-6-carboxy-1,2-dihydro-benzofuran in Sodium Hydroxide.**—A suspension of 0.3185 g. of the 6-carboxy compound in 50 cc. of water was titrated with 0.103 *N* sodium hydroxide solution. For complete solution 15.2 cc. was required. A faint alkaline reaction to litmus resulted. This is almost exactly 2 molecular equivalents of sodium hydroxide. Upon titration of the solution with 0.0952 *N* hydrochloric acid, no permanent precipitate was observed until 8.2 cc. (8.1 cc. = 1 molecular equivalent) had been added. After a total of 16.5 cc. had been added, precipitation was complete and the solution was filtered. The filtrate contained no mercuric ions.

**Methyl Mercuric Hydroxide from Methyl Mercuric Chloride and Sodium Hydroxide.**—A solution of 10 g. of methyl mercuric chloride in 75 cc. of warm absolute

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[11] Adams and Rindfusz, THIS JOURNAL, **41**, 655 (1919).

methyl alcohol was treated with 1.6 g. of sodium hydroxide in 16 cc. of absolute methyl alcohol. An immediate precipitate of sodium chloride was formed. An equal volume of dry ether was added to complete the precipitation of the sodium chloride and the mixture filtered. The precipitate weighed 2.4 g. which is 100% of the calculated amount of sodium chloride. Upon evaporation of the ether and alcohol from the filtrate at room temperature in a vacuum there remained 8.3 g. of grayish-white crystals which melted at 95° after one precipitation from methyl alcohol by means of ether, proving the product obtained to be methylmercuric hydroxide.[12] Dil. hydrochloric acid converted the hydroxide instantaneously into methylmercuric chloride.

**4-Allyloxy Methyl Cinnamate:** ($p$)$CH_2{=}CH{-}CH_2OC_6H_4CH{=}CHCO_2CH_3$.—A mixture of 25.3 g. of the methyl ester of *p*-cumaric acid,[13] 18 g. of allyl bromide, 21 g. of anhydrous potassium carbonate and 30 g. of acetone was refluxed on the steam cone. The completion of the reaction was determined by withdrawing a sample, diluting it with ether, extracting this with dil. sodium hydroxide solution and neutralizing the sodium hydroxide layer with dil. hydrochloric acid. A precipitate indicated the presence of unchanged *p*-cumaric acid. When the mixture was poured into 400 cc. of cold water the 4-allyloxymethyl cinnamate separated and was recrystallized from 80% alcohol. The yield was 22.5 g. or 73%. The material formed white, glistening plates melting at 65.5°.

*Analysis.* Subs., 0.3231: 495.8 cc. of $CO_2$ (25.5°, 725.9 mm.). Calc. for $C_{13}H_{14}O_3$: C, 71.52. Found: 71.83.

**3-Allyl-4-hydroxy Methyl Cinnamate:** 3-$(CH_2{=}CHCH_2)$4-$(HO)C_6H_3CH{=}CHCO_2CH_3$.—When 8.5 g. of the allyl ether of methyl *p*-coumarate was heated under a reflux condenser in an oil-bath for 2 hours at 230–245°, rearrangement took place. The amber-colored residue was dissolved in ether, extracted with 10% sodium hydroxide solution and the alkaline solution run into dil. hydrochloric acid at 0°. 3-Allyl-4-hydroxy methyl cinnamate separated as a brown, soft mass which gradually hardened after a few hours' exposure to the air. This substance was not purified further but was used directly in the preparation of the free acid. The yield was 7 g. of crude material.

**3-Allyl-4-hydroxycinnamic Acid,** 3-$(CH_2{=}CHCH_2)$4-$(HO)C_6H_3CH{=}CHCO_2H$.—A solution of 4 g. of the crude 3-allyl-4-hydroxy methyl cinnamate in 25 cc. of 10% sodium hydroxide solution was refluxed gently for 4 hours. The mixture was then poured slowly into dil. hydrochloric acid at 0°. The precipitate was filtered, washed with water, dried, dissolved in ether and extracted with 10% sodium bicarbonate solution. The aqueous solution was poured into cold dil. hydrochloric acid solution and the precipitate recrystallized from 80% alcohol. The yield was 2.1 g. of pure white crystals, m. p. 169°, and 0.5 g. of impure crystals, or a total of 63%.

*Analysis.* Subs., 0.2409: 361.2 cc. of $CO_2$ (25.5°, 725.9 mm.). Calc. for $C_{12}H_{12}O_3$: C, 70.57. Found: 70.22.

## Summary

1. The addition of mercuric salts to *o*-allylphenols has been shown to be a general one. Several substituted *o*-allylphenols have been treated with mercuric salts with the formation of mercurated-methyl-1,2-dihydro-benzofurans.

2. The reactions of these compounds have been extensively studied and compared with the reactions of alkyl mercuric halides and compounds from mercuric salts and olefins.

3. The 1-acetoxy- or 1-halogen-mercurimethyl-1,2-dihydro-benzofurans

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[12] Sneed and Maynard, This Journal, **44**, 2946 (1922).

[13] Fischer and Nouri, *Ber.*, **50**, 619 (1917).

react with alcoholic or aqueous sodium or potassium bromide or iodide to give the corresponding bromo- or iodomercuri compounds; with alcoholic potassium cyanide and alcoholic potassium thiocyanate, to give the corresponding cyanomercuri or thiocyanatemercuri compounds. In none of these reactions was it possible with excess of reagent to convert the compounds into mercury-bis derivatives.

4. The 1-chloromercurimethyl-1,2-dihydro-benzofurans react readily with potassium or sodium hydroxide in alcohol to give the corresponding hydroxymercuri compounds and sodium or potassium chloride. The method is apparently general for alkyl mercuric chlorides since methyl mercuric chloride was converted to methylmercuric hydroxide by a similar procedure. The 1-hydroxymercurimethyl-1,2-dihydro-benzofurans react with acids to form the corresponding salts and, in general, show the typical reactions of any of the known hydroxymercuri compounds.

5. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with sodium stannite to give a quantitative yield of the corresponding allylphenol and metallic mercury.

6. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with ammonium sulfide, potassium hydrosulfide or hydrogen sulfide in dil. acid solution to give quantitative yields of the corresponding allylphenols and mercuric sulfide.

7. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with sodium thiosulfate to give 1-sodiumthiosulfate-mercurimethyl-1,2-dihydro-benzofurans which are unstable compounds decomposing readily into mercuric sulfide and the corresponding allylphenol.

8. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with sodium amalgam and alcohol to give the corresponding mercuri-bis compounds.

9. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans do not react with methyl iodide or acetyl chloride.

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## NEW BOOKS

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