

2. The mercurization of 3-bromo-5-nitrosalicylic acid and of 3,5-dinitrosalicylic acid gave mixtures of mono- and dimercury compounds from which it was impossible to separate pure substances.

3. Modifications in the preparation of 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid are described.

PHILADELPHIA, PENNSYLVANIA

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

A STUDY OF THE NITRO-ANILINES

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The purpose of this investigation, as it developed, was twofold. It was desired, in the first place, to obtain additional information bearing upon the chemical constitution of the nitro-anilines and, second, to test the hypothesis advanced in a previous paper⁴ as to the mechanism of mercurization of aromatic amines. It was pointed out in that paper that mercurization of aromatic amines proceeds probably in two stages: first, the addition of the mercury salt to the amino group forms an ammonium salt; this ammonium compound then rearranges, the most strongly positive group migrating to the *para* position or, that position being occupied, to the *ortho* position.

While this point of view seems to be generally applicable in the case of aromatic amines, it is quite conceivable that mercurization of amines capable of existing in the quinoid form, *e. g.*, the *ortho* and *para* nitro-anilines, might take place by the absorption of the mercury salt at the double bond.⁵ Evidence of this type of substitution might well be obtained in the study of mercurization of the nitro-anilines and of the mono-nitro-diphenyl-amines. The present paper deals with the former phase of the problem.

As a general principle, one writes different structural formulas to indicate the tautomeric forms of a given compound. In the case of the *ortho* and *para* nitro-anilines, we might assume that, in solution, we are dealing with a mixture of the following tautomers in equilibrium,

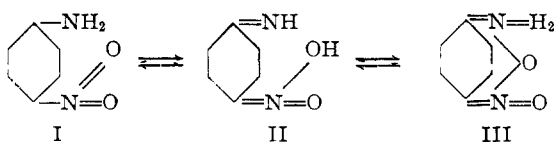
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² The material presented here is used by Frederick W. M. Lommen in his dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

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

⁵ The absorption of mercuric acetate by quinone, and also the behavior of the mercury salts of unsaturated aliphatic acids containing the double bond in the α - β , β - γ and γ - δ positions will be discussed in a subsequent paper by Kharasch.



the *para* compound being taken for illustration. In the case of *m*-nitro-aniline, however, structural formulas do not permit us to write such a simple quinoid arrangement. The question naturally arises whether our chemical reactions are compatible with the ordinary benzenoid structures for the 3 nitro-anilines, or whether the behavior of the *ortho* and *para* isomers is sufficiently different from that of the *meta* compound, and in agreement with a quinoid structure for those compounds.

It must be stated, however, that the present investigation is more of a qualitative nature and the real issue in question, as far as the present authors are concerned, is whether any of the tautomeric form II exists in solution. The presence of tautomer III in this solution should then follow, as in the case of sulfanilic acid, *p*-aminobenzoic acid, etc.

The only work of which the present writers are aware concerning the nitronic acid structures of the nitro-anilines is that of Baly and his collaborators on the absorption spectra of these compounds. In the first paper on the nitro-anilines, Baly, Edwards and Stewart⁶ arrive at the conclusion that, since the nitro-anilines, in alcoholic solution, show the absorption bands present in quinones and diketones, while, in hydrochloric acid solution, they show none of these characteristics, the substances in alcoholic solution must have the quinoid form (II). This latter structure for the nitro-anilines has been criticized by Hantzsch,⁷ since he claims that it is not applicable to the dialkyl nitro-anilines which also show similar absorption curves. Baly⁸ in collaboration with Tuck and Marsden, in a subsequent paper, abandons the quinoid structures for the nitro-anilines and ascribes the absorption band to the "isorropesis between the nitro group and the aniline residue."

The main reason given by Baly for rejecting the quinoid structure for the nitro-anilines is as follows: "While it may be urged that the absorption of the free base and the monomethyl derivative (3-nitro-*p*-toluidine) is due to their existing in the quinoid form, it is difficult to see how the dimethyl compound can exist in this form, and yet the absorption spectra of all three are almost identical. The only difference is the shift toward the red accompanying the introduction of the methyl group." And, about the nitro-anilines, they say, "There is no difference at any moment between the free compounds and the dimethyl derivatives. The con-

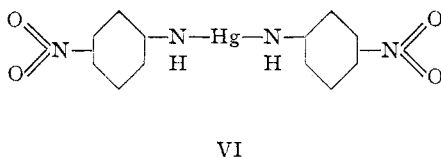
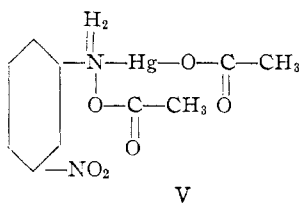
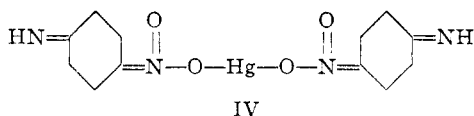
⁶ Baly, Edwards and Stewart, *J. Chem. Soc.*, **89**, 517 (1906).

⁷ Hantzsch, *Ber.*, **43**, 1668 (1910).

⁸ Baly, Tuck and Marsden, *J. Chem. Soc.*, **97**, 581 (1910).

clusion, therefore, is forced upon us that the same explanation of the color and absorption must be given in each. A simple quinoid compound is ruled out in the case of the dimethyl compound and hence we are compelled to abandon it in the case of the parent substances."

In spite of the later views advanced by Baly and the objections raised by Hantzsch to the nitronic acid structure for the *o*- and *p*-nitro-anilines, it may be profitable to examine the structure of the nitro-anilines in the light of the writers' work upon the mercury derivatives of these compounds. If the original view held by Baly as to the structure of the nitro-anilines in alcoholic solution were correct, then, in this solvent, the conditions would be most favorable for the formation of the tautomer II and, if a sufficiently insoluble salt of this tautomer could be produced by the addition of some base, it should precipitate. As a matter of fact, when an alcoholic solution of *o*- or *p*-nitro-aniline is treated with an aqueous solution of mercuric acetate, intensely colored compounds are precipitated in the course of a few seconds.⁹ They behave as mercuric salts, reacting readily with ammonium sulfide in the cold to give a precipitate of mercuric sulfide. Their structures, from the viewpoint advanced would then be according to Formula IV, the para compound being taken for illustration. On the other hand, for the *meta* nitro-aniline, in which the formation of a quinoid compound of this type is not possible, the reaction with mercuric acetate is much slower, and the product, instead of being highly colored, as in the case of the *ortho* and *para* isomers, is almost white. Its analysis corresponds to Formula V, a different type of compound from that obtained from the *ortho* and *para* nitro-anilines.



It is interesting to note here that Jackson and Peakes¹⁰ have obtained, in the case of *m*-nitro-aniline, as well as with its *ortho* and *para* isomers, a highly colored compound upon treating with nascent mercuric oxide. The analysis of the products, however, has led them to conclude that,

⁹ The *ortho* and *para* isomers react, in this manner, not only with mercuric acetate, but in alcoholic solution they unite directly with mercuric oxide to give the same compounds.

¹⁰ Jackson and Peakes, *Am. Chem. J.*, 39, 567 (1908).

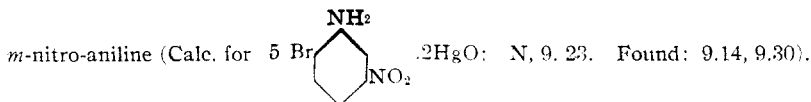
while the *o*-, *m*- and *p*-nitro-aniline salts probably have the structure shown in Formula VI, the *m*-nitro-aniline derivative must also contain a molecule of water of crystallization.

The formation of such a colored derivative in the case of *m*-nitro-aniline, using nascent mercuric oxide, and also of a *maroon* compound when an alcoholic solution of *o*-bromo-*m*-nitro-aniline (*i. e.*, a substituted *m*-nitro-aniline) is treated with an aqueous solution of mercuric acetate, as observed by the writers, is hardly compatible with the concepts developed above. Therefore, it became necessary either to reject the very tempting idea of quinoidation, as derived from the behavior of the *o*-, *p*- and *m*-nitro-anilines in alcohol solution with mercuric acetate, or to show that these *maroon* products obtained from *m*-nitro-aniline are chemically different from compounds capable of existing in the quinoid form, *e. g.*, *o*- and *p*-nitro-anilines, and substituted nitro-anilines such as nitro-toluidines, *p*-bromo-*o*-nitro-anilines, etc.

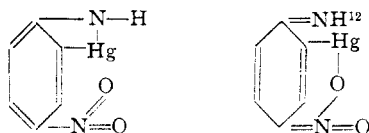
It is very significant in this connection that, while the colored compounds obtained from *o*- and *p*-nitro-anilines always give analyses which correspond to one mercury for two molecules of the nitro-aniline, those obtained from *m*-nitro-aniline and its bromo substitution products do not.¹¹ This suggests the possibility that the *m*-nitro-aniline and its derivatives yield addition compounds, while the *o*- and *p*-nitro-anilines yield true mercury salts of the nitronic acids. To test this deduction, the different colored compounds of the *o*-, *p*- and *m*-nitro-anilines were put into extraction thimbles in a Wiley extractor. Since neither ether nor benzene would wet the compounds satisfactorily, acetone was used as the extracting solvent. The deductions made were wholly verified since the acetone completely extracted the *m*-nitro-aniline and *p*-bromo-*m*-nitro-aniline from their respective colored mercury compounds, leaving in the thimble yellow mercuric oxide. The *o*- and *p*-nitro-aniline mercury salts, however, remained unchanged. This illustrates that there must also be a difference in the chemical formulas of these various colored compounds. Therefore, although the color of the *m*-nitro-aniline compounds with mercuric oxide resembles that of the *ortho* and *para* isomers, the facts advanced in support of quinoidation are not thus invalidated.

As further evidence of the nitronic acid structure for *o*- and *p*-nitro-anilines, the examination of the reactions of their mercurized products

¹¹ While the colored derivative of *m*-nitro-aniline gives analyses which correspond to two molecules of *m*-nitro-aniline to one molecule of mercuric oxide, the analysis of the reaction product obtained from *o*-bromo-*m*-nitro-aniline is more compatible with a formula corresponding to two molecules of mercuric oxide and five of the *o*-bromo-



toward alkalies and alkali carbonates is of considerable importance. Thus, when these derivatives, which are yellow, are treated with dil. alkali, red compounds are obtained whose analyses would correspond to either of the following structures,



VII

the derivatives obtained from *p*-nitro-aniline *ortho* mercuric chloride or acetate and sodium carbonate being taken for illustration.

However, if Formula VII were correct, one would expect that the compound would have undergone no color change. There are a few cases on record where we might suspect such an inner linkage between mercury and nitrogen as that expressed in Formula VII, but these compounds do not differ in color from the compound from which they are derived.¹²

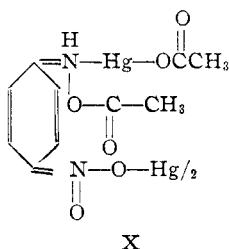
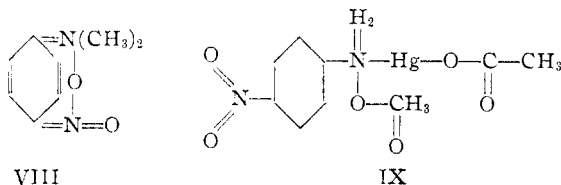
We find thus that the chemical behavior of the nitro-anilines suggests that in solution the *ortho* and *para* isomers might exist in the quinoid form. Of course, as with other tautomeric compounds, the solvent plays an important rôle in determining the amount of each of the tautomers present. For example, in alcoholic solution, tautomer II is favored, as indicated by the fact that the *o*- and *p*-nitro-anilines react quite readily with mercuric acetate to give quinone imide aci-nitro salts, while, in water solution, it is necessary to add alkali in order to obtain the same products. The objection raised by Baly to the nitronic acid structures for the *o*- and *p*-nitro-anilines may be overruled since it is possible to write the structures of the methylated nitro-anilines in the nitronic acid form. Thus, for *p*-nitro-dimethylaniline, we may write Formula VIII. A structure of this type is really more in accord with the chemical behavior than that usually written. Since it is an internal salt, we would not expect it to form salts with acids very readily. The only way in which the authors have been able to make the hydrochloride of this compound was by passing dry hydrogen chloride into its solution in anhydrous solvents. However, Hantzsch⁷ has rejected the structure given above for *p*-nitro-dimethylaniline and thereby the theory of quinoidation in the case of the *o*- and *p*-nitro-anilines, on the basis that these compounds give absorption spectra similar to those obtained from the addition (?) compounds of polynitro benzols and aniline bases which cannot be formulated in that way. We do not believe that this objection invalidates

¹² This formula is quite comparable with that given by Hantzsch and Auld, *Ber.*, 39, 1115 (1906), for the aci-anhydrides of the mercurized nitrophenols.

¹³ Pesci, *Gazz. chim. ital.*, 22, I, 373 (1892). Piccinini and Ruspaggiari, *ibid.*, 22, II, 609 (1892).

our conclusions as to the structures of the nitro-anilines. This matter will be discussed in greater detail in a subsequent paper.

The mechanism of mercurization of the nitro-anilines is, as yet, not definitely settled. There are at least three possible ways in which *o*- and *p*-nitro-anilines might be mercurized. In the first place, we might have the nitro-aniline molecule add on a molecule of mercuric acetate to form the ammonium salt (Formula IX).

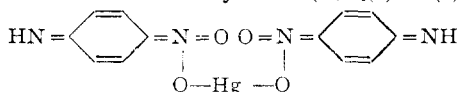


This would then rearrange, the mercury migrating to the *ortho* position. In favor of this supposition, we have the fact that the quinone-imide aci-nitro mercury salts of *o*- and *p*-nitro-anilines are not mercurized when heated with alcohol, while the addition of a little acetic acid effects the mercurization in a very short time, even in the cold.

The other possible mechanisms are the addition of mercuric acetate, in a similar manner to the above, but to the imido nitrogen of the mercury salt of the quinone-imide aci-nitronic salt, (Formula X). This compound then rearranges in the manner outlined above. Finally, we may also have direct absorption of the mercuric acetate by the double bond in the quinone-imide aci-nitro salt. As a guide in deciding the true mechanism of the mercurization of the nitro-anilines, the mercurization of mononitro-diphenylamines will be undertaken.

The positions taken by the mercury in the nitro-anilines is always *ortho* or *para* or *ortho-para* to the amino group.¹⁴ This was established by preparing the acetyl derivatives of the various mercurized products, and subsequent replacement by bromine. The bromo derivatives were then compared with the respective synthetic products, prepared by other methods, and were found not to depress their melting points.

¹⁴ It is of considerable interest, in this connection, that in the case of the dimercury compound of *m*-nitro-aniline the positions taken by the mercury are 2,4 ($\text{NH}_2=1$, $\text{NO}_2=3$) and not 4,6 as one might expect.

Experimental Part¹⁵*p*-Quinone-imide Acini-nitro Mercury Salt $(C_6H_4(1)NH(4)NOO)_2Hg$ 

This compound has already been prepared by Jackson and Peakes.¹⁰ However, the following method of preparation has been found to be more practical than the one given by the above writers.

To a solution of 4.7 g. of *p*-nitro-aniline in 60 cc. of alcohol 4.6 g. of mercuric acetate dissolved in 8 cc. of water was added. Within the course of a few seconds a maroon precipitate was formed. This was collected on a filter, washed well with alcohol and ether and dried *in vacuo* over sulfuric acid to constant weight. Yield, 5.5 g.

Analyses. Subs., 0.2462: 25.6 cc. of dry N_2 (23.5° and 745.4 mm.). Subs., 0.2204: Hg, 0.0923. Calc., for $C_{12}H_{10}O_4N_2Hg$: N, 11.82; Hg, 42.19. Found: N, 11.74; Hg, 41.88.

The compound is almost insoluble in cold water and the common organic solvents. However, when it is boiled with water or alcohol the filtrate is found to give a black precipitate when treated with ammonium sulfide, indicating that the mercury has not been substituted in the nucleus. It is decomposed immediately by acetic acid into mercuric acetate and *p*-nitro-aniline. When allowed to stand in alcohol, it remains for months without change. However, when a little acetic acid or mercuric acetate is added to the alcoholic suspension it is converted gradually in the cold, more rapidly in the hot, to a yellow compound described below. It decomposes at 300°.

o-Acetoxymercuri-*p*-nitro-aniline, $[C_6H_3(1)NH_2(4)NO_2(2)HgO_2C_2H_3]$.—This compound can be prepared by treating the above-mentioned salt with mercuric acetate or acetic acid. However, it was obtained in better yield by the following procedure. A solution of 9.2 g. of mercuric acetate in 15 cc. of water, to which a little acetic acid had been added, was mixed with a solution of 4.7 g. of *p*-nitro-aniline in 60 cc. of alcohol and the mixture was boiled for one hour. After this time the reaction was completed, as indicated by the fact that the filtrate gave no test for inorganic mercury when treated with ammonium sulfide. The reaction mixture was filtered hot. Upon cooling, the compound separated and was collected on a filter. It was recrystallized from hot alcohol to which a little acetic acid had been added. A beautiful yellow crystalline compound was thus obtained. This was washed with alcohol containing a few drops of acetic acid, and finally with ether. For analysis, the compound was dried *in vacuo* to constant weight.

Analysis. Subs., 0.2061: 12.80 cc. of dry N_2 (20° and 721.7 mm.). Calc. for $C_8H_5O_4N_2Hg$: N, 7.08. Found: 6.89.

The compound is soluble in alcohol to which a few drops of acetic acid have been added. Upon treatment with solutions of sodium hydroxide or sodium carbonate, and even upon boiling with alcohol, the compound changes into a maroon substance which will be described in greater detail later in the paper. The compound turns red when heated, but does not melt below 300°.

o-Chloromercuri-*p*-nitro-aniline, $[C_6H_3(1)NH_2(4)NO_2(2)HgCl]$.—This compound may be obtained upon treating the alcoholic solution of the acetate, described above,

¹⁵ Julius Rother, in his Inaugural Dissertation (Berlin, 1911) calls attention to a series of color changes which take place upon treating the nitro-anilines in alcoholic solution with mercuric acetate and to the stability of the various products to ammonium sulfide. Beyond that, however, no investigation was undertaken by him.

with an aqueous solution of sodium chloride or an alcoholic solution of calcium chloride. The yield is quantitative. For analysis, the compound was dried *in vacuo* to constant weight at 100°.

Analysis. Subs., 0.4440: AgCl, 0.1687. Calc. for $C_6H_5N_2O_2HgCl$: Cl, 9.50. Found: 9.37.

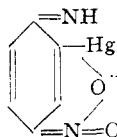
The compound is yellow. It is less soluble in alcohol than the acetate. It does not melt, even when heated to 300°. Like the corresponding acetate, it turns maroon when treated with sodium hydroxide.

o,o'-Di-acetoxymercuri-*p*-nitro-aniline, $[C_6H_2(1)NH_2(4)NO_2(2,6)(HgO\cdot OC_2H_3)_2]$.—When an alcoholic solution of 9 g. of *p*-nitro-aniline was boiled with an aqueous solution containing 18.4 g. of mercuric acetate, a disubstituted mercury derivative was obtained. To remove any of the monomercury compound which was formed the product was extracted with hot alcohol containing a little acetic acid. It was then dissolved in pyridine in order to remove a small amount of metallic mercury which had been formed in the reaction. The compound was then precipitated from this solvent by the addition of acetone. For analysis, it was dried *in vacuo* to constant weight.

Analysis. Subs., 0.2558: 10.40 cc. of dry N_2 (22° and 738.3 mm.). Calc. for $C_{16}H_{10}O_6N_2Hg_2$: N, 4.28. Found: 4.57.

This compound is orange colored. It does not melt below 300°. When treated with sodium hydroxide or sodium carbonate solutions, and even upon boiling a suspension of the compound in alcohol, it changes into a red compound similar in structure to that described below.

Quinone-(1)-imide Aci-(4)-nitro-(2)-mercury,



—When the various

mercury derivatives of *p*-nitro-aniline described above are heated or when they are treated with dilute solutions of sodium hydroxide or of sodium carbonate, and also when heated with alcohol, they are converted into maroon compounds. *o*-Acetoxymercuri-*p*-nitro-aniline furnishes a typical example of this reaction. This compound was dissolved in alcohol containing a little acetic acid, and upon treatment with an aqueous solution of sodium hydroxide, a maroon product was obtained in quantitative yield. For analysis, the compound was washed with alcohol and ether and dried *in vacuo* to constant weight.

Analyses. Subs., 0.2425: 18.30 cc. of dry N_2 (24° and 728.9 mm.). Subs., 0.2305: Hg, 0.1362. Calc. for $C_6H_4O_2N_2Hg$: N, 8.34; Hg, 59.60. Found: N, 8.32; Hg, 59.09.

The compound is insoluble in all common organic solvents. When treated with acetic or hydrochloric acids, it turns yellow giving the acetate or chloride, respectively. It is stable to ammonium sulfide in the cold. It does not melt even when heated to 300°.

o,o'-Mercury-bis-*p*-nitro-aniline, $[(C_6H_3(1)NH_2(4)NO_2)_2Hg]$.—To prepare this compound, 1 g. of *o*-acetoxymercuri-*p*-nitro-aniline was moistened with alcohol and suspended in water. To this suspension an aqueous solution containing 3 g. of sodium thiosulfate was added. Within the course of a few minutes the compound was completely dissolved. The solution was then diluted with 20 cc. of water and the whole boiled for 6 minutes. A yellow precipitate soon formed. In order to test the completeness of the reaction a sample portion of the suspension was treated with sodium hydroxide solution. No color change was observed at the end of the period stated. However, should the color of the suspended solid change from yellow to orange or red, the reaction is incomplete and the solution should be boiled until no such test is obtained.

The compound was then extracted a few times with alcohol. Yield, 86%. For analysis the product was dried to constant weight *in vacuo*.

Analyses. Subs., 0.2798, 0.2055: 28.54 cc. of dry N₂ (23° and 741.4 mm.), 20.80 cc. (23.5° and 746.5 mm.). Calc. for C₁₂H₁₀O₄N₄Hg·N, 11.76. Found: 11.52, 11.45.

The compound is greenish-yellow. It is insoluble in all common organic solvents. With sodium hydroxide it gives no color reaction, in distinction to unbridged compounds.

o-Acetoxymercuri-acetyl-*p*-nitro-aniline. [C₆H₃(1)NH·(CO·CH₃)(4)NO₂(2)HgO·OC₂H₅].—To prepare this compound 4 g. of *o*-acetoxymercuri-*p*-nitro-aniline was boiled under a reflux condenser with 10 cc. of acetic anhydride and 30 cc. of ethyl acetate. After a short time the solid was completely dissolved. The solution was then filtered hot, and upon cooling a white crystalline product separated. This was collected on a filter and washed with alcohol. Yield, 50%. For analysis, the compound was dried *in vacuo* at 100° to constant weight.

Analysis. Subs., 0.2071: 12.10 cc. of dry N₂ (21.5° and 731.8 mm.). Calc. for C₁₀H₁₀O₆N₂Hg: N, 6.40. Found: 6.53.

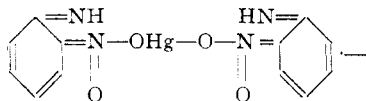
The compound is white and crystalline. It is soluble in ethyl acetate. With sodium hydroxide it gives no color change.

Determination of the Position of the Mercury in the Mercurized *p*-Nitro-aniline

The position of the mercury in the mono-mercury-substituted *p*-nitro-aniline was determined in the following manner. One mol of *o*-acetoxymercuri-acetyl-*p*-nitro-aniline was treated with 1 mol of potassium perbromide solution and the whole shaken until the color of the bromine had disappeared. The solid product of the reaction was collected on a filter and washed with water. It was then extracted with ether, the ethereal extract was evaporated to dryness, and the residue was recrystallized from hot water; m. p. 130°. When mixed with *p*-nitro-*o*-bromo-acetanilide prepared by synthetic methods, the melting point was not lowered. The position of the mercury is thus established as *ortho* to the amino group.

To determine the position of the mercury in the dimercury-substituted *p*-nitro-aniline the compound was first acetylated, in ethyl acetate suspension with acetic anhydride. The reaction was considered complete when the whole became almost white.¹⁶ The acetylated compound thus obtained was treated with two mols of potassium perbromide in a manner similar to that used for the monomercury substituted derivative. A product was obtained which melted at 225–227°. When mixed with 4-nitro-2,6-dibromo-acetanilide the melting point was not lowered. The position of the mercury is thus established as being in the 2,6 positions (NH₂ = 1).

Quinone-(1)-imide Aci-(2)-nitro Mercury Salt,¹⁷ [(C₆H₄(1)NH(2)NO·O)₂Hg]



This compound was prepared from *o*-nitro-aniline by the same procedure as that used for the preparation of the corresponding *p*-nitro-aniline compound. The precipitation, however, was much slower than in the case of the latter compound. For analysis, the compound was washed with alcohol and ether, and dried *in vacuo* to constant weight.

¹⁶ The compound thus obtained was insoluble in the common organic solvents and, owing to the presence of an appreciable quantity of metallic mercury formed in the course of the acetylation, was not analyzed.

¹⁷ This compound has been prepared previously by Jackson and Peakes¹⁰ using nascent mercuric oxide.

Analysis. Subs., 0.4769: 50.20 cc. of dry N_2 (20° and 739.6 mm.). Calc. for $C_{12}H_{10}O_4N_2Hg$: N, 11.82. Found: 11.94.

The compound is scarlet-red. With ammonium sulfide it gives in the cold an immediate precipitate of mercuric sulfide. When allowed to stand suspended in alcohol it undergoes no change even after several months. However, when acetic acid or mercuric acetate is added it changes gradually in the cold, more rapidly in the hot, into the yellow compound described below.

***p*-Acetoxymercuri-*o*-nitro-aniline**, $[C_6H_3(1)NH_2(2)NO_2(4)HgO \cdot OC_2H_3]$.—This compound was prepared from *o*-nitro-aniline and mercuric acetate in the same manner as was the corresponding *p*-nitro-aniline derivative. The compound was recrystallized from alcohol, to which a little acetic acid had been added. For analysis, it was dried *in vacuo* to constant weight.

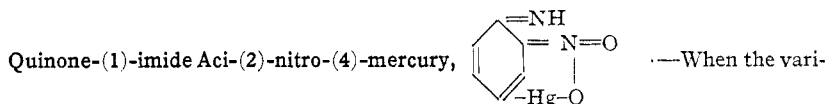
Analysis. Subs., 0.1657: 10.60 cc. of dry N_2 (24° and 733.2 mm.). Calc. for $C_6H_5O_4N_2Hg$: N, 7.09. Found: 7.10.

This is a yellow crystalline compound, soluble in alcohol containing a little acetic acid. The compound is stable to ammonium sulfide. When treated with a dilute solution of sodium hydroxide or sodium carbonate and upon boiling with alcohol the compound turns red. The preparation thus obtained will be described in greater detail later in the paper. The compound does not melt, even when heated to 300° . However, upon heating it turns red.

***p*-Chloromercuri-*o*-nitro-aniline**, $[C_6H_3(1)NH_2(2)NO_2(4)HgCl]$.—This compound was prepared from *p*-acetoxymercuri-*o*-nitro-aniline in the same manner as the chloride of the mercurized *p*-nitro-aniline. For analysis, this compound was dried at 100° *in vacuo* to constant weight.

Analyses. Subs., 0.2183: 13.92 cc. of dry N_2 (18° and 748.3 mm.). Subs., 0.2985: $AgCl$, 0.1131. Calc. for $C_6H_5N_2O_2HgCl$: N, 7.52; Cl, 9.50. Found: N, 7.37; Cl, 9.37.

The compound is orange colored. When treated with a dilute solution of sodium hydroxide or sodium carbonate, an intensely red compound is formed. It has no melting point.



ous mercury derivatives of *o*-nitro-aniline are heated dry or treated with a dilute solution of sodium hydroxide, or even upon boiling with alcohol, an intensely red compound is obtained, in quantitative yield. As an illustration of this reaction, the behavior of *p*-acetoxymercuri-*o*-nitro-aniline may be taken. When it is dissolved in alcohol containing a little acetic acid and treated with a dilute solution of sodium hydroxide a red precipitate separated immediately. The compound was collected on a filter and washed with a little alcohol and ether. For analysis, the compound was dried *in vacuo* to constant weight.

Analyses. Subs., 0.2111: 14.96 cc. of dry N_2 (23° and 743.8 mm.). Subs., 0.1886: Hg , 0.1134. Calc. for $C_6H_4O_2N_2Hg$: N, 8.31; Hg , 59.60. Found: N, 8.06; Hg , 60.11.

The compound is a brilliant red. It is insoluble in the common organic solvents. With ammonium sulfide it gives no test for inorganic mercury. When treated with acetic acid, it is converted into the yellow acetate derivative.

***p*-Acetoxymercuri-diacetyl-*o*-nitro-aniline**, $[C_6H_2(1)N(CO \cdot CH_3)_2(2)NO_2(4)HgO \cdot OC_2H_3]$.—This compound was prepared from *p*-acetoxymercuri-*o*-nitro-aniline, using the same procedure as that already used for the preparation of the corresponding *p*-nitro-

aniline derivative. The reaction in this case was found to take place much more slowly. For analysis the compound was dried *in vacuo* to constant weight.

Analysis. Subs., 0.2654: 13.8 cc. of dry N_2 (22° and 737.0 mm.). Calc. for $C_{12}H_{11}O_6N_2Hg$: N, 5.84. Found: 5.87.

The compound is of a straw-yellow color. It is soluble in sodium hydroxide solution imparting to the solution a yellow coloration. M. p. 194° with decomposition.

p-Acetoxymercuri-acetyl-*o*-nitro-aniline, $[C_6H_3(1)N \cdot H \cdot CO \cdot CH_3](2)NO_2(4)HgO \cdot OC_2H_5]$.—To prepare this compound, a water suspension of *p*-acetoxymercuri-diacetyl-*o*-nitro-aniline was treated with a dilute solution of sodium hydroxide. The compound dissolved, giving the solution a yellow color. The solution was then filtered immediately into dil. acetic acid. A yellow crystalline precipitate formed immediately. This was collected on a filter and washed with water and alcohol. For analysis the compound was dried *in vacuo* over sulfuric acid to constant weight.

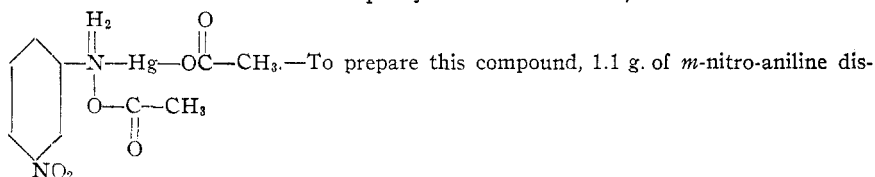
Analysis. Subs., 0.2835: 16.42 cc. of dry N_2 (20° and 737.2 mm.). Calc. for $C_{10}H_9O_5N_2Hg$: N, 6.40. Found: 6.55.

The compound is yellow and crystalline. It dissolves in sodium hydroxide, forming a yellow solution. After a short time this solution yields a red precipitate, further de-acetylation having taken place. It melts with decomposition at 194°.

Determination of the Position of the Mercury in the Mercurized *o*-Nitro-aniline Derivative

To determine the position of the mercury in the mercury derivative, the diacetyl compound was treated with potassium perbromide in the same manner as already described for the corresponding *para* compound. A lemon colored compound was obtained which, when recrystallized from water, melts at 104°. When mixed with some known *o*-nitro-*p*-bromo-acetanilide the melting point was not lowered. The mercury is shown thus to be in the position *para* with respect to the amino group.

N-iso-Mercuric-acetate-*m*-nitrophenylammonium Acetate,



solved in 14 cc. of alcohol was added to a solution of 1.8 g. of mercuric acetate in 8 cc. of water. The solution soon acquired a dark color and considerable heat was evolved. After standing for 4 minutes a yellow solid separated and in a short time the entire mass became semi-solid. The compound was collected in a filter and washed well with acetone. For analysis it was dried *in vacuo* over sulfuric acid to constant weight.

Analyses. Subs., 0.2771, 0.3007: 14.00 cc. dry N_2 (21° and 738.8 mm.), 15.40 cc. (25° and 717.0 mm.). Calc. for $C_{10}H_{12}O_6N_2Hg$: N, 6.12. Found: 5.70; 5.43.

The compound is slightly yellow. When treated with alcohol or water it decomposes to give a red substance. The filtrate when treated with ammonium sulfide gives a test for inorganic mercury.

m-Nitro-aniline-*p*-mercuric Acetate, $[C_6H_3(1)NH_2(3)NO_2(4)HgO \cdot OC_2H_5]$.—To prepare this compound, 9.6 g. of mercuric acetate dissolved in 40 cc. of water was added to a solution of 4.2 g. of *m*-nitro-aniline in 60 cc. of alcohol. The solution soon changed into a pasty mass. Upon heating on the water-bath for 3 hours it gave no immediate test for

inorganic mercury with ammonium sulfide. The hot solution was then filtered and the solid residue extracted repeatedly with alcohol which contained a little acetic acid. A dark red residue remained which melted at 225°. This residue, which is the dimercurey-substitution product, will be described in more detail later in the paper. The first alcoholic extract was evaporated to dryness and the residue recrystallized from alcohol which contained a little acetic acid. For analysis the compound was dried *in vacuo* to constant weight.

Analysis. Subs., 0.1094: 7.00 cc. of dry N₂ (19° and 731.4 mm.). Calc. for C₈H₈O₄N₂Hg: N, 7.09. Found: 7.20.

The compound is yellow; m. p. 183°. A darkening of color is observed when it is treated with sodium hydroxide.

o-p-Diacetoxymercuri-m-nitro-aniline, [C₆H₂(1)NH₂(3)NO₂(4,2)(HgO·OC₂H₃)₂].—This compound was prepared by boiling an alcoholic solution of 4.2 g. of *m*-nitro-aniline with 19.4 g. of mercuric acetate dissolved in water, until the solution gave no further test for inorganic mercury with ammonium sulfide. The precipitated compound was extracted repeatedly in order to remove any monomercurey substituted derivative which might have been present. For analysis the compound was dried *in vacuo* to constant weight.

Analysis. Subs., 0.6292: 25.36 cc. of dry N₂ (24° and 733.5 mm.). Subs., 0.2520: Hg, 0.1531. Calc. for C₁₀H₁₀O₆N₂Hg₂: N, 4.28; Hg, 61.17. Found: N, 4.47; Hg, 60.76.

The compound is red; m. p. 225°. It is insoluble in the common organic solvents.

p-Acetoxymercuri-acetyl-m-nitro-aniline, [C₆H₃(1)NH·(COCH₃)(3)NO₂(4)HgO·OC₂H₃].—This compound was prepared from *p*-acetoxymercuri-*m*-nitro-aniline in the same manner as that described for the *p*-nitro-aniline derivative above. For analysis it was dried *in vacuo* over sulfuric acid to constant weight.

Analysis. Subs., 0.2522: 14.24 cc. of dry N₂ (18° and 739.5 mm.). Calc. for C₁₀H₁₀O₅N₂Hg: N, 6.40. Found: 6.45.

This compound is white. It melts with decomposition at 230°.

Determination of the Position of the Mercury in the Mercurized *m*-Nitro-aniline

The method of procedure used in determining the position of the *m*-nitro-aniline derivatives was similar to that used for the *para* compound. The compound obtained when recrystallized from water melted at 135–139°. When mixed with some known *p*-bromo-*m*-nitro-acetanilide the melting point was not lowered. The position of the mercury is thus shown to be *para* to the amino group.

To determine the position of the mercury in the dimercurey-substituted *m*-nitro-aniline, the latter compound was suspended in ethyl acetate and boiled under a reflux condenser with acetic anhydride until the whole became white.¹⁸ The acetyl derivative thus prepared was treated with 2 mols of potassium perbromide, in the manner previously described. The product obtained was then filtered, dried and extracted with ether. The ethereal extract was evaporated to dryness, leaving a residue of melting point 141–146°. Upon recrystallization from 50% alcohol it melted at 150°. When mixed with known 2,4-dibromo-3-nitro-acetanilide the melting point was not lowered. The compound was then de-acetylated with conc. sulfuric acid at 120°. Upon dilution of this reaction mixture with water, a yellow product melting at 84–87° was obtained. Upon recrystallization from 50% alcohol, a product melting at 89° was obtained. When mixed with known 2,4-dibromo-3-nitro-aniline, the melting point was not lowered. This identifies the position of the mercury as being 2,4 with respect to the amino group (NO₂=3).

¹⁸ In the course of the reaction, an appreciable amount of metallic mercury was formed. Since the compound thus obtained is insoluble in the common organic solvents, it could not be purified, and therefore was not analyzed.

Summary

1. The nitronic acid structure for the nitro-anilines is discussed. Evidence is given that is compatible with the assumption that, in alcoholic solution, the *o*- and *p*-nitro-anilines exist in two or more tautomeric forms. The fundamental difference between the mercury salts of the *o*- and *p*-nitro-anilines and that formed by the *meta* compound is pointed out.

2. The mercurization of the nitro-anilines is discussed.

3. The positions taken by the entering mercury in the nitro-anilines has been established as *ortho* or *para*, or *ortho-para*, to the amino group.

4. The preparation of the following compounds is described: *p*-quinone-imide-aci-nitro mercury salt, *o*-acetoxymcuri-*p*-nitro-aniline, *o*-chloromcuri-*p*-nitro-aniline, *o*-,*o'*-di-acetoxymcuri-*p*-nitro-aniline, quinone-(1)-imide-aci-(4)nitro-(2)-mercury, *o*-,*o'*-mercury-*bis-p*-nitro-aniline, *o*-acetoxymcuri - acetyl - *p*-nitro - aniline, quinone-(1) - imide - aci - (2)-nitro mercury salt, *p*-acetoxymcuri-*o*-nitro-aniline, *p*-chloro-mercuri-*o*-nitro-aniline, quinone-(1)-imide-aci-(2)nitro-(4)-mercury, *p*-acetoxymcuri-di-acetyl-*o*-nitro-aniline, *p*-acetoxymcuri-acetyl-*o*-nitro-aniline, *N*-*iso*-mer-curic acetate *m*-nitrophenylammonium acetate, *p*-acetoxymcuri-*m*-nitro-aniline, *o*, *p*-diacetoxymcuri - *m* - nitro-aniline, *p*-acetoxymcuri-acetyl-*m*-nitro-aniline.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]
**ALIPHATIC ARSONIC AND ARSINIC ACIDS, AND ALIPHATIC-
AROMATIC ARSINIC ACIDS¹**

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The extensive development of aromatic arsenicals as compared with those of the aliphatic series is in part explained by the fact that the most active and most effective trypanocidal drugs belong to the aromatic series. Another cause for the unbalanced development is found in the ease and convenience with which aromatic arsenicals can be synthesized. The methods of preparation for the arsenic compounds belonging to the aliphatic series are very numerous,² but they are quite unsatisfactory.

The arsonic (RAsO_3H_2) and, to a less extent, the arsinic acids ($\text{R}_2\text{AsO}_2\text{H}$) are substances from which many different types of compounds may be made, so that the lack of a satisfactory method of preparation of these has limited development in this field. The object of this research was to find an easy method for preparing these compounds and to apply such a method

¹ This communication is an abstract of a thesis submitted by A. J. Quick in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² See THIS JOURNAL, 28, 347 (1906) for a list of the known methods.