[Contribution from the School of Chemistry, University of Minnesota.]

ORGANIC MERCURY COMPOUNDS DERIVED FROM *p*-BROMODIMETHYLANILINE.

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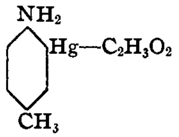
The present paper is the first of a series in which the introduction of mercury in the *ortho* position to various substituted amino groups will be studied. The work with the organic mercury compounds so obtained will deal especially with two fundamental reactions of organic mercury compounds in general. These reactions may be represented by the single equilibrium equation

$$R_2Hg + HgX_2 \rightleftarrows 2RHgX$$

in which R represents any organic residue which has its free bond attached to carbon, and X represents any univalent acid radical. The reaction normally runs to completion to the right because of the slight solubility of the organo-mercuric salt RHgX in the organic solvents used. The reaction may be reversed by using reagents which remove HgX_2. Such substances are alkaline reducing agents such as sodium stannite solution, and compounds like potassium iodide and sodium thiosulfate which form mercuric complexes of considerable stability.

The introduction of mercury into a *para*-substituted aromatic amine has been studied only in the cases of *p*-toluidine and its dimethyl derivative.[1] Klein mixed solutions of *p*-toluidine and mercuric chloride in ether and obtained crystals to which he assigned the formula $HgCl_2.2C_6H_4(CH_3)NH_2$. He obtained similar compounds with the bromide and the iodide of mercury. Pesci treated an alcoholic solution of *p*-toluidine with an aqueous-alcoholic solution of mercuric acetate and obtained crystals of mercury (2-amino-5-methyl phenyl) acetate.



This substance is insoluble in water but is readily soluble in organic solvents. The corresponding hydroxide and chloride were made by treating it with conc. aqueous potassium hydroxide and with alcoholic calcium chloride, respectively. Pesci suggested that Klein's addition compound was really made up of one molecule of this chloride and one molecule of *p*-toluidine hydrochloride. However he did not attempt to verify this conclusion by making Klein's compound from these substances. When

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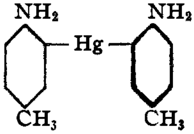
[1] Klein, *Ber.*, 11, 744 (1878); 13, 835 (1880); Pesci, *Gazz. chim. ital.*, 28, II, 101, 111, 460 (1898); *Z. anorg. Chem.*, 17, 276, 281 (1898); Vecchiotti, *Gazz. chim. ital.*, 48, II, 78 (1918).

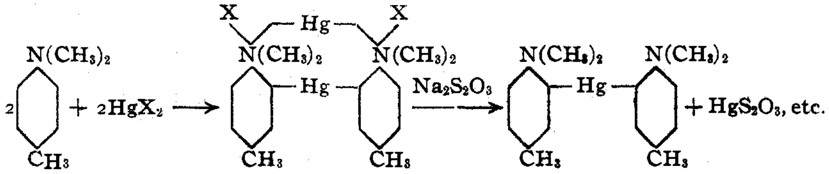
the hydroxide was treated with a concentrated solution of sodium thiosulfate it was changed to mercury di-(2-amino-5-methyl phenyl).



Vecchiotti obtained the same results as did Pesci. Indeed the experimental data in the two papers are identical except in a few minor points.

Pesci treated dimethyl-*p*-toluidine with mercuric acetate and obtained mercury (2-dimethylamino-5-methyl phenyl) acetate from which he made the corresponding hydroxide, nitrate, chloride, bromide, and iodide. The hydroxide with sodium thiosulfate yielded the mercury diphenyl derivative, mercury di-(2-dimethylamino-5-methyl phenyl). Pesci briefly states that the acetate when treated with an excess of ammonium hydroxide gave the mercury diphenyl derivative.[1] He does not mention this reaction in the summary of his work published later.[2] This method of changing RHgX to R_2Hg has apparently not been observed by any other worker with organic mercury compounds. Pesci proved the constitution of the mercury diphenyl derivative obtained from mercury (2-dimethylamino-5-methyl phenyl) hydroxide by synthesizing it from 3-bromo-dimethyl-*p*-toluidine and 1.5% sodium amalgam according to the method of Otto for making mercury diphenyl compounds.[3]

Pesci misinterpreted all of his reactions because he assigned incorrect structural formulas to all of his compounds except the mercury diphenyl derivatives. He believed that the salts which he had prepared each contained two benzene rings and two atoms of mercury in the molecule. He thought that one mercury was attached to two carbon atoms and the other was attached to two nitrogen atoms. The sodium thiosulfate was supposed to remove only the mercury attached to nitrogen. The difference between Pesci's views and the more modern one can best be shown by equations illustrating the formation of the acetate and the mercury diphenyl derivative.



Pesci's formulas.

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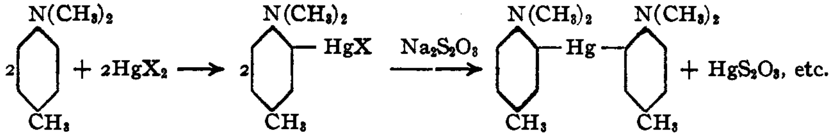
[1] *Gazz. chim. ital.*, **28**, II, 106 (1898).

[2] *Z. anorg. Chem.*, **17**, 176–281 (1898).

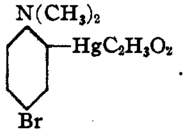
[3] Otto, *Ann.*, **154**, 94 (1870). This method was first developed by Frankland and was used by him in work in the aliphatic series. *Ann.*, 130, 105 (1864).



Modern formulas.

It will be seen that Pesci had the correct formulas for the mercury diphenyl compounds but did not correctly interpret their formation. Pesci's ideas were plausible enough when applied to the aromatic amines which he studied but they had to be discarded when Dimroth showed that "mercuration" is as general a reaction of aromatic compounds as sulfonation or nitration.[1] The best positive evidence that Pesci's double formulas are incorrect is that given Jacobs and Heidelberger who proved that the mercury compound obtained from aniline contains a primary amino group which can be diazotized and then coupled in the usual way with dimethylaniline or phenols.[2]

In the present investigation the starting point is *p*-bromo-dimethyl aniline. The dimethyl derivative was chosen as being likely to give fewer side reactions than any of the other substituted amines which are to be studied later. When an aqueous-alcoholic solution of mercuric acetate is allowed to stand with an alcoholic solution of *p*-bromo-dimethylaniline for several days there crystallizes out the organo-mercuric salt, mercury (2-dimethylamino-5-bromo-) acetate



The fine needle crystals of this substance are mixed with a certain amount of mercurous acetate. The mother liquor yields only tarry substances and more mercurous acetate. Thus at least two reactions are taking place, the introduction of the mercuri-acetate group into the ring and the oxidation of the *p*-bromo-dimethylaniline by the mercuric acetate. It was not found possible to eliminate this oxidation reaction completely. When *p*-bromo-diethylaniline is used instead of the dimethyl compound the oxidation becomes the chief reaction.[3] It was at first thought that the formation of mercurous acetate was due to a reducing action of the alcohol. This was disproved by the fact that boiling mercuric acetate for days with alcohol gave only minute traces of mercurous acetate. The use of more concentrated solutions of mercuric acetate with the *p*-bromo-dimethylaniline gave larger amounts of mercurous acetate. Heating the reaction mixture had a similar effect. To avoid a large concentration of

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[1] *Z. anorg. Chem.*, 32, 227ff (1902); 33, 311ff (1903).

[2] *J. Biol. Chem.*, 20, 513 (1915); *C. A.*, 9, 1609 (1915).

[3] This reaction is being studied by Mr. A. R. Cade of this laboratory.

mercuric acetate and thus to cut down its oxidizing action experiments were carried out in which the acetate was added very slowly and the mixture was stirred by a powerful mechanical stirrer. This did indeed cut down the amount of mercurous acetate formed but it also cut down the yield of the organo-mercuric salt.

Various other salts were prepared from the acetate by treating the alcoholic solution of the latter with alcoholic solutions of suitable inorganic salts. In preparing the base alcoholic sodium hydroxide was used. The base was found useful in making salts which were not easily prepared by the precipitation method. This could be done by treating the base with the appropriate acid or better still with an ester of the acid. The formate was made in this way by heating the hydroxide with ethyl formate. This proved more convenient than the treatment of the hydroxide with formic acid or the treatment of the acetate with a formate solution. A slight excess of formic acid tends to remove some of the mercury from the ring while an excess of the ester does no harm. The purest sample of the acetate obtained was made from the hydroxide and ethyl acetate.

The change of the acetate or the hydroxide into the corresponding mercury diphenyl derivative, mercury di-(2-dimethylamino-5-bromo phenyl), was tried by all the usual methods. The reagents which bring about this change may be divided into two classes: The first class consists of alkaline reducing agents like sodium stannite solution. This reagent gave the mercury diphenyl derivative in 63% yield.

$$2R - Hg - X + 2NaOH + Na_2SnO_2 = R_2Hg + Na_2SnO_3 + 2NaX + H_2O + Hg.$$

The second class consists of those inorganic salts which form stable complex mercuric ions. Such substances are iodides, sulfides, and thiosulfates. Pesci usually employed the sulfides and thiosulfates in preparing his mercury diphenyl compounds. In the present research these substances gave very poor yields. Apparently the sulfide and thiosulfate of the organo-mercury base are more stable than those studied by Pesci and do not readily break up giving a molecule of an inorganic mercury compound according to the equation

$$(RHg)_2S + Na_2S = R_2Hg + Na_2HgS_2.$$

Potassium iodide proved to be the best reagent for preparing mercury di-(2-dimethylamino-5-bromo phenyl) as it gave a yield of 86% and a reaction mixture much easier to work up than did the sodium stannite which gave the next best yield.

$$2R - Hg - C_2H_3O_2 + 4KI = R_2Hg + 2KC_2H_3O_2 + K_2HgI_4.$$

It will be noted that all the products are water soluble except the desired substance.

If the theory that the formation of R_2Hg from RHgX depends on the removal of HgX_2 by the formation of a complex is true there should be a marked difference in the efficiency of iodides, bromides, and chlorides in bringing about this change. As is well known the iodide complex is by far the most stable and the chloride complex is the least stable. Experiments showed that while the iodide gave an 86% yield the bromide gave only a 3% yield and the chloride gave none of the mercury diphenyl compound. In the equation

$$2RHgX + 2MX = R_2Hg + M_2HgX_4$$

it will be seen that half of the mercury appears in an inorganic form which would give a precipitate with hydrogen sulfide. The filtrate from the reaction of sodium bromide with the organo-mercuric acetate gave an immediate black precipitate with hydrogen sulfide. The filtrate from the mixture of the acetate with a very large excess of alcoholic calcium chloride gave no precipitate with hydrogen sulfide, showing that no inorganic mercury compound had been formed.

It was thought that the organo-mercuric iodide might be changed to the mercury diphenyl derivative and mercuric iodide by long heating in a solvent in which the latter substance is much less soluble than the organic iodide. Such does not seem to be the case. Long boiling of a benzene solution of the organo-mercuric iodide gave no trace of mercuric iodide. Evidently the strong tendency for the formation of R-Hg-X depends not merely on the slight solubility of that type of substance but also on some peculiarity of the mercury atom which favors union with two groups at least as different as a hydrocarbon residue and an acid radical.

The formate was heated to see if it would yield the mercury diphenyl compound. The reduction did not stop at that point as almost all of the mercury appeared as metal and only a small amount of the mercury diphenyl compound was obtained. The chief organic product was *p*-bromodimethylaniline.

$$R—Hg—OCHO = Hg + RH + CO_2.$$

When the acetate was heated with zinc dust the products were mercury, zinc oxide, *p*-bromo-dimethylaniline, and unchanged acetate. Copper powder gave little action even on long boiling.

$$R—Hg—C_2H_3O_2 + Zn + H_2O = RH + ZnO + Hg + HC_2H_3O_2.$$

The acetic acid probably united with the large excess of alcohol present.

In all the reactions in which the mercury diphenyl compound was obtained after long boiling in an alcoholic solution small amounts of mercury metal were obtained. Usually this amounted to less than 0.1 g. The reaction which gives rise to this free mercury is evidently a very slow one as long boiling of the mercury di-(2-dimethylamino-5-bromo phenyl) with an excess of alcoholic potassium iodide or with alcohol alone only gave a very small amount of metallic mercury. Small amounts of *p*-bromo-dimethylaniline were sometimes obtained in these experiments. The reaction is possibly due to a slight reducing action of the alcohol on the organo-mercury compound.

The reaction of mercury di-(2-dimethylamino-5-bromo phenyl) with mercuric salts of monobasic inorganic acids was proved to proceed quantitatively according to the equation

$$R_2Hg + HgX_2 = 2R—Hg—X.$$

The reaction was carried out with mercuric chloride, bromide, iodide, and thiocyanate. When mercuric salts of dibasic acids were used no satisfactory results were obtained. Thus mercuric sulfate when heated with the mercury diphenyl compound gave mercuric oxide and *p*-bromo-dimethylaniline. Probably the reaction proceeded as follows:

$$HgSO_4 + C_2H_5OH = HgO + (C_2H_5)HSO_4$$

The ethylsulfuric acid would then react with the organic mercury compound liberating its mercury in inorganic form and leaving the *p*-bromo-dimethylaniline. The reaction of less easily hydrolyzable mercury salts of dibasic acids with mercury diphenyl and its derivatives will be studied later.

EXPERIMENTAL PART.

Reaction of Mercuric Acetate with *p*-Bromo-dimethylaniline.

Reaction in Cold Dilute Solution.—80 g. of 85% mercuric acetate was dissolved in 150 cc. of hot water containing 5 cc. of glacial acetic acid to prevent the hydrolysis of the acetate. A small amount of mercurous acetate formed and was filtered off. A solution of 40 g. of *p*-bromo-dimethylaniline in 700 cc. of hot 95% alcohol was prepared and filtered into a one-quart fruit jar. When both solutions had cooled to 30° the mercuric acetate solution was added to the solution in the fruit jar and the latter was stoppered tightly. If the solutions were mixed at a higher temperature yellow mercuric oxide separated, as mercuric acetate reacts almost completely with hot alcohol undergoing "alcoholysis." No change was evident on mixing the cool solutions. After standing at room temperature for about 6 hours long needle crystals began to form slowly. At the end of 6 days the formation of crystals had ceased. After filtration by suction the crystalline residue (75 g.) was heated under a reflux condenser for 15 minutes with 250 cc. of benzene, and then filtered through a steam funnel. The residue (7.5 g.) from this extraction on treatment with 100 cc. more of benzene gave no more soluble material. This residue insoluble in benzene was practically pure mercurous acetate. The benzene extract gave large amounts of pure white crystals as soon as it passed through the steam funnel. When thoroughly cold it formed a solid mass of crystals. Filtration left 62 g. of fine, pure white needles melting at

138 to 140°. 110 cc. of benzene was distilled off from the mother liquor and the residue was allowed to evaporate spontaneously giving 5.5 g. of crystals melting at 135°. The alcoholic mother liquor from the original reaction mixture gave no more crystals on long standing. 750 cc. of alcohol was distilled off. On cooling a black tar was obtained which left 7.7 g. of mercurous acetate after extraction with hot alcohol. The alcoholic extract on standing gave 4.4 g. of an unmanageable black tar. In later preparations the mother liquor from the original reaction mixture was worked up only for the recovery of the alcohol. All the easily obtainable organo-mercuric acetate separated during the long standing. The evaporation of the mother liquor on the steam bath increased the oxidizing action of the mercuric acetate which resulted in the formation of mercurous acetate and the objectionable tar. Even without recovering any organic mercury compound from the original mother liquor, 40 g. of *p*-bromo-dimethylaniline gave 67.5 g. of mercury-(2-dimethylamino-5-bromo phenyl) acetate (74% yield).

Effect of Greater Concentration and Heating.—Two g. of *p*-bromo-dimethylaniline was heated with 10 cc. of alcohol and treated with a hot solution of 3.2 g. of mercuric acetate in 4 cc. of water and 2 cc. of glacial acetic acid. An oil separated at once. After heating for 5 minutes on the steam bath the oil disappeared and white, flaky crystals appeared. After heating for two hours the mixture was filtered. The white crystals proved to be mercurous acetate (1.2 g.). The alcoholic filtrate on evaporation gave a brown oil which did not crystallize even on standing for 3 months.

Effect of Slow Addition of the Mercuric Acetate with Vigorous Stirring.—77 g. of mercuric acetate was dissolved in 150 cc. of hot water containing 2 cc. of glacial acetic acid. The nearly clear solution was treated with 250 cc. of alcohol and filtered. 40 g. of *p*-bromo-dimethylaniline was dissolved in 500 cc. of alcohol and filtered into a large wide-mouth bottle provided with a powerful mechanical stirrer. The mercuric acetate solution was added in 10 cc. portions with constant stirring for 3 days. The crystals which had separated were treated in the usual way. The amount of mercurous acetate obtained from the first crystals was 4.2 g. as compared with 7.5 g. in a run in which all of the mercuric acetate was added at once without stirring. However only 53.6 g. of the organo-mercuric acetate was obtained as compared with 67.5 g. in the other experiment.

Action of Mercuric Acetate with Alcohol.—Seven g. of mercuric acetate was treated with one cc. of acetic acid and 50 cc. of alcohol and heated until no more dissolved. About 0.1 g. of mercurous acetate was filtered off and the solution was heated under reflux for 5 days and nights. Filtration left less than 0.1 g. of mercurous acetate. Evaporation of the filtrate gave no more mercurous acetate.

Properties of Mercury 2-Dimethylamino-5-bromo Phenylacetate.

The acetate forms white, needle crystals melting at 144°.[1] It is almost insoluble in water and in petroleum ether (b. p. 35-45°). It is difficultly soluble in toluene, ethyl ether, and chloroform even on heating. It is fairly soluble in hot ethyl acetate, benzene, and carbon tetrachloride. It is very soluble in hot methyl alcohol, ethyl alcohol, and acetone. Carbon disulfide dissolves it readily even in the cold. The best crystals are obtained from methyl alcohol, ethyl alcohol, and benzene. Benzene is the best solvent for purification as it does not dissolve mercurous acetate, the impurity most likely to be present. The acetate is also soluble in cold conc. ammonium hydroxide.

Action of the Acetate with Hydrogen Sulfide.—A suspension of the organo-mercuric acetate in water gave no black precipitate with hydrogen sulfide. A small amount of a white, gelatinous precipitate formed showing that the sulfide of the mercury base is even less soluble than the acetate. An alcoholic solution of the acetate gave no black precipitate with hydrogen sulfide. A solution of the acetate in ammonium hydroxide was saturated with hydrogen sulfide and stoppered. The pure white precipitate which formed first had not changed at the end of 3 hours. At the end of 5 hours it had turned gray. These tests show that the mercury in mercury-(2-dimethylamino-5-bromo phenyl)-acetate is very completely "masked" or non-ionized. Similar experiments with the other organic mercury compounds prepared in this work showed that their mercury atoms were in the same masked condition.

Analysis of the Acetate for Bromine and for Mercury.—The organic mercury compounds mentioned in this paper were analyzed in the following way: A sample of the substance was decomposed in a Carius tube by means of fuming nitric acid. For complete decomposition heating at about 200° for at least 36 hours was required. In samples which were heated for shorter periods organic material was often left undecomposed. This apparently consisted of water-soluble nitro compounds which interfered with the quantitative precipitation of the mercury sulfide by ammonium sulfide. The contents of the Carius tube were diluted, transferred to a beaker, and nearly neutralized by sodium hydrogen carbonate free from halogen. Freshly prepared ammonium sulfide made from 10 cc. of conc. ammonium hydroxide was then added with stirring. The reaction mixture was allowed to stand on a steam bath overnight and was then filtered through a weighed Gooch crucible and dried at 110° for one hour. This method of analysis gave better results than the ordinarily recommended method of dissolving the mercury sulfide in sodium hydrox-

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[1] All melting points given in this paper are "uncorrected."

ide and reprecipitating it with ammonium nitrate in order to get the precipitate in a more easily filterable form. By using the method indicated there was no trouble in filtering the precipitate. Moreover the mercury sulfide contained practically no free sulfur. This was shown by extracting the weighed precipitate for an hour with carbon disulfide. The loss in weight seldom exceeded 0.2 mg. The extraction with carbon disulfide was carried out in an extraction flask having a wide neck and provided with a reflux condenser. The Gooch crucible with a piece of filter paper tied around it was set in a support of heavy copper wire by means of a pair of long, straight tongs. A cone of filter paper was then placed on top of the crucible and the condenser was put in place. The purpose of the filter paper cone is to prevent the dropping of the condensed carbon disulfide from becoming rapid enough to wash the asbestos mat loose. Even with this precaution mercury sulfide might be washed through if the mat were unusually thin. In this case the outside filter paper will show the mercury sulfide and the analysis can be discarded. This happened only once in the analysis of the substances mentioned in this paper.

The filtrate and washing from the mercury sulfide, about 400 cc., were made barely acid with dil. nitric acid. In most cases no sulfur separated. When sulfur did appear it was usually from a sample which had not been thoroughly heated on the steam bath. The slightly acid solution was then warmed on the steam bath until no odor was perceptible, after which the clear solution was treated with silver nitrate and the silver halide was determined gravimetrically.

Calc. for $C_{10}H_{12}O_2NBrHg$: Hg, 43.7; Br, 17.5. Found: Hg, 43.9; Br, 18.2.

Preparation of Other Salts from the Acetate.

The chloride, bromide, iodide, and thiocyanate were prepared by treating alcoholic solutions of the acetate with alcoholic solutions of calcium chloride, sodium bromide, potassium iodide, and potassium thiocyanate, respectively. In the cases of the chloride, bromide, and thiocyanate the product precipitated out of the hot solutions. As the iodide was much more soluble it was found desirable to mix the calculated amounts of the acetate and potassium iodide in a small volume of alcohol and reflux until most of the material had gone into solution. After filtering and cooling crystals separated which were freed from any potassium acetate by washing with a little water.

Properties of Mercury (2-Dimethylamino-5-bromo Phenyl) Chloride. —The chloride separated from alcohol or benzene in felted masses of very fine needles, m. p. 183°. Its solubilities are about the same as those of the acetate.

Subs., 0.3231: HgS, 0.1716; mixed AgBr + AgCl, 0.2498.

Calc. for $C_8H_9NClBrHg$: Hg, 46.0; Br + Cl (1:1), 26.6. Found: Hg, 45.8; Br + Cl, 26.9.

Properties of the Bromide.—The bromide tends to form larger crystals than the chloride and does not assume the "felted" appearance of the latter. M. p. 182°. It is rather more soluble in all the organic solvents than the chloride.

Calc. for C_8H_9NBrHg: Hg, 41.8. Found: 41.8.

Properties of the Iodide.—The appearance of the iodide is very much like that of the bromide. It is very much more soluble in organic solvents. M. p. 169°.

Calc. for $C_8H_9NBrIHg$: Hg, 38.0. Found: 37.8.

Properties of the Thiocyanate.—The thiocyanate separated from the reaction mixture in fine, white, gritty crystals, m. p. 135°, decomposing at 140°. It is insoluble in water and petroleum ether, slightly soluble in carbon tetrachloride, difficultly soluble in ether, soluble in acetic acid and carbon disulfide, very soluble on heating in methyl alcohol, ethyl alcohol, ethyl acetate, benzene, toluene, and chloroform. It dissolves readily in cold acetone. The only solvent which gives good crystals is ethyl acetate.

Calc. for $C_9H_9N_2BrSHg$: Hg, 43.8; Br, 17.5. Found: Hg, 43.4; Br, 17.4.

Preparation and Properties of the Base, Mercury (2-Dimethylamino-5-bromo Phenyl-)hydroxide.—An alcoholic solution of the acetate when treated with the calculated amount of sodium hydroxide in alcohol slowly deposited hard, wart-like masses of crystals. These melt at 162° and give off bubbles without blackening at 165°. No method was found for purifying this substance as it is practically insoluble in all solvents except acetic acid and ethyl acetate which, of course, change it back to the acetate. The powdered crystals were dried over soda lime and analyzed.

Calc. for $C_8H_{10}ONBrHg$: Hg, 48.1. Found: 48.4.

Preparation and Properties of the Formate.—Five g. of the hydroxide was heated under a reflux condenser with 50 cc. of ethyl formate for half an hour. Most of the hydroxide dissolved. When filtered and cooled the solution gave fine felted needles, m. p. 145°, decomposing at 150°. On standing the pure white crystals turned black, possibly due to the liberation of a small amount of mercury. The solubilities of the formate are similar to those of the acetate except that it is rather more soluble, notably so in water, chloroform, and carbon tetrachloride.

Calc. for $C_9H_{10}O_2NBrHg$: Hg, 45.1; Br, 18.0. Found: Hg, 45.4; Br, 18.8.

Preparation of the Mercury Diphenyl Derivative. Mercury Di-(2-dimethylamino-5-bromo Phenyl).

27.6 g. of mercury(2-dimethylamino-5-bromo phenyl) acetate was mixed with 23 g. of powdered potassium iodide and heated with 200 cc. of alcohol under a reflux condenser for 8 hours. At the end of the heating most of the material had dissolved giving a pale yellow solution. A small insoluble residue was colored dark by metallic mercury. After filtration the residue was extracted with cold benzene giving a solution which left 7.5 g. of crystals melting at 95 to 105°. The residue insoluble in benzene contained 0.5 g. of metallic mercury and a water-soluble inorganic compound (K_2HgI_4). The original yellow alcoholic solution deposited 8.2 g. of crystals melting at 114 to 119°. The mother liquor from these crystals was treated with 200 cc. of water and allowed to stand. 2.6 g. of crystals melting at 55° were obtained. This substance was proved to be *p*-bromo-dimethylaniline. The water-alcohol mother liquor gave no more solid even on evaporation. The yield of the mercury diphenyl derivative was 86%.

The 15.5 g. of crystals melting over 95° was dissolved in 30 cc. of hot benzene and mixed with 50 cc. of petroleum ether (b. p. 35 to 45°). The mixture was only slightly turbid. On standing, 12 g. of crystals melting 115° separated. Three more crystallizations raised the melting point to 123°. The mother liquors yielded a small amount of *p*-bromo-dimethylaniline.

Properties of the Diphenyl Derivative.—The substance crystallizes in fine, white needles, m. p. 123°. It dissolves in the same solvents as the acetate but to a much greater extent. It is readily soluble even in the cold in benzene, toluene, ether, carbon disulfide, and acetone.

Calc. for $C_{16}H_{18}N_2Br_2Hg$: Hg, 33.5; Br, 26.8. Found: Hg, 33.3; Br, 26.5.

Other Methods of Obtaining the Mercury Diphenyl Derivative.

Action of the Acetate with Ammonium Bromide.—9.2 g. of mercury-(2-dimethylamino-5-bromo phenyl) acetate was mixed with 4 g. of ammonium bromide and 200 cc. of alcohol and heated under a reflux condenser for 3 hours. The reaction mixture was worked up in the same way as that obtained by means of potassium iodide. The products obtained were 3.2 g. of the bromide, 0.2 g. of the mercury diphenyl compound, and 2.6 g. of *p*-bromo-dimethylaniline. The aqueous washings from the last substance contained large amounts of inorganic mercury compounds probably formed by the hydrobromic acid liberated by the dissociation of the ammonium bromide.

Action of the Acetate with Sodium Bromide.—The experiment was carried out in the same way as with the ammonium bromide. An insoluble residue consisted of 0.8 g. of metallic mercury and 6.4 g. of the bromide. The original solution deposited 1.2 g. of the bromide on cooling. Evaporation of the mother liquor left a sticky solid from which some inorganic mercury compound was extracted by water.

Action of the Acetate with Large Excess of Calcium Chloride.—2.3 g. of the acetate with 2 g. calcium chloride, and 25 cc. water and 100 cc. of alcohol were heated under a reflux condenser for 12 hours. The solid residue (0.8 g.) consisted of impure chloride (m. p. 171–4°). The solution on cooling deposited 1.1 g. of the chloride, m. p. 181°. Evaporation of the mother liquor gave 1.2 g. of solid, most of which dissolved in water. The water solution gave no action with hydrogen sulfide showing that *no inorganic mercury compound had been formed.*

Effect of Heat on the Iodide in Benzene Solution.—1.7 g. of the iodide in 50 cc. of benzene was heated under a reflux condenser for 6 hours. Only unchanged iodide was recovered. There was no evidence of the formation of any mercuric iodide or of metallic mercury.

Heating of the Mercury Diphenyl Compound with Excess of Potassium Iodide.—Long refluxing (15 hours) of the mercury diphenyl derivative with a large excess of potassium iodide in alcohol gave a very small amount (less than 0.1 g.) of metallic mercury and a very small amount of a water-soluble inorganic mercury compound. Most of the mercury diphenyl compound was recovered unchanged. When the mercury diphenyl derivative was refluxed with alcohol for 30 hours a slight amount of metallic mercury was formed. No inorganic mercury compound was obtained. Pure potassium mercuric iodide was refluxed for 10 hours with alcohol without the formation of any metallic mercury. These experiments show that the formation of metallic mercury is due to the action of the organo-mercury compounds with the alcohol. The reaction is in all cases a very slight one.

Action of the Acetate with Sodium Thiosulfate.—Five g. of the acetate in a mixture of 100 cc. of alcohol and 100 cc. of benzene was treated with 7 g. of sodium thiosulfate in 10 cc. of cold water. At first there was no change apparent on shaking. On standing the mixture turned black. An excess of conc. sodium thiosulfate solution was added. The black precipitate did not change. Filtration gave a clear solution which turned black on standing. The black substances were tarry and unmanageable. Probably they were mixtures of the organo-mercuric thiosulfate, the mercury diphenyl compound, metallic mercury, etc.

Action of the Acetate with Potassium Sulfide.—When an alcoholic solution of the acetate is treated with alcoholic potassium sulfide a pure, white precipitate forms at once. This almost instantly turns yellow, then gray, and finally black. This change is very rapid if the solutions are warm when mixed. Attempts were made to filter off the precipitate made from cold solutions before it had a chance to darken. These were unsuccessful as the sulfide is very gelatinous and filters slowly. During this slow filtration the precipitate always turned yellow. The white sulfide was finally obtained in the following way: 2.3 g. of the acetate dissolved in 250 cc. of cold alcohol was mixed with 20 cc. of alcohol containing 0.28 g. of potassium sulfide. The mixture was *immediately* poured into cold water. The precipitate remained white. It was filtered through a fluted filter paper and dried between several thicknesses of filter paper. When wet the sulfide formed a thick, gelatinous mass; when dry it formed hard, white flakes which turned slightly gray on long standing. When heated in a melting point tube it turned gray at about 97° and partly melted 115 to 120°. This behavior is probably due to the change of the sulfide into mercuric sulfide and the mercury diphenyl derivative (m. p. 123°). The sulfide was not soluble in any cold solvent. All hot solvents turned it gray except ether and petroleum ether in which it was not appreciably soluble. The other solvents dissolved part of it on heating but gave very tarry substances on evaporation. Evidently the decomposition of the organo-mercuric sulfide into mercuric sulfide and the mercury diphenyl derivative is not readily brought to completion.

Action of the Acetate and the Hydroxide with Stannous Compounds.—9.2 g. of the acetate in 400 cc. of alcohol treated with aqueous sodium stannite made from 2.3 g. of crystallized stannous chloride and an excess of sodium hydroxide gave 3.8 g. of the mercury diphenyl compound, a 63% yield.

When the hydroxide was refluxed in alcohol with stannous chloride the chief products were the organo-mercuric chloride, metallic mercury and *p*-bromo-dimethylaniline. The formation of the last named substance was probably due to hydrochloric acid liberated by the hydrolysis of the stannous chloride.

When the base was treated with freshly precipitated stannous hydroxide suspended in alcohol only a very small amount of the mercury diphenyl compound was obtained. This was probably due to the slight solubility of both substances in alcohol.

Effect of Heat on the Formate.—One g. of the formate was heated for 30 hours with 20 cc. of benzene and 20 cc. of alcohol. 0.4 g. of metallic mercury was formed. The filtrate on standing gave less than 0.1 g. of the mercury diphenyl compound and about 0.5 g. of *p*-bromo-dimethylaniline.

Action of the Acetate with Zinc Dust.—4.6 g. of the acetate mixed with 0.4 g. of zinc dust and 100 cc. of alcohol was heated under a reflux condenser for 2 hours. The residue weighed 0.9 g. and consisted of metallic mercury and some zinc oxide (or hydroxide). The solution gave 1.3 g. of unchanged acetate and 0.9 g. *p*-bromo-dimethylaniline. When the experiment was repeated, using copper powder, no product but the original acetate and a very small amount of metallic mercury was obtained.

Action of Mercuric Salts with the Mercury Diphenyl Derivative, Mercury Di-(2-dimethylamino-5-bromo Phenyl).

One g. of the mercury diphenyl compound mixed with 0.5 g. of mercuric chloride and 50 cc. of alcohol and refluxed for 4 hours gave 1.5 g. of the chloride, melting at 181°. Yield, 100%.

A similar experiment using mercuric bromide gave 1.5 g. of the bromide, melting at 179°. Yield, 94%.

Using mercuric iodide instead of the chloride, 1.7 g. of the iodide was obtained, melting at 160°. Yield, 95%. It will be noted that the iodide obtained in this way is not as nearly pure as are the corresponding bromide and chloride.

When mercuric thiocyanate was used in place of the halides the organo-mercuric thiocyanate melting at 130° was obtained in 87% yield.

One g. of the mercury diphenyl compound refluxed with 0.5 g. of mercuric sulfate in alcohol gave a yellow solid which proved to be basic mercuric sulfate and a small amount of *p*-bromo-dimethylaniline.

Summary.

1. Mercuric acetate reacts with *p*-bromo-dimethylaniline introducing the mercuri-acetate group, —Hg—O—CO—CH_3, into the *ortho* position. Yield, 74%.

2. The mercury-(2-dimethylamino-5-bromo phenyl-) acetate obtained in this way readily yields other salts by double decomposition reactions. The chloride, bromide, iodide, and thiocyanate were prepared and their properties studied.

3. The organo-mercuric hydroxide of this series was prepared. From it was made the corresponding formate by treatment with ethyl formate. This treatment of an organo-mercuric hydroxide with an ester gives a new method for making organo-mercuric salts which cannot conveniently be made in any other way.

4. The mercury diphenyl derivative was made and its properties studied.

5. The change of compounds of the type R—Hg—X to those of the mercury diphenyl type, R_2Hg, may be brought about by alkaline reducing agents and by substances like iodides, sulfides, and thiosulfates It is suggested that this reaction depends upon the ability of these substances to form very stable complex ions of mercury. In confirmation of this it has been found that the iodides are most efficient of the halides in bringing about this reaction. Bromides bring it about to only a very slight extent and chlorides do not do so at all.

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