

Conclusions previously drawn regarding the distribution of the sulfur in arsphenamine have been substantiated.

The ease of solution of arsphenamine in water depends partly upon the acidity of the reduction medium during the formation of arsphenamine base. Specimens prepared by use of pure hydrosulfite are much more readily soluble than similar ones in the preparation of which commercial hydrosulfite has been used.

The writer is indebted to Dr. Reid Hunt for examining the product toxicologically and to Mr. Arthur J. Norton for assisting in some of the experiments.

BOSTON 17, MASSACHUSETTS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PREPARATION OF THE MERCURY COMPOUNDS OF THE PHENYL HALIDES

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Received January 30, 1923

The preparation of the simple halogen-benzene-mercury compounds is not recorded in the literature. The problem can be attacked in at least two ways: (1) by the direct mercuration of the phenyl halide, such as the treatment of the phenyl halide with mercuric acetate, resulting in the replacement of a hydrogen atom of the benzene ring by mercury; (2) by the indirect introduction of mercury, that is, the replacement by mercury of some group already present in the benzene ring, such as the sulfinic acid group.

In 1920 Kharasch² found that when phenyl halides are heated with mercuric acetate, mercury compounds are formed. Since then the direct mercuration of the phenyl halides has been more closely investigated by the writer. It has been found that although the *p*-halogen-phenylmercuric acetates can easily be isolated in fairly good yield, the separation of the remaining *ortho* and *meta* compounds, and possibly other products, is extremely difficult, and requires a tedious process of fractional crystallization. The reaction is one of great theoretical interest, but as a source of mercury compounds of the phenyl halides it thus far appears to be impractical.

In the hope of finding a more expedient method for preparing these compounds the reaction of heating the mercuric salt of the halogen-ben-

¹ This work was done by Martin E. Hanke as National Research Fellow in Organic Chemistry at the University of Chicago from September, 1921, to August, 1922.

² Private communication.

zene-sulfinic acid³ was tried. Every attempt was entirely successful. The reactions are quick, the yields good, and the products can be isolated directly in pure condition.

The Sulfinic Acid Method

In every case the halogen-benzene-sulfinic acid was made from the corresponding halogen aniline by the diazo reaction according to Gattermann's⁴ method. The sulfinic acid was then boiled with three equivalents of mercuric acetate in glacial acetic acid, the solution filtered to remove the mercurous salts which are formed in the reaction, and the halogen-phenylmercuric acetate precipitated from the filtrate by the addition of water or alkali. The halogen-phenylmercuric chlorides can be prepared by the addition of sodium chloride to aqueous or alcoholic solutions of the corresponding acetates. All the products, sulfinic acids as well as mercury compounds, are white crystalline solids. The sulfinic acids are usually best recrystallized from benzene, while the mercury compounds, both acetates and chlorides, crystallize very well from alcohol.

It is interesting to note that the melting points⁵ of the *o*-chloro- and -bromobenzene sulfinic acids are distinctly higher than those of the corresponding *para* compounds, while those of the *meta* compounds are lowest of all. These melting points are probably decomposition temperatures, and it may be that the relatively high melting points of the *o*-sulfinic acids are an index of their greater stability. This is in agreement with the fact that the *meta* compounds, with the lowest melting sulfinic acids, give distinctly the poorest yields of mercury compounds.

The mercury compounds have been identified by replacing the mercury by bromine and identifying the resulting dihalogen benzene by its melting or boiling point.

The preparation of the *o*- and *m*-iodo compounds is now in progress.

Direct Mercuration of the Phenyl Halides

The method is to heat the phenyl halide with 0.1 molecular equivalent of mercuric acetate⁶ at 140° under a reflux condenser until a sample portion no longer gives a positive test for inorganic mercury by the sulfide test.⁷

³ This reaction was discovered by Peters [(a) *Ber.*, **38**, 2567 (1905)]. Kharasch and Chalkley applied the method with good success to the preparation of nitrobenzene mercury compounds [(b) *THIS JOURNAL*, **43**, 608 (1921)]. See also Whitmore, Hamilton, and Thurman [(c) *ibid.*, **45**, 1067 (1923)].

⁴ Gattermann, *Ber.*, **32**, 1136 (1899).

⁵ For data see experimental part.

⁶ This great excess of phenyl halide is used in order to cut down the formation of dimercury compound and thus allow for a maximum yield of the monomercurated product.

⁷ These and other experimental details are included here because there is no experimental part with this section of the paper. It was thought well to postpone publication of complete practical details, until the methods had been worked out better, and the nature of the reactions and products understood more clearly.

About 2.5 hours' heating is required with phenyl chloride and bromide, while the reaction is complete in less than 1.5 hours with phenyl iodide. This fact may be related to the relative stability of the mercurated products, that is, that mercurated phenyl iodide is decomposed by ammonium sulfide in the cold, while the corresponding products from phenyl chloride and bromide require heat for decomposition by this reagent. The mixture is distilled with steam to remove the excess phenyl halide, and a yellow-to-brown sticky solid remains. This residue can be separated by fractional extraction and crystallization from alcohol, benzene or ether.

In all cases small quantities of very insoluble gray-to-brown residues were isolated, which do not melt, but decompose at about 250°. They probably contain dimercury compounds.

The first compounds to crystallize are the *p*-halogen-phenylmercuric acetates. They can easily be purified by recrystallization from benzene and from alcohol. The melting points are in each case slightly lower than those of the same compounds made by the sulfinic acid method, being 188.5°, 192° and 188°, respectively, for the *p*-chloro-, *p*-bromo- and *p*-iodo-phenylmercuric acetates, while the melting points of the same compounds made by the sulfinic acid method are 192°, 196° and 191°. ⁸ It appears that the compounds made by direct mercuration probably contain persistent impurities which cannot well be removed by fractional crystallization. The yields of the *para* compounds are about 40% with phenyl chloride, 25% with phenyl bromide, and only about 4% with phenyl iodide. All of the compounds have been identified by replacing the mercury with halogen and isolating the expected *p*-dihalogen-benzene in quantity. The *p*-chloro-phenylmercuric acetate was analyzed.

Subs., 0.3753, 0.3085: HgS, 0.2371, 0.1935. Calc. for C₆H₅O₂ClHg: Hg, 54.04. Found: 54.45, 54.05.

The mother liquors from the *para* compounds contain in each case a mixture of several lower-melting halogen-benzene-mercury compounds which are not readily separable. The products with phenyl bromide were the only ones investigated in any detail.

By repeated fractional extraction with ether, in which all the products are somewhat soluble, the lower melting ones more, the higher melting ones less, the following products were isolated: a white solid, m. p. 123°, which was identified as *o*-bromo-phenylmercuric acetate; and a white solid, m. p. 160°, which was identified as *m*-bromo-phenylmercuric acetate. For the identification of the *meta* compound a mixed melting point was taken with the *m*-bromo-phenylmercuric acetate prepared by the sulfinic acid method, and this mixed melting point was also 160°. In addition,

⁸ This is entirely similar to the observations on *o*-nitrobenzene-mercuric chloride. Dimroth, who made this compound by the direct mercuration of nitrobenzene, reports a melting point of 181–182° [(a) *Ber.*, 35, 2036 (1902)], while Kharasch and Chalkley, who used the sulfinic acid method, report a melting point of 185° (Ref. 3b, p. 611).

the *chloride* was prepared from the acetate by treatment in alcoholic solution with sodium chloride. The resulting product melted at 198°, as did the corresponding compound prepared by the sulfinic acid method. This is a notable exception to the rule that mercury *never* enters the benzene ring in the *meta* position, about which there has been considerable discussion in the literature.⁹ This observation will be repeated, and *meta* compounds will also be looked for among the products made with phenyl chloride and phenyl iodide.

Other lower-melting products were also obtained, but these are probably mixtures of those identified above. They will be further investigated.

In the mercuration of phenyl chloride, a product is formed which has an extremely corrosive action on the skin. It persists in the mother liquors, rather than in any of the isolated compounds. Its presence makes certain stages in the purification of the products of the direct mercuration of phenyl chloride a problem requiring great care in manipulation. No such physiological action was observed with any other of the preparations, either by the sulfinic acid method, or by the mercuration of phenyl bromide or iodide.

Replacement of Mercury by a Nitro Group in Aromatic Compounds

When *p*-chloro-phenylmercuric acetate is treated with conc. nitric acid at 65° for 10 minutes, the mercury is replaced by a nitro group, and *p*-chloro nitrobenzene is formed in quantity. With *p*-bromo-phenylmercuric acetate and nitric acid under similar conditions, *p*-bromonitrobenzene is the product. Similarly, *o*-chloro-phenylmercuric acetate yields *o*-chloronitrobenzene; and *o*-bromo-phenylmercuric acetate yields *o*-bromonitrobenzene. With the *meta* compounds, however, the reactions do not proceed so smoothly. The *meta* mercury compounds are decomposed by the nitric acid, but the products isolated, high boiling oils, could not be identified by their melting or boiling points.

The failure to isolate the *m*-halogen-nitrobenzenes from the reaction of the *m*-halogen-benzene-mercury compounds with nitric acid, leads one to speculate about the nature of the reaction with the *ortho* and *para* compounds. Possibly it is not a simple replacement of the mercury by a nitro group. That it cannot be first a replacement of the mercury by hydrogen, a common reaction of mercury compounds with strong acids, and then a nitration of the resulting halogen benzene, is indicated by the following facts. The *p*- and *o*-halogen-phenylmercuric compounds yield exclusively *p*- and *o*-halogen-nitrobenzenes, respectively, although a monohalogen-benzene on nitration yields a mixture of *ortho* and *para* compounds. Also, no *o*- or *p*-nitro-halogen-benzenes are formed from the *m*-halogen-benzene-mercury compounds. The writer believes that

⁹ See Dimroth, Ref. 8a, p. 2032. Also Ref. 3b, and Kharasch and Jacobsohn, THIS JOURNAL, 43, 1894 (1921).

the replacement of the *meta* mercury by a nitro group is entirely similar in nature to the reactions with the *ortho* and *para* compounds, and will resolve itself simply into developing the proper conditions for the reactions.

Whatever the mechanism of the reactions, these are the first definite replacements of mercury by a nitro group recorded,¹⁰ and it is hoped that this reaction may be of value in synthesizing nitro compounds as well as in identifying mercury compounds. The replacement of mercury by other groups like the sulfonic and arsonic acid groups is also contemplated.

Experimental Part

p-Chloro-phenylmercuric Acetate by the Sulfinic Acid Method¹¹

In a 500cc. Erlenmeyer flask, 7.4 g. of *p*-chloro-aniline (equivalent to 10.0 g. of bromo-aniline or 12.7 g. of iodo-aniline) is dissolved in 160 cc. of water and 44 cc. of conc. sulfuric acid by heating. On cooling, white *p*-chloro-aniline sulfate crystallizes. The mixture is cooled well in ice, and 4.5 g. of sodium nitrite dissolved in 25 cc. of water is added gradually with constant mechanical stirring. After the nitrite has been added all of the solid disappears, and the solution gives a positive starch-iodide test. A previously well-cooled solution of 22 cc. of conc. sulfuric acid and 15 cc. water is then added. The flask and contents are weighed, and sulfur dioxide is passed in under pressure until the weight increase is 50 to 60 g. (20 g. of sulfur dioxide in 100 cc. of solution). It is important to have the liquid very cold in order to expedite the absorption of the sulfur dioxide. In fact, anything that can be done to reduce the time of the reactions will help the yield, since both the diazo compound and the sulfinic acid are unstable. The sulfur dioxide absorption is complete in about 1 hour.

The mixture, which should be only slightly colored and free from solid, is transferred to a liter beaker immersed in a freezing mixture. About 50 g. of catalytic copper¹² is now added gradually with constant stirring until the violent gas evolution resulting from the decomposition of the diazo compound is complete. During the addition of the copper a slow stream of sulfur dioxide is passed through the liquid to insure an excess of this gas in solution. The *p*-chlorobenzene-sulfinic acid which is formed at this stage is practically insoluble in the liquid, and is present as a solid with the copper.

The mixture is filtered, and the residue, after being washed with a little cold water to remove excess sulfuric acid, is extracted with 250 cc. of 10% sodium carbonate solution, which dissolves the sulfinic acid as the sodium salt. The copper is removed by filtration and discarded. The clear, well-cooled sodium carbonate solution is neutralized carefully by cold¹³ 50% sulfuric acid, and the *p*-chlorobenzene-sulfinic acid separates as white glistening flakes. It is collected on a Büchner funnel, and washed with a little water, *m. p.*,¹⁴ 99°.

¹⁰ Dreher and Otto, *Ann.*, **154**, 97, 124 (1870) observed a violent reaction between mercury diphenyl and nitric acid, resulting in the formation of nitro derivatives of benzene.

¹¹ The first part of this preparation, involving the preparation of the sulfinic acid, is very similar to the method of Gattermann, *Ref. 4*, and his paper should be consulted for the details of the reaction.

¹² This is prepared by the action of finely powdered zinc on copper sulfate solution according to Gattermann's method, *Ber.*, **23**, 1219 (1890).

¹³ The sulfinic acid decomposes rapidly even at slightly elevated temperatures. Low temperature also decreases the solubility of the sulfinic acid.

¹⁴ Gattermann gives 93°. *Ref. 4*.

The crude sulfinic acid (weighing 11.3 g., damp) is dissolved at once in 50 cc. of glacial acetic acid, and a solution of 50 g. of mercuric acetate (at least 3 molecular equivalents) in 100 cc. of glacial acetic acid is added. A white precipitate of the mercuric sulfinate forms at once. The mixture is heated to boiling for 15 minutes, during which time the mercuric salt of the *p*-chlorobenzene-sulfinic acid is completely converted into the *p*-chloro-phenylmercuric acetate. This compound is very soluble in glacial acetic acid, while mercurous acetate and mercurous sulfate, which are also formed in the reaction, remain as solids. The mixture is filtered free from these mercurous salts, and the *p*-chloro-phenylmercuric acetate is precipitated from the filtrate, by the addition of water or alkali, as a white crystalline solid; m. p., 193°; yield, 14.0 g. For analysis it was recrystallized once from hot alcohol, and dried in a vacuum over sulfuric acid.

Analysis. Subs., 0.2379: HgS, 0.1470. Calc. for $C_6H_4O_2ClHg$: Hg, 54.04. Found: 53.29.

The mother liquors from the sulfinic acid contain a small amount of this substance. They are treated with 100 cc. of 10% aqueous mercuric acetate solution which causes the precipitation of the white mercuric salt of the sulfinic acid. This mercuric sulfinate (weight, 4.7 g., wet), is collected on a filter, mixed with 40 cc. of glacial acetic acid and 4 g. of mercuric acetate, heated to boiling, and the *p*-chloro-phenylmercuric acetate isolated as described above. The additional yield is 1.5 g. This, with the 14.0 g. noted above, is a total yield of 15.5 g., or 70%.

For the preparation of *p*-chloro-phenylmercuric chloride, 1 g. of the acetate was dissolved in 50 cc. of hot 75% alcohol, and 10 cc. of a 10% sodium chloride solution was added gradually with constant stirring. The chloride of the organic mercury compound is precipitated as a white crystalline solid; m. p., 225°. It can easily be recrystallized from hot alcohol.

For the further identification of the acetate, 4.0 g. of the compound is suspended¹⁵ in 120 cc. of 10% aqueous potassium bromide solution, and 20 cc. of 10% bromine in 10% potassium bromide solution (3 cc. excess) is added. The mixture is shaken for 1 hour, preferably in a shaking machine. The bromine replaces the mercury and *p*-chloro-bromobenzene is formed, as a white solid. It is collected on a filter, washed with water, and recrystallized once, best from ligroin, to remove undecomposed mercury compound; m. p., 67°.

***m*-Chloro-phenylmercuric Acetate.**—This and the subsequent "sulfinic acid method" preparation are very similar to the *p*-chloro-phenylmercuric acetate preparation described above. Only the differences in details will be given.

At the very beginning, for 7.4 g. of the *m*-chloro-aniline, 125 cc. of water is used instead of 160 cc. *m*-Chloro-aniline is more soluble than the *para* compound. The smaller volume is desirable since it shortens the time required later for saturation with sulfur dioxide, and thus improves the yield.

m-Chlorobenzene-sulfinic acid crystallizes in long, white needles when the cold solution of its sodium salt is acidified; m. p., 81°. It is more soluble in water than is the corresponding *para* compound. In fact, more than half the product remains in the mother liquors; this can be recovered by precipitating the mercuric salt of the sulfinic acid, and converting this into the benzene-mercury compound by heating with mercuric acetate and acetic acid.

m-Chloro-phenylmercuric acetate is a white, crystalline solid, best recrystallized

¹⁵ Under the heading "*m*-chloro-phenylmercuric acetate," below, a method is described for carrying out this replacement of the mercury by bromine in acetic acid solution instead of aqueous suspension as given here. The acetic acid method is probably superior, since the reaction is much quicker and more complete in solution than it is in suspension.

from alcohol, soluble in glacial acetic acid, benzene, acetone, and slightly soluble in ether; m. p., 133°.

Analysis. Subs., 0.4319: HgS, 0.2696. Calc. for $C_8H_7O_2ClHg$: Hg, 54.04. Found: 53.85.

m-CHLORO-PHENYLMERCURIC CHLORIDE, prepared from the acetate by the addition of sodium chloride to a dil. alcoholic solution of the acetate, as described above for the *para* compound, is a white crystalline solid. It is best recrystallized from hot alcohol; m. p., 210°.

Analysis. Subs., 0.3772: HgS, 0.2504. Calc. for $C_6H_4Cl_2Hg$: Hg, 57.71. Found: 57.25.

For the further identification of the compound, 3.0 g. of the acetate was dissolved in 30 cc. of 90% acetic acid, and 15.0 cc. of 10% bromine in 50% acetic acid¹⁶ was added gradually with constant stirring. The bromine is decolorized almost immediately. It displaces the mercury with the formation of *m*-chlorobromobenzene. The resulting pale yellow solution was made alkaline with sodium hydroxide and sodium carbonate, which neutralized the acetic acid and caused the precipitation of the inorganic mercury. The mixture was distilled with steam, and about 2 cc. of a colorless oil was obtained. This was distilled directly from a side-neck test-tube fitted with an Anschließtz thermometer, using a sulfuric acid bath. The boiling point was 197°, and the compound was thus identified as *m*-chlorobromobenzene.

o-Chloro-phenylmercuric Acetate.—Here only 100 cc. of water is required for 7.4 g. of *o*-chloro-aniline. The *o*-chlorobenzene-sulfinic acid crystallizes very well as a white crystalline solid; m. p., 120°. It can well be recrystallized from benzene. It is only slightly soluble in water, even less so than the *para* compound, and it is, therefore, not worth while to work up the mother liquors. *o*-Chloro-phenylmercuric acetate is a white, crystalline solid; m. p., 115°; yield, 15.0 g., or 70%.

Analysis. Subs., 0.3615: HgS, 0.2265. Calc. for $C_8H_7O_2ClHg$: Hg, 54.04. Found: 54.04.

o-CHLORO-PHENYLMERCURIC CHLORIDE was made from the acetate in the usual way; m. p., 145°.

The mercury was replaced by bromine in acetic acid solution, exactly as described above for the *meta* compound. The resulting oil boiled at 204°, which identified it as *o*-chlorobromobenzene.

p-Bromo-phenylmercuric Acetate.—Ten g. of *p*-bromo-aniline was dissolved in 160 cc. of water and 44 cc. of conc. sulfuric acid, and the rest of the reaction was carried out as described above for the *p*-chloro compound. *p*-Bromobenzene-sulfinic acid is a white crystalline solid; m. p., 114°. It is appreciably soluble in water, about 20% of the total yield remaining in the mother liquors. *p*-Bromo-phenylmercuric acetate is a white crystalline solid; m. p., 196°; yield, 14 g., or 60%.

Analysis. Subs., 0.4919: HgS, 0.2752. Calc. for $C_8H_7O_2BrHg$: Hg, 48.26. Found: 48.24.

p-BROMO-PHENYLMERCURIC CHLORIDE was made from the acetate in the usual way, m. p., 250°.

The mercury was replaced by bromine in aqueous suspension, by the method described for the *p*-chloro compound. The resulting solid had a melting point of 88°, and was thus identified as *p*-dibromo-benzene. When 4.0 g. of the *p*-bromo-phenylmercuric acetate is shaken with 120 cc. of 10% potassium iodide solution and 28 cc. of

¹⁶ That is, 1.5 g. of bromine in approximately 7.5 cc. of glacial acetic acid and 7.5 cc. of water.

10% iodine in 10% potassium iodide solution, the mercury is replaced by iodine, and *p*-bromo-iodobenzene, m. p., 91°, is the product. When 4.0 g. of the *p*-bromo-phenylmercuric acetate is suspended in 120 cc. of water and shaken while a slow stream of chlorine gas is passed through the solution, the mercury is replaced by chlorine, and *p*-chlorobromobenzene, m. p., 66°, is the product.

***m*-Bromo-phenylmercuric Acetate.**—Ten g. of *m*-bromo-aniline was dissolved in 140 cc. of water and 44 cc. of conc. sulfuric acid. *m*-Bromobenzene-sulfinic acid melts at 88°. About 1/4 of the yield is in the mother liquors from the sulfinic acid. *m*-Bromophenylmercuric acetate is a white crystalline solid; m. p., 160°; yield, 10 g., or 40%.

Analysis. Subs., 0.3913: HgS, 0.2167. Calc. for C₈H₇O₂BrHg: Hg, 48.26. Found: 47.77.

***m*-BROMO-PHENYLMERCURIC CHLORIDE** made by the addition of sodium chloride to a dil. alcoholic solution of the acetate, as described under the *p*-chloro compound above, melts at 198°.

The mercury was replaced by bromine in acetic acid solution as described under the *m*-chloro-compound, above. An oil was isolated, which was identified as *m*-dibromobenzene by the boiling point, 220°.

***o*-Bromo-phenylmercuric Acetate.**—One hundred cc. of water was used for 10 g. of *o*-bromo-aniline. *o*-Bromobenzene-sulfinic acid melts at 130°. It crystallizes well on cooling a hot benzene solution, and is practically insoluble in cold water. *o*-Bromophenylmercuric acetate is a white crystalline solid; m. p., 124°; yield, 16 g., or 66%.

Analysis. Subs., 0.3261: HgS, 0.1806. Calc. for C₈H₇O₂BrHg: Hg, 48.26. Found: 47.77.

***o*-BROMO-PHENYLMERCURIC CHLORIDE** made in the usual way melts at 155°. When this compound is heated under a glass vessel in a drying oven at 100° for several days, it sublimes, and long white needles of a very pure product are formed. When the mercury was replaced by bromine in acetic acid solution, *o*-dibromo-benzene, b. p. 225°, was isolated.

***p*-Iodo-phenylmercuric Acetate.**—To a solution of 12.7 g. of *p*-iodo-aniline in 380 cc. of water (much more water than was required for the solution of any other of the halogen anilines) and 50 cc. conc. sulfuric acid, is added 4.5 g. of sodium nitrite in 25 cc. of water. After the diazotization, 50 cc. of conc. sulfuric acid and 20 cc. of water are added, instead of the quantities given for the *p*-chloro compound. This increased quantity of acid is required to keep the acid concentration sufficiently high. The absorption of sulfur dioxide and addition of copper powder take place in the usual manner, except of course that greater quantities are required, 100 g. of the former, and 70 g. of the latter.

p-Iodobenzene-sulfinic acid separates as a white crystalline solid on acidifying its alkaline solution. It can be well recrystallized from hot water. When heated in a melting-point tube it seems to change state at about 100°, although it does not liquefy completely. It is appreciably soluble in cold water, and about half the yield is in the mother liquors.

p-Iodo-phenylmercuric acetate separates first as pinkish crystals which can, however, be entirely decolorized by recrystallization from alcohol with charcoal; yield, 14 g., or 50%; m. p., 191°.

Analysis. Subs., 0.3375: HgS, 0.1701. Calc. for C₈H₇O₂IHg: Hg, 43.35. Found: 43.46.

The mercury was replaced by bromine in aqueous suspension as described under the *p*-chloro compound. One g. of *p*-iodo-phenylmercuric acetate was suspended in 30 cc. of 10% potassium bromide solution; 4.0 cc. of 10% bromine in 10% potassium bromide solution was added, and the mixture shaken vigorously for 1 hour. The solid was col-

lected on a filter, dried in a desiccator, and dissolved in ligroin; the ligroin solution was filtered and evaporated. White crystals of *p*-iodo-bromobenzene remained; m. p., 92°. A mixed melting point of these crystals with the *p*-bromo-iodobenzene (m. p., 91°) obtained by the replacement of mercury by iodine in *p*-bromo-phenylmercuric acetate, is 91°.

Replacement of Mercury by a Nitro Group

One g. of *p*-chloro-phenylmercuric acetate is added to 5 cc. of conc. (68%) nitric acid. The mixture is stirred well, warmed to 65°, and kept at that temperature for 10 minutes, during which the solid gradually dissolves, and the liquid becomes reddish brown. On cooling, a solid crystallizes. The mixture is poured into much water, the precipitated solid collected on a filter and washed with water. When recrystallized from alcohol, the product separates as long, slightly yellow needles, m. p., 85°. It is pure *p*-nitrochlorobenzene. *p*-Bromo-phenylmercuric acetate with nitric acid under the same conditions yields *p*-bromonitrobenzene, a white crystalline solid; m. p., 125°.

The *o*- and *m*-chloro- and bromonitrobenzenes do not readily crystallize directly, so the experimental detail here is somewhat different from that for the *para* compounds. One g. of *o*-chloro-phenylmercuric acetate is treated with 5 cc. of conc. nitric acid at 65° for 10 minutes, as described above. The mixture is diluted with water, neutralized with sodium carbonate, and distilled with steam. The distillate contains a slightly greenish oil which soon solidifies. The product is transferred to a side-neck test-tube fitted with an Anschütz thermometer and distilled; b. p., 244.5°. This distillate is a yellowish-brown oil which solidifies when cooled; m. p., 33°. The product is thus identified as *o*-chloronitrobenzene. *o*-Bromo-phenylmercuric acetate with nitric acid under the same conditions yields *o*-bromonitrobenzene; m. p., 43°.

With the *meta* compounds the course of the reaction could not be followed so easily. One g. of *m*-bromo-phenylmercuric acetate was treated with 5 cc. of conc. nitric acid at 65° for 10 minutes. On cooling the mixture and diluting it with water, a dark brown oil separated which solidified on stirring and further cooling. This solid was collected on a filter, and recrystallized from alcohol. Yellowish crystals were thus obtained; m. p., 118°. This certainly is *not m*-bromonitrobenzene, the melting point of which is given as 56.4°. On evaporating the alcoholic mother liquors, a small drop of a brown oil was obtained which was not further investigated. From the reaction mixture of 1 g. of *m*-chloro-phenylmercuric chloride and 5 cc. of nitric acid kept at 65° for 10 minutes, a brown solid was isolated, which on recrystallization from alcohol melted at 110°. The alcoholic mother liquors were evaporated, and the residue distilled with steam, but no oil passed over. The residue from the distillation was extracted with ether, the ether evaporated, and a solid thus obtained; m. p., 102–104°. This is probably an impure form of the product described above melting at 110°. Certainly, none of these products is *m*-chloronitrobenzene, the melting point of which is given as 44°.

Summary

1. The preparation of *o*-, *m*-, and *p*-chloro-phenylmercuric acetates, *o*-, *m*-, and *p*-bromo-phenylmercuric acetates, and *p*-iodo-phenylmercuric acetate from the corresponding halogen anilines by the sulfinic acid method has been described.

2. An account of the beginning of an extensive investigation of the direct mercuration of the phenyl halides has been given. (a) *p*-Chloro-, *p*-bromo-, *o*-bromo-, *m*-bromo-, and *p*-iodo-phenylmercuric acetates have been isolated and identified. (b) The isolation of *m*-bromo-phenylmercuric

acetate from the reaction of phenyl bromide with mercuric acetate is important, as it is the first case of the formation of a *meta* mercury compound by direct mercuration. (c) Whether or not *ortho* and *meta* compounds are formed from phenyl chloride and phenyl iodide has not yet been determined.

3. The replacement of mercury by a nitro group has been carried out with *p*- and *o*-chloro-, and *p*- and *o*-bromo-phenylmercuric acetates. This reaction was not so simple with the *meta*-chloro- and bromo-mercury compounds. The limits of this reaction are being studied with other mercury compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS
OF NORTHWESTERN UNIVERSITY]

MERCURY DERIVATIVES OF SALICYLALDEHYDE AND THE NITRO-SALICYLALDEHYDES¹

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Received February 15, 1923

Aromatic aldehydes cannot, as a rule, be mercurated by mercuric acetate because of its oxidizing action. At the time the present work was done the only mercurated aromatic aldehyde was a mercury vanillin of undetermined structure.³ More recently the 3 hydroxybenzaldehydes have been mercurated.^{1a} Definite mercuration products have also been obtained from vanillin.⁴ Salicylaldehyde was chosen for the present study because of its resistance to oxidation and because of the activating effect of the phenolic hydroxyl.

Salicylaldehyde reacts readily with two molecular proportions of mercuric acetate in alcohol to form 3,5-diacetoxymercuri-salicylaldehyde. No oxidation takes place, as shown by the absence of mercurous acetate and metallic mercury from the products. The dichloromercuri compound is made in the usual way from an acetic acid solution of the acetate and a chloride solution. Even when only 1 molecular proportion of mercuric acetate is used the chief product is the dimercurated compound, although a small amount of a monomercurated product can be obtained from the

¹ Presented at the Birmingham Meeting of the American Chemical Society, April, 1922. Since the presentation of this paper an article has appeared by Henry and Sharp on the mercury derivatives of the three hydroxybenzaldehydes. (a) *J. Chem. Soc.*, **121**, 1055 (1922).

² Research Fellow under a grant from the U. S. Interdepartmental Social Hygiene Board, General M. W. Ireland, Chairman. Some of the compounds prepared are being investigated pharmacologically under the direction of Dr. A. S. Loevenhart of the Department of Pharmacology of the University of Wisconsin.

³ "Realenzyklopaedie für Pharmazie," vol. VII, p. 100.

⁴ Paolini, *Gazz. chim. ital.*, **51**, II, 188 (1921); *C. A.*, **16**, 557 (1922).