solves in ammonium hydroxide to give the intensely blue solution characteristic of cupri-ammonium ion. The writer has found, however, that when dilute ammonium hydroxide is slowly added to precipitated copper ferrocyanide, and the mixture shaken after each addition, the mahogany-brown precipitate is completely converted to a silky, dark brown solid, probably a substance of the formula $Cu_2Fe(CN)_6.4NH_3$.[2] This precipitate does not dissolve in concd. ammonium hydroxide, and is only slowly changed to copper sulfide when treated with hydrogen sulfide. Acetic acid, however, restores the copper ferrocyanide.

Scott[3] also states that the ferrocyanide of copper is soluble in ammonium hydroxide, and hence its presence must be avoided in the detection of traces of copper by the ferrocyanide method. When to two exceedingly dilute solutions of cupric sulfate, only one of which contained a trace of free ammonia, potassium ferrocyanide was added, the one without the trace of ammonia showed the usual characteristic deep red color, but the other developed a light brown color from which the silky, brown precipitate noted above settled on standing. These results could be duplicated as often as desired. They are to be interpreted as indicating that even the slightest trace of ammonia will seriously impair, if not completely obscure, the delicacy (1 part in 2,500,000) of the ferrocyanide test.

CONTRIBUTION FROM
COLUMBIA UNIVERSITY
NEW YORK CITY
RECEIVED AUGUST 13, 1923
E. D. CRITTENDEN

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE OTHO SPRAGUE MEMORIAL INSTITUTE]

FACTORS AFFECTING THE STABILITY OF MERCURIALS AND THE MERCURATION OF SUBSTITUTED PHENYLAMMONIUM SALTS

BY MORRIS S. KHARASCH AND LYMAN CHALKLEY, JR.

RECEIVED AUGUST 30, 1923

It is a well established fact that amino and hydroxyl groups in a benzene ring enhance the ease of substitution of the *para* and *ortho* hydrogen atoms. We should expect, therefore, that any positive group,[1] *para* or *ortho* to an

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[2] Bunsen, *Pogg. Ann.*, **34**, 134 (1835). See also Messner, *Z. anorg. Chem.*, **8**, 393 (1895).

[3] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, **1918**, 2nd ed., p. 166.

[1] The term positive group is rather indefinite. There are various degrees of "positivity" of positive groups depending upon the position of the pair of electrons with respect to the carbon atom. The arrangement of positive groups in the order of their "positivity" will be given in a subsequent paper by one of us (Kh.) in conjunction with the heats of combustion of organic compounds.

amino or hydroxyl group would be more or less labile. That such is the case is well demonstrated by the ease of substitution of halogens *ortho* or *para* to these negative groups. We find also that the lability is quite pronounced in the case of iodine, but not so striking for bromine. Chlorine, moreover, does not seem to be loosened to any extent when *ortho* or *para* to one or two negative groups.[2] This difference in behavior of the various members of the halogen family, when attached *ortho* or *para* to a negative group, is most probably due to the fact that while the iodine, and to some extent the bromine, tends to remain positive, the positive chlorine undergoes at once intramolecular oxidation reduction with the carbon atom.

While the essentials of the relationships developed are quite evident, it is by no means certain that the inability of the chlorine atom to be removed from the nucleus is due to a change in polarity of that atom. Furthermore, it is impossible to ascertain what effect acetylation, or methylation of the amino or hydroxyl groups exercises over the stability of the atom already in the nucleus.

It was with the idea of testing out some of these relationships and in order to elucidate the mechanism of removal of these groups that certain mercuri-organic compounds were prepared. In the case of organic mercurials we have almost an ideal case. First, the grouping —HgX in mercuri-organic compounds is undoubtedly positive and if any intramolecular oxidation-reduction reaction takes place we are warned immediately, for metallic mercury separates at once. Second, it is possible to prepare mercurials in which the mercury is held more or less loosely by the carbon atom. Third, the stability of the carbon-to-mercury linkage in methylated or acetylated compounds can be determined without removing the "protecting" group from the amino or hydroxyl group.

m-Dimethylamino-phenol was selected for the work in question, for preliminary tests have shown that the compound mercurates with the greatest ease, indicating an extremely high degree of lability of the hydrogen atom *para* to the dimethylamino group. The difference in stabilities of the various mercurials was ascertained by the addition of hydrogen sulfide water to a pyridine solution of the compounds, and noting the time of blackening, due to the formation of mercuric sulfide.

In working with the aminophenols we find that an amino group exercises a much greater labilizing effect on the mercury *ortho* or *para* to it than an hydroxyl group. This is brought out particularly well in the case of the derivatives of *m*-dimethylamino-phenol. Thus we find that the mercury compound of dimethylamino-phenol (I) reacts with hydrogen sulfide instantly; the speed of reaction is quite similar to that for any inorganic mercury salt. If we acetylate the hydroxyl group, the compound II

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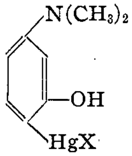
[2] Nicolet, THIS JOURNAL, **43,** 2081 (1921).

I


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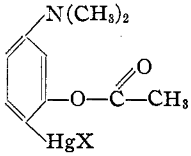

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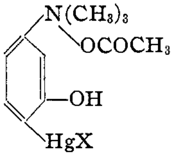
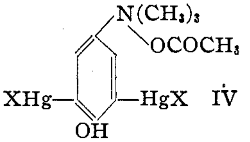


thus formed reacts much less readily with hydrogen sulfide water, the reaction taking about two minutes.[3] On the other hand, if we prepare the quaternary ammonium compound (III), the product thus formed does not give a test for mercury when treated with hydrogen sulfide for about 12 minutes. The same relationship holds in the case of the mercury derivatives of other aminophenols. Thus, diacetoxy-mercuri-*p*-hydroxyphenyl-trimethylammonium acetate (IV) and dichloro-mercuri-*o*-oxyphenyl-trimethylammonium anhydride (V) are stable to the action of hydrogen sulfide for more than 24 hours.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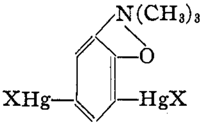
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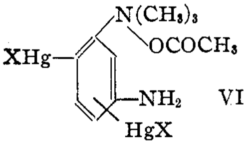
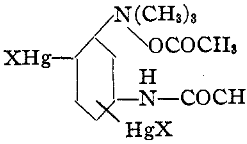

VI


VII

As a further check upon the difference in labilizing the mercury, induced by amino and hydroxyl groups, (and thus indirectly indicating the lability of the particular hydrogen which the mercury has displaced), *m*-amino-trimethyl-phenylammonium acetate was mercurized (VI). The mercury compound of this substance darkens immediately, while that in which the hydroxyl group occupies the position now occupied by the amino group, namely, Compound III, is stable to hydrogen sulfide for 12 minutes. We also found that acetylation of the amino group in the mercury compound of *m*-aminophenyl-trimethylammonium acetate (VII) makes the mercury less labile so that it reacts with hydrogen sulfide only in the course of 15 minutes.

The effect of the amino group in increasing the lability of the hydrogen atoms or other positive groups *para* or *ortho* to it, and the fact that acetylation or quaternary salt formation decreases this effect are of considerable theoretical interest. An explanation that is particularly applicable to

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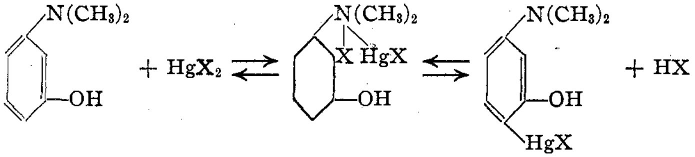
[3] Methylation of an hydroxyl group has a greater stabilizing effect upon the groups *ortho* or *para* to it than acetylation. This is quite evident from the behavior of the mercury compounds of resorcinol. The mercury compound of the dimethyl ether of resorcinol is stable to hydrogen sulfide for 24 hours, while the mercury compound of resorcinol reacts instantly with the latter reagent.

mercurials is that the process of *ortho, para* substitution is reversible in nature. In this respect the hypothesis, advanced by Kharasch and Jacobsohn,[4] that mercuration of aromatic amines proceeds in two stages, namely, first the formation of the quaternary ammonium salt and second, the rearrangement of the positive group to the *ortho* or *para* positions, is particularly instructive. Perhaps this would be better illustrated by considering the mercuration of *m*-dimethylamino-phenol. The mercuration of this product probably takes place in two stages (see Experimental Part). First, the mercuric acetate adds to the nitrogen atom to give a quaternary ammonium compound (VIII); this compound then rearranges to one in which the mercury is attached to a carbon atom (IX).



If the above process is reversible then the methylation of the nitrogen atom to give a quaternary ammonium compound should prevent this reversible reaction taking place. As a matter of fact, we do find that in the quaternary ammonium compound the mercury is much more firmly held to the carbon atom. Acetylation of an amino group in decreasing the salt-forming properties of the amino group prevents reversibility in a manner similar to the action of methylation of the dimethylamino group, and thus also decreases the lability of the positive group *para* or *ortho* to it. The reactions of these compounds are thus in complete accord with the hypothesis advanced to explain the mercuration of aromatic amines.

The authors also wish to call attention here to a rather unusual experience with one of the compounds, namely, *m*-hydroxyphenyl-trimethylammonium acetate. When this compound was treated with mercuric acetate the mercuri-bis compound was obtained instead of the mercuriacetoxy derivative. This is the first instance in which a mercuri-bis compound was formed by the direct treatment of a compound with mercuric acetate. The result, however, is not entirely puzzling if we recall the type reagents usually used to prepare mercuri-bis compounds; they are salts, such as potassium iodide, etc. In *m*-hydroxyphenyl-trimethylammonium acetate the ammonium salt part of it could have had the same effect as other salts.

Experimental Part

Acetoxymercuri-*m*-dimethylamino-phenol, $C_6H_3(1)N(CH_3)_2(3)OH(4)HgOCOCH_3$. —A solution of 2.8 g. (1 molecular equivalent) of *m*-oxy-dimethylaniline in 10 cc. of

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[4] Kharasch and Jacobsohn, THIS JOURNAL, **43,** 1894 (1921).

alcohol is mixed at room temperature with a solution of 7 g. (1 molecular equivalent) of 90% mercuric acetate in 30 cc. of water. In the course of a minute the solution, unless it is quite warm, sets to a jelly. The gelatinous mass is warmed for a minute or two, not longer, on the water-bath, whereupon the jelly melts and yellow crystals immediately begin to precipitate. The precipitation is complete in a few minutes. The precipitate is collected on a filter, washed well with water and dried in a vacuum over sulfuric acid; yield, 7.4 g., or 92%.

Analyses. Subs., 0.6587: 20.6 cc. of dry N_2 (22°, 736.8 mm.). Subs., 0.4482: HgS, 0.2602. Calc. for $C_{10}H_{13}O_3NHg$: N, 3.54; Hg, 50.69. Found: N, 3.51; Hg, 50.48.

The substance forms dirty yellow crystals that are insoluble in the usual organic solvents except pyridine, in which they are readily soluble. It is slightly soluble in water, giving a yellow solution which immediately precipitates mercuric sulfide on addition of ammonium sulfide. It is soluble in sodium hydroxide, giving a clear solution which is relatively stable, and can be boiled. When the dry material stands for ten days or two weeks, decomposition takes place with separation of metallic mercury; and when the substance is heated slowly it melts with decomposition at about 100–110°. An alcohol-soluble pink dye, with yellow fluorescence, is formed as a product of this decomposition.

The position of the mercury group in this compound was not determined directly. However, the fact that acetyl-*m*-dimethylamino-phenol mercurizes just as rapidly as the free phenol (see below), while *m*-oxyphenyl-trimethylammonium acetate is mercurated much more slowly (see below) indicates that the predominating orienting influence is that of the amino group, especially since dimethylaniline is mercurated immediately in the cold,[5] while phenol is mercurated much more slowly.[6] As dimethylaniline is mercurated in the *para* position it seems reasonable to assume that the acetoxymercuri group occupies the *para* position to the amino group in the compound under discussion.

Action of Mercuric Acetate upon Meta-Dimethylamino-Phenol in Glacial Acetic Acid

When *m*-dimethylamino-phenol and mercuric acetate in equal molecular proportions are boiled in glacial acetic acid for 15 minutes, metallic mercury is precipitated and a mercury-free, pink dye is formed. The dye base can be precipitated with ammonium hydroxide. It seems to have the empirical formula, $C_{18}H_{22}O_2N_2$.

Analyses. Subs., 0.3942: 32.30 cc. of dry N_2 (21°, 741.9 mm.). Subs., 0.2423, 0.2275: CO_2, 0.6326, 0.5937; H_2O, 0.1498, 0.1320. Calc. for $C_{18}H_{22}O_2N_2$: N, 9.29; C, 72.44; H, 7.44. Found: N, 9.30; C, 71.20, 71.17; H, 6.92, 6.49.

The dye base dissolves in acids to give a deep pink solution with a strong yellow fluorescence. It dyes silk readily. The dye is also soluble in concd. alkali forming a deep red, non-fluorescent solution which smells of dimethylamine. The dye is extremely difficult to reduce; not even magnesium and hydrochloric acid decolorize it. However, boiling with sodium hydrosulfite bleaches it in a few minutes. The work on this dye is being continued.

Methylation of Acetoxymercuri-Meta-Dimethylamino-Phenol

Fourteen g. of acetoxymercury-*m*-dimethylamino-phenol is placed in a small bottle and treated with 5.04 g. of methyl iodide (1 molecular equivalent) and 20 cc. of methyl

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[5] Dimroth, *Ber.*, **35**, 2044 (1902).

[6] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., **1921**, p. 254.

alcohol. The mixture is allowed to stand with an occasional shaking for 24 hours. It is then poured into an evaporating dish and allowed to stand overnight. The pasty residue is shaken with an aqueous suspension of silver oxide from 12 g. of silver nitrate. After about one-half hour the solution is filtered and neutralized with acetic acid. The solution is allowed to stand overnight, when a brown gelatinous precipitate forms. This is collected on a filter. The filtrate, which has a volume of about 35 cc., is heated to 45–50°, treated with a solution of sodium chloride and, after being stirred for a few minutes, filtered from a red powder. The filtrate is a light pink solution from which pink crystals separate on cooling. The crystals are collected on a filter; they weigh 1.5 g. They are crystallized from 20 cc. of boiling water, giving 1 g. of faintly pink, beautifully formed, leaf-like crystals.

Analysis. Subs., 0.6432: 18.6 cc. of dry N_2 (24°, 732.1 mm.). Calc. for $C_{11}H_{16}O_3NClHg$: N, 3.14. Found: 3.21.

An aqueous solution of the substance gives a yellow precipitate with ammonium sulfide and is much more stable than acetoxymercuri-*m*-dimethylamino-phenol. When heated, the substance melts to a deep red, viscous liquid at about 140–150°. When heated further to 190° it gives off a gas. A pink, fluorescent dye is formed as a result of this decomposition.

Acetoxymercuri-*m*-dimethylamino-phenyl Acetate, $C_6H_3(1)N(CH_3)_2(3)OCOCH_3(4)HgOCOCH_3$.—A solution in 30 cc. of alcohol of 1.8 g. (1 molecular equivalent) of *m*-dimethylamino-phenyl acetate, prepared by acetylation of *m*-dimethylamino-phenol,[7] is mixed with a solution of 3.5 g. (1 molecular equivalent) of 90% mercuric acetate in 15 cc. of water. The compound is mercurated as soon as the solutions are mixed (sulfide test), but no precipitate forms. The clear solution is treated with 60 cc. of water and allowed to stand overnight in the ice box and then cooled in an ice-bath. The large, colorless crystals that have precipitated are collected on a filter and dried in a desiccator; yield, 3.45 g., or 78%.

Analyses. Subs., 0.4736: 13.8 cc. of dry N_2 (23°, 733.6 mm.). Subs., 0.5353: HgS, 0.2826. Calc. for $C_{12}H_{15}O_4NHg$: N, 3.20; Hg, 45.82. Found: N, 3.24; Hg, 45.52.

The compound is readily soluble in hot alcohol; it precipitates again on cooling or upon addition of water. The cold alcoholic or aqueous-alcoholic solution gives with ammonium sulfide a yellow precipitate which turns black in the course of two minutes. The substance melts at 110° (corr.) without decomposition. On standing for some months the dry compound gradually blackens. When the substance is warmed for a few minutes on the water-bath with dil. aqueous sodium hydroxide, the mixture cooled and neutralized with acetic acid and then treated with ammonium sulfide, mercuric sulfide is immediately precipitated. This is undoubtedly due to the hydrolysis of the acetyl group by the alkali and the formation of the much less stable mercury derivative of *m*-dimethylamino-phenol.

Diacetoxymercuri-resorcinol-dimethylether, $C_6H_2(1,3)(OCH_3)_2(4,6)(HgOCOCH_3)_2$.—An alcoholic solution of equal molecular proportions of resorcinol-dimethylether and mercuric acetate is boiled until mercuration is complete. This requires only a short time. On cooling, beautiful, white, feathery crystals separate from the solution, which smells of resorcinol-dimethylether. The solid is collected on a filter and crystallized from alcohol.

Analysis. Subs., 0.4089: HgS, 0.3205. Calc. for $C_{12}H_{14}O_6Hg_2$: Hg, 61.21. Found: 60.73.

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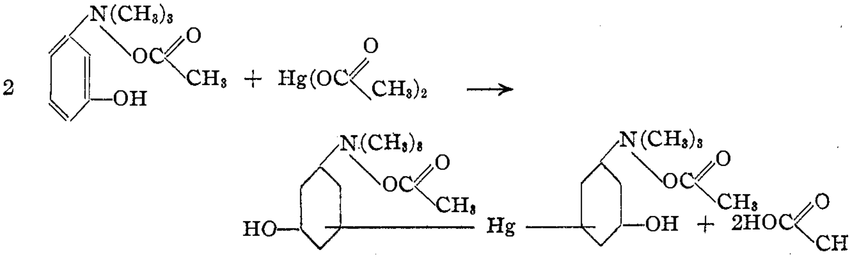
[7] Meyenburg, *Ber.*, **29**, 508 (1896).

The substance melts at 218–220° (corr.). It is quite stable to ammonium sulfide, the alcoholic solution giving a yellow precipitate with the reagent.

Mercuri-bis-*m*-oxyphenyl-trimethylammonium Acetate, $[C_6H_3(1)OH(3)N(CH_3)_3OCOCH_3]_2Hg$.—A solution of 5.6 g. (1 molecular equivalent) of *m*-oxyphenyl-trimethylammonium iodide, prepared by methylation of *m*-dimethyl-amino-phenol,[8] in 20 cc. of water is shaken with the washed silver oxide from 4.6 g. of silver nitrate. The solution is filtered after about ten minutes and the filtrate neutralized with acetic acid. It is free from iodine and silver. It is mixed with a solution of 7.1 g. (1 molecular equivalent) of 90% mercuric acetate. The resulting solution is heated on the water-bath until a cooled sample of it gives a yellow and not a black precipitate with ammonium sulfide. This requires about half an hour. The solution is then evaporated to dryness in a vacuum, since evaporation on the water-bath causes considerable decomposition. The gummy, glass-like residue is dissolved in the least possible amount of absolute alcohol, about 15 cc., and mixed, without filtration from the suspended mercurous acetate, with about 275 cc. of acetone. The resulting cloudy solution is warmed on the water-bath until it is clear. The clear liquid is decanted from the dark, oily material that has collected on the sides of the flask, and then mixed with about 450 cc. more of acetone. In the course of 24 hours the sides and bottom of the flask are covered with colorless crystals. These are collected on a filter and dried over sulfuric acid and phosphorus pentoxide. The yield is 2.2–2.8 g. If the equation



is taken for a basis of calculation, this is a 53–69% yield. The substance may be recrystallized by solution in alcohol and precipitation with acetone, but this does not seem to change its properties much.

The acetone used in this preparation cannot contain much water, but it must contain a trace. When perfectly dry alcohol and acetone are used, neither the first oily precipitate nor the last crystal one form at all, even after 48 hours. On very prolonged standing an impure product separates, probably due to the absorption of moisture from the air by the acetone which, in the experiments, was not completely excluded by the cork stoppers used. When a drop of water is added to the clear solution of the compound in dry acetone and alcohol, a precipitate forms; too much water redissolves the precipitate. In this work Mallinckrodt's U. S. P. acetone was used, as it seemed to contain the optimum amount of water. The necessity of the presence of water for the precipitation of the compound, and the fact that the substance loses its crystalline form on drying, indicate that the substance is precipitated as a hydrate.

In the analysis of the compound considerable difficulty was experienced because of the extremely hygroscopic nature of the substance, even though a drying bottle was used with a side tube that would fit directly into the mixing bottle or Carius sample tube. A different sample was used for each of the following determinations.

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[8] (a) Hantzsch and Davidson, *Ber.*, **29**, 1533 (1896); (b) Otto Fischer, *J. prakt. Chem.*, [2] **73**, 435 (1906).

Analyses. Subs., 0.2962: 11.6 cc. dry N_2 (22°, 729.6 mm.). Subs., 0.3950, 0.4738, 0.7012: HgS, 0.1383, 0.1683, 0.2563. Calc. for $C_{22}H_{32}O_6N_2Hg$: N, 4.45; Hg, 32.30. Found: N, 4.35; Hg, 30.17, 30.66, 31.52.

The dry substance is a white powder which melts with decomposition and evolution of a gas at 116–117° (corr.). In contrast to the behavior of the other mercurated phenylammonium salts prepared, this decomposition point seems to be constant and sharp. The substance is stable in the dry state, but it decomposes on standing in aqueous solution for a week, forming a white precipitate and leaving inorganic mercury in solution. The substance is extremely hygroscopic, and is soluble in water in all proportions; it is also extremely soluble in alcohol. It is insoluble in ether. It seems to be even more hygroscopic than the unmercurated *m*-oxyphenyl-trimethylammonium acetate, which can be easily prepared from the iodide by treatment with silver acetate, titration of the solution, precipitation of the silver with hydrogen sulfide, and evaporation. The aqueous solution of the compound slowly precipitates mercury with sodium stannite; it gives no precipitates with chlorides or sulfides unless boiled with the latter, when mercuric sulfide is formed.

Chloromercuri-*m*-oxyphenyl-trimethylammonium Anhydride, $C_6H_3(1)N(CH_3)_3(3)$-O(?)HgCl.—A solution of 2.3 g. (1 molecular equivalent) of mercuri-bis-*m*-oxyphenyl-trimethylammonium acetate in 5 cc. of 60% (by volume) alcohol is treated with a solution of 0.9 g. (0.9 molecular equivalent) of mercuric chloride in 12 cc. of 60% alcohol. The mercuric chloride reacts immediately and the solution gives no mercuric sulfide with ammonium sulfide. A white precipitate forms during the addition of the mercuric chloride. This partially redissolves on being shaken with the solution. The suspension is very gently warmed until almost all of the precipitate has gone into solution. If the suspension is heated too rapidly the solid forms a resinous mass which becomes discolored and insoluble. The warm solution is decanted from any remaining particles of solid; this is easily done, since the warm solid sticks to the flask. The solution is allowed to stand for 24 hours and is then cooled in an ice-bath. The white solid that forms is collected on a filter and dried over sulfuric acid and phosphorus pentoxide. The yield is 0.6 g., which represents 25% of the calculated amount.

Analysis. Subs., 0.4671: HgS, 0.2799. Calc. for $C_9H_{12}ONClHg$: Hg, 51.96. Found: 51.67.

The dry compound is quite insoluble in cold water, and only very difficultly soluble in hot. This is in strong contrast to the behavior of the substance when it is first formed in solution and corresponds to the formation of the internal salt. The substance is readily soluble in dil. acetic acid. It gives a yellow precipitate with ammonium sulfide. When heated the substance melts and decomposes, turning purple, at about 130–150°. Like all the other ammonium compounds prepared in this work, it gives off a gas when it decomposes.

2,6-Diacetoxymercuri-*p*-oxyphenyl-trimethylammonium Acetate, $C_6H_2(1)OH(4)N$-$(CH_3)_3OCOCH_3(2,6)(HgOCOCH_3)_2$.—A solution in a little water of 5 g. (1 molecular equivalent) of *p*-oxyphenyl-trimethylammonium iodide monohydrate, prepared by methylating *p*-aminophenol,[9] is shaken with the washed silver oxide precipitated from 5 g. of silver nitrate, and filtered. The alkaline filtrate, which contains neither iodine nor silver, is neutralized with acetic acid and then mixed with a solution of 5.9 g. (1 molecular equivalent) of 90% mercuric acetate in 30 cc. of water and a little acetic acid. The resulting solution, which through addition of filter washings has a volume of about 125 cc., is allowed to stand at room temperature until it ceases to give mercuric sulfide with ammonium sulfide. This requires about 24 hours. The solution is then evapo-

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[9] (a) Auwers and Wehr, *Ann.*, **334**, 308 (1904). (b) Griess, *Ber.*, **13**, 246 (1880).

rated to dryness in a vacuum. The glassy residue may be dissolved in alcohol, but acetone precipitation is unsatisfactory, while the addition of ether to the alcoholic solution precipitates an oil. The substance is best purified by the following method. It is dissolved in 40–50 cc. of boiling absolute methyl or ethyl alcohol, and the solution filtered into a 150cc. beaker, which is placed in an empty desiccator. There is then placed in the desiccator a beaker of pure ether, and the desiccator is closed and allowed to stand for 24 hours. The colorless, needle crystals which form are removed by filtration, redissolved in alcohol, and reprecipitated with ether by the same method. The resulting crystals are collected on a filter and dried over sulfuric acid and phosphorus pentoxide. The yield is 4.5 g., which represents 74.5% of the mercury used.

Analyses. Subs., 0.2852: 7.25 cc. of dry N_2 (23°, 734 mm.). Subs., 0.4917, 0.4252: HgS, 0.2482, 0.2903. Calc. for $C_{15}H_{21}O_7NHg_2$: N, 1.92; Hg, 55.07. Found: N, 2.10; Hg, 54.03, 54.51.

Each analysis is of a different sample.

The compound forms large, colorless needles which, when slowly heated, decompose with evolution of gas at about 155–160°. The substance is extremely soluble in water; it is quite soluble in hot alcohol, and much less soluble in cold; it is insoluble in benzene, acetone and ether. With ammonium sulfide the aqueous solution gives a yellow precipitate which becomes black on heating. The compound is stable in the dry state.

Chloromercuri-*p*-oxyphenyl-trimethylammonium Acetate, $C_6H_3(1)OH(4)N(CH_3)_3$-$OCOCH_3(2)HgCl$.—The alcohol-ether filtrates from the above precipitation of the diacetoxymercuri-*p*-oxyphenyl-trimethylammonium acetate are combined and the ether vapor treatment is continued until the solution divides into two layers. The whole liquid is then decanted from any crystals of dimercury compound that may have formed, and heated on the water-bath to drive off the ether. When the ether has been removed, the remaining solution is diluted to about 100 cc. with water and treated with sodium chloride solution. A precipitate is formed. The suspension of this is heated to boiling, and the precipitate collected on a filter. From the filtrate, small, slightly brownish needles precipitate on cooling. These are collected on a filter and dried in a desiccator. The yield is 1 g., which represents 13.5% of the mercury used. There is no evidence of the formation of a mercuri-bis compound in the mercuration of *p*-oxyphenyl-trimethylammonium acetate.

Analysis. Subs., 0.3253: HgS, 0.1689. Calc. for $C_{11}H_{16}O_3NClHg$: Hg, 45 04. Found: 44.77.

When heated, the compound decomposes at 155–160°, turning blue-green, and gives off a gas. The substance is sparingly soluble in water, and is soluble in pyridine. It is stable when dry.

Dichloromercuri-*o*-oxyphenyl-trimethylammonium anhydride, $C_6H_2(1)O(2)N(CH_3)_3(4,6)(HgCl)_2$.—An aqueous solution of 5 g. (1 molecular equivalent) of *o*-oxyphenyl-trimethylammonium iodide monohydrate, prepared by methylation of *o*-aminophenol,[9b,8b] is treated with silver oxide and acetic acid as in the other preparations, and then mixed with a solution of 5.9 g. (1 molecular equivalent) of mercuric acetate (90%). The resulting solution is allowed to stand at room temperature until it ceases to give mercuric sulfide with ammonium sulfide, which requires about 20 minutes. The mercurated products cannot be separated and purified by the methods used with the *meta* and *para* compounds. If the solution is evaporated to dryness in a vacuum and the glassy residue dissolved in alcohol, the addition of acetone induces decomposition, while the addition of ether causes the liquid to separate into two layers without the formation of an appreciable amount of crystals even on long standing. Therefore, the aqueous mercurized solution is treated immediately with an excess of sodium chloride solution. A white gelatinous precipitate is formed. The suspension is cooled in an ice-bath for some time and the precipitate collected on a filter. The filtrate is allowed to stand and is treated separately (see below). The precipitate when dried weighs 5.9 g. Two and a half g. of this precipitate is ground in a mortar with a little water and added to 500 cc. of boiling water. The boiling liquid is stirred vigorously for a minute or two, whereupon most of the solid dissolves. The solution is filtered as rapidly as possible, and allowed to stand for three days. The amorphous solid which has separated is collected on a filter and dried in a desiccator. The yield is 0.9 g. If in recrystallizing the precipitate thrown down by sodium chloride the solution is boiled more than a very short time, the substance after going into solution precipitates out again, and nothing comes out of the filtrate. The substance which precipitates on boiling is the same as that obtained by the recrystallization described above. As the final product obtained in each case is the insoluble anhydride, these reactions indicate that the substance first precipitated by sodium chloride from the original reaction mixture is the ammonium acetate which hydrolyzes on boiling with water or standing in solution for some time to give the anhydride.

Analysis. Subs., 0.4873: HgS, 0.3690. Calc. for $C_9H_{11}ONCl_2Hg_2$: Hg, 64.58. Found: 65.29.

The compound is practically insoluble in water; it is soluble in dilute sodium hydroxide and acetic acid solutions, and in pyridine. When heated, it becomes violet-colored at about 200–210°, and 5° or 10° higher it suddenly turns brick red and decomposes, giving off a gas.

The filtrate from the sodium chloride precipitation of the dimercury compound of *o*-oxyphenyl-trimethylammonium acetate (see above) has been investigated by several methods with the isolation of the unmercurized starting product. One experiment will be described. The filtrate was allowed to stand for two or three weeks and filtered from about 0.6 g. of precipitate. This filtrate was then treated at room temperature with an excess of potassium iodide solution and the mixture allowed to stand overnight. It was then filtered from a small amount of crystals. The filtrate contained no mercury. This shows that the iodide has not removed any mercury from its organic combination, since any inorganic mercury would be present in the filtrate as potassium mercuric iodide. It is also a good indication that a mercuri-bis compound was not formed in the mercuration of *o*-oxyphenyl-trimethylammonium acetate, since such a compound should not be quantitatively precipitated by iodides. The mercury-free filtrate was cooled in an ice-bath and filtered from 0.3 g. of crystals which had formed. These crystals decomposed at about 240°, and in other ways resembled the compound $(C_6H_4N(CH_3)_3O)_2HI$ prepared by Griess.[10] The substance was therefore recrystallized from 5 cc. of water containing a little potassium iodide and acetic acid. The substance thus obtained was compared with the oxyphenyl-trimethylammonium iodide monohydrate used in the experiment. This substance does not have a constant melting point, as has been reported,[8b,11] but the melting point varies with the rapidity with which the substance is heated. Therefore, the product to be identified, the pure starting product, and a mixture of the two were all heated in the same bath at the same time. On very slow heating, the substances melted at 181.5°, 183° and 182.5°, respectively.

m-**Aminophenyl-trimethylammonium Chloride Hydrochloride**, $C_6H_4(1)N(CH_3)_3Cl(3)NH_3Cl$.—This compound is recorded in the patent literature,[12] but no analyses or properties of it are given. The starting product is *m*-nitrophenyl-trimethylammonium bromide. This is readily prepared by methylating *m*-nitroaniline,[13] but it was found

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[10] Ref. 9b, p. 247.

[11] The melting point given is 198–200°.

[12] Ger. pat. 87,997; *Chem. Zentr.*, [2] **1896**, 1069.

[13] Staedel and Bauer, *Ber.*, **19**, 1940 (1886).

convenient to use a modified form of Staedel and Bauer's method, as follows. Forty g. of *m*-nitroaniline is warmed with 48 cc. of constant-boiling hydrobromic acid until it is almost all in solution. This mixture is then cooled and the crystals of hydrobromide are collected on a filter and dried overnight between porcelain plates. The substance should not be exposed directly to the air longer than is necessary. The dry hydrobromide is heated in a bomb tube with 55 cc. of absolute methyl alcohol for 25 hours at 90–100°. The contents of the tube are then removed and heated on the water-bath to drive off the excess of alcohol, and the crystals drained by suction. The crystals are suspended in a little dil. ammonium hydroxide and extracted with ether. On evaporating the ether, a small amount of pure *m*-nitro-dimethylaniline is obtained. The ammonium salt after the ether extraction is washed with water and dried. The product weighs 58.5 g., which represents a 77% yield, and consists of well-formed, faintly brownish crystals. The substance may be recrystallized from water, but this is not at all necessary for the subsequent preparation of the amino compound. Fifteen g. of this nitro compound is suspended in 90 cc. of about 15% hydrochloric acid and reduced with 30 g. of tin. This requires only about half an hour. Most of the water and hydrogen chloride are evaporated in a vacuum, the residue is dissolved in about 450 cc. of water, and the tin precipitated with hydrogen sulfide. The hydrogen sulfide is volatilized from the filtrate on the water-bath, and the resulting solution shaken with the silver oxide precipitated from 20 g. of silver nitrate; the solution is kept acid with hydrochloric acid. The filtrate, which should contain no bromine, is evaporated to dryness in a vacuum. The residue is taken up in about 100 cc. of boiling methyl or ethyl alcohol, the solution filtered, and the pure salt precipitated by ether. The yield is 10.4 g., which is 82% of the calculated amount.

Analysis. Subs., 0.3824: 42.5 cc. of dry N_2 (24.5°, 732 mm.). Calc. for $C_9H_{16}N_2Cl_2$: N, 12.56. Found: 12.29.

The substance forms pale yellow needles which are deliquescent and extremely soluble in water; they are less soluble in alcohol, and insoluble in ether. When heated, the substance decomposes at about 190–200°. An aqueous solution of the substance when shaken with silver oxide forms the hydroxide without decomposing, in contrast to *m*-nitrophenyl-trimethylammonium bromide.[13]

The halogen in the compound cannot be determined by dissolving the substance in water and titrating with silver nitrate and a chromate indicator because, although the solution retains the yellow color of the added potassium chromate, even a great excess of silver nitrate does not precipitate the red silver chromate. When chromate is added after an excess of the silver nitrate has been added, silver chromate is precipitated.

The use of silver chloride for removing the bromine in the preparation of the compound is quite essential, since if it is not used the final product gives a test for bromine, and, judging from the following nitrogen analysis, a good deal of bromide salt is present.

Analysis. Subs., 0.1978: 20.25 cc. of dry N_2 (24°, 733.5 mm.). Calc. for $C_9H_{16}N_2Cl_2$: N, 12.56; calc. for $C_9H_{16}N_2ClBr$: N, 10.48. Found: 11.32.

Dichloromercuri-*m*-aminophenyl-trimethylammonium Acetate, $C_6H_2(1)NH_2(3)N(CH_3)_3OCOCH_3(4,6?)(HgCl)_2$.—A solution of 1 g. (1 molecular equivalent) of *m*-aminophenyl-trimethylammonium chloride hydrochloride in a little water is shaken with the silver oxide precipitated from 2 g. of silver nitrate, and filtered. The filtrate is neutralized with acetic acid and treated with a solution of 1.59 g. (1 molecular equivalent) of 90% mercuric acetate. The resulting solution is allowed to stand until it gives no precipitate with sodium hydroxide. This requires two or three days. The solution then gives with hydrogen sulfide water an orange-colored precipitate which darkens on standing for a minute; it gives with ammonium sulfide an immediate black precipitate, and with sodium chloride a white precipitate. The whole solution is treated with sodium chloride, cooled in an ice-bath, and filtered. The precipitate is recrystallized from 50 cc. of boiling water and dried in a desiccator. The yield is 0.65 g., which represents 36% of the mercury used.

Analysis. Subs., 0.4808: HgS, 0.3219. Calc. for $C_{11}H_{16}O_2N_2Hg_2Cl_2$: Hg, 58.97; calc. for $C_{11}H_{16}O_2N_2Hg_2Cl_2 + H_2O$: Hg, 57.46. Found: 57.70.

The substance forms colorless or pale brown crystals which on heating decompose at about 200°. It is difficultly soluble in water. The aqueous solution gives an immediate black precipitate with ammonium sulfide.

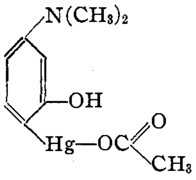
The original mercurated compound before conversion into the chloride may be easily benzoylated by making the solution alkaline and treating with benzoyl chloride. No inorganic mercury is formed, and the solution gives a yellow, fairly stable precipitate with ammonium sulfide.

Relative Stabilities of the Compounds Described Above to Hydrogen Sulfide in Pyridine Solution.—Samples of the compounds weighing 0.05 g. were each dissolved in 10 cc. of pyridine. This solvent was chosen because it was the only one that would dissolve all of the compounds. To each sample was added in saturated aqueous solution a little less than 0.5 molecular equivalent of hydrogen sulfide to each mercury atom. In the case of compounds marked with an asterisk (*) about 0.25 volume of water had to be added to the pyridine to make substances dissolve. The time recorded is measured from the time of addition of hydrogen sulfide to the time of blackening.

Table I

Relative Stabilities of Compounds at 23–25°

Substance



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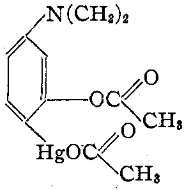

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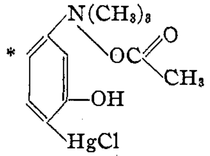

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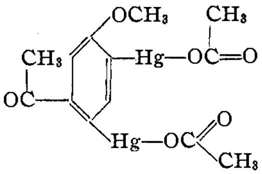

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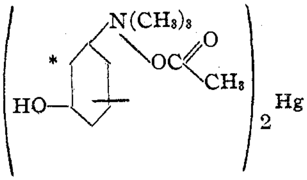

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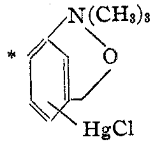
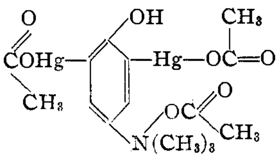
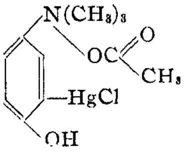


VI

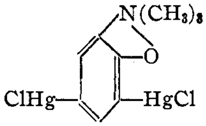


VII

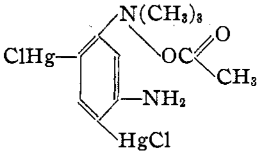


VIII

TABLE I (*Concluded*)



IX



X

Substance	Mol. wt.	H_2S required (calc.) Mg.	H_2S used in cc. of sat. sol. at 18°	Time of blackening Hours:minutes
I	386	2.1	0.42	0
II	438	1.9	.37	0:2
III	446	1.9	.36	0:12
IV	655	2.6	.5	24:
V	621	1.3	.26	>5:
VI	386	2.2	.32	0:6–8
VII	728	2.3	.44	24:
VIII	445	1.9	.36	0:5
IX	621	2.7	.52	>5:
X	680	2.5	.47	0

Summary

1. The influence of amino and hydroxyl groups upon the lability of the *ortho* and *para* hydrogen atoms is discussed.

2. An amino group has a much greater labilizing effect upon the hydrogen atoms, or positive groups, *ortho* and *para* to it than an hydroxyl group.

3. The increase in stability of various mercurials caused by acetylation and quaternary compound formation has been studied.

4. It has been shown that the removal of positive groups from the benzene nucleus is well in accord with the hypothesis of the mercuration of amines advanced by Kharasch and Jacobsohn.

5. The formation of a "mercuri-bis compound" by direct mercuration of *m*-hydroxyphenyl-trimethylammonium acetate has been observed.

6. The preparation of a number of new compounds is described.

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