knows, however, that it is an easy matter to make an error of half a milligram in any method involving a precipitation and the transfer of a precipitate ; Croasdale's results and those of Richards show that the error involved is much less when copper is determined by the battery method, and that we can probably determine copper more accurately than any other element, consequently that our method should be taken as the standard and others referred to it."

No question need be raised in regard to the exactness of the electrolytic assay of copper. It is a direct and absolute method for the determination of copper, but the method, based upon that determination, of using the liberated acid for standardizing a permanent acid solution by making two volumetric determinations, and computing from the low equivalent weight of copper (as compared with that of silver chloride) is very indirect and not exceedingly accurate; and this comparative study of methods of standardizing acids has convinced the writer that the objections mentioned to the copper sulphate method are applicable and valid ; also that the silver chloride method (as described) and the ammonium sulphate method are extremely accurate and satisfactory for standardizing solutions of hydrochloric and sulphuric acids, respectively.

UNIVERSITY OF ILLINOIS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 32.]

SOME EXPERIMENTS WITH THE MONONITROORTHOPHTHALIC ACIDS.

BY MARSTON TAYLOR BOGERT AND LEOPOLD BOROSCHEK.

Received August 1, 1901.

ALTHOUGH both mononitro-*o*-phthalic acids have long been well known, yet, of their derivatives, with the exception of their salts and esters, only the anhydride, imide, and anil have been described. It seemed, therefore, of interest to prepare some of the other derivaties of these acids and to study their properties, and the present paper records our first experiments along this line.

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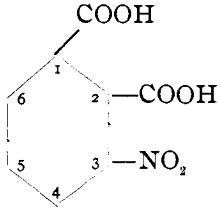
[1] The iron-permanganate method gave fairly accurate results as a method for standardizing oxalic acid. It is no more indirect and no less accurate (if the purity of the iron be known) than the copper sulphate method. It is thought that a detailed description here of the work done upon the iron-permanganate method would not be of special interest or value.

Naturally, the first question to be decided was as to the best method for the preparation of the pure acids themselves. Our experience has shown that the direct nitration of phthalic acid itself, or of its anhydride, gives good yields of the pure 3,nitro-*o*-phthalic acid, but that as a method for the preparation for the isomeric 4,nitro acid it is not so good as that depending upon the oxidation of *p*-nitrophthalide with alkaline potassium permanganate.

Of the derivatives of the 3,nitro-*o*-phthalic acid, we have prepared and studied the acid aniline and *o*-toluidine salts, a new acid ethyl ester, the imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, and the hydrazide.

Of the 4,nitro-*o*-phthalic acid the following derivatives are described: Acid aniline salt, a new acid ethyl ester, anhydride, imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, *p*-tolilic acid, and hydrazide; also the corresponding azophthalic acid and azophthalide.

By the action of phosphorus pentachloride upon the anhydride of the 3,nitro-*o*-phthalic acid, the anhydride of the 3,chlor-*o*-phthalic acid was formed, and from this the free acid and imide were prepared.



α, OR 3,NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

Method of Beilstein and Kurbatow.[1]—One part of α-nitronaphthalene is dissolved in 7 parts of 90 per cent. acetic acid, and 5 parts of chromic anhydride gradually added. When the reaction is over, dilute with water, filter out unchanged nitronaphthalene, extract the filtrate with chloroform, to remove nitrophthalide,[2] boil the acetic acid solution with barium carbonate, decompose

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[1] *Ann. Chem.* (Liebig), **202**, 217 (1880).

[2] *Ber. d. chem. Ges.*, **18**, 3452 (1885).

the precipitated barium nitrophthalate with sodium carbonate, acidify with sulphuric acid, collect the liberated nitrophthalic acid in ether, evaporate the ether, and crystallize the residue from water.

We have found this method unsatisfactory for several reasons. In the first place, the reaction proceeds with considerable violence, prohibiting the use of large amounts of materials, while attempts to moderate its violence only result in the formation of more resinous by-products, as was likewise the experience of Beilstein and Kurbatow ;[1] yet, in spite of the apparent energy of the reaction, considerable of the nitronaphthalene is recovered unchanged, in some cases as much as 25 per cent. Then, the method is rather long and tedious, the yield small (25 per cent. of theory) and the quality of the resulting acid poor, the crystals invariably showing a low melting-point and carrying a small amount of a red coloring-matter from which they are freed with difficulty.

Method of Miller.[2]—This is the process generally employed for the simultaneous preparation of both nitro-*o*-phthalic acids. It is as follows:

Fifty grams of *o*-phthalic acid are nitrated in a roomy flask by a mixture of 75 grams concentrated sulphuric acid and 75 grams fuming nitric acid, the flask being heated two hours upon the water-bath. The result of this nitration is a mixture of the two nitro-*o*-phthalic acids and picric acid, together with unchanged phthalic acid, acetic acid, etc. Towards the close of the heating some of the 3,nitro acid begins to separate in prisms. The mass is then allowed to cool and is precipitated by the addition of water. The composition of the precipitate varies with the amount of water added, as the two nitro-*o*-phthalic acids possess very different solubilities in dilute mineral acids: 240 cc. of water precipitate mainly the 3,nitro acid, while half this amount throws down the 4,nitro acid also. This difference in solubility cannot, however, be used as a means of separation (for the 4,nitro acid, at least), since picric acid remains in solution with the 4,nitro acid and combines with it in recrystallization; hence, it is better to precipitate both nitrophthalic acids together, although some picric acid is thus always carried down, apparently in union with the 4,nitro acid. The reaction mixture is, therefore, diluted

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[1] *Loc. cit.*

[2] *Ann. Chem.* (Liebig), **208**, 223 (1881).

with 120 cc. of water, allowed to stand twelve hours in a cool place, the precipitate filtered out upon cloth, and the acid mother-liquor removed as completely as possible by suction and pressure. The precipitate is then rubbed up with a little water and extracted repeatedly with ether. The first ether extracts contain mainly the 4,nitro acid and picric acid, and are, therefore, yellow in color, while the more difficultly soluble 3,nitro acid is extracted last. Evaporation of the ether leaves a yellow acid mixture, melting at 154°–186°, in a yield of 85 per cent. of the theory, from which the 3,nitro acid may be obtained by frequent crystallization from water, the 4,nitro acid and picric acid remaining in the mother-liquors. The yield of pure 3,nitro acid thus obtained is about 50 per cent. of the weight of the crude acid mixture.

As pointed out by Miller,[1] this process can be considerably shortened if it is not desired to recover the 4,nitro acid, by taking the first precipitate of crude acids, removing the mineral acids by careful washing, pressing, and draining upon a clay plate, and then separating the difficultly soluble 3,nitro acid by crystallizing this cake repeatedly from water.

In carrying out this method, the phthalic acid dissolves after about a half hour's heating, to a clear amber solution, with evolution of copious fumes of oxides of nitrogen. After heating for about an hour longer, the 3,nitro acid begins to crystallize out, and the contents of the flask soon change to a mass of crystals. Sufficient water is then added to precipitate mainly the 3,nitro acid, the mixture is allowed to stand twenty-four hours in a cool place, and the precipitate then separated as thoroughly as possible from the acid mother-liquor, giving a cake of crude 3,nitro acid. This is dissolved in hot water and the solution concentrated until crystals begin to separate from the hot liquid. It is then allowed to cool slowly and is left four or five hours in a cool place. Most of the 3,nitro-*o*-phthalic acid is thus separated in small hard transparent crystals of a faint yellowish cast, which are further purified by recrystallization from water, the yield then being about 30 per cent. of the theory.

As there is usually some unnitrated phthalic acid in the first precipitate of crude acids, this precipitate was subjected to a second nitration in similar manner. Only a small amount of the crude acid then dissolved in the hot nitrating solution, showing the

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[1] *Ber. d. chem. Ges.*, **11**, 393 (1878).

presence of but little phthalic acid. The yield of 3,nitro acid was increased by this second nitration to about 32 per cent. of that theoretically obtainable from phthalic acid.

Method of May,[1] *Edinger*[2] *and Leupold.*[3]—This is quite similar to that of Miller, except that phthalic anhydride is used instead of the acid.

As might be expected from the smaller amount of water present in this reaction, the precipitation of the nitro acids begins much sooner, and after an hour's heating upon the water-bath the mixture in the flask is a nearly solid mass of crystals. This rapid separation of the nitro acids seems to prevent complete nitration, as the yield of pure 3,nitro acid by this process was only about 25 per cent. of the theory, while a renitration raised this figure to nearly 38 per cent. It is quite possible that by the careful addition of water during the first nitration the separation of the nitro acids could be retarded, thereby increasing the yield and obviating the necessity for a second nitration.

In renitrating the crude nitro acids no complications need be feared from formation of dinitrophthalic acids, as Beilstein and Kurbatow[4] have shown that it is exceedingly difficult to further nitrate 3,nitro-*o*-phthalic acid.

The nitration of phthalic acid or of its anhydride thus readily gives good yields of pure 3,nitro-*o*-phthalic acid, and it is the method by which we have prepared the acid for conversion into the derivatives described later.

As thus prepared, 3,nitro-*o*-phthalic acid forms hard transparent prisms, of a very pale yellow color. Its behavior when heated resembles that of the unsubstituted phthalic acid; in an open tube, it decomposes at 207°, or lower, into water and the anhydride, the point at which this decomposition begins depending upon the rapidity of the heating, while in a sealed tube it melts at 222° (corr.). It is quite readily soluble in hot water, much less so in cold; easily soluble in cold acetone; moderately soluble cold, easily hot, in methyl or ethyl alcohols, and ethyl acetate; sparingly soluble in cold isoamyl alcohol, moderately in hot; difficultly soluble in ether; nearly insoluble in petroleum ether, benzene, chloroform, carbon tetrachloride, ethyl nitrate,

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[1] Inaug. Dissertation, Freiburg, (1880).

[2] *J. prakt. Chem.*, (2), **53**, 382 (1896).

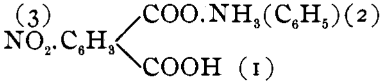
[3] Inaug. Dissertation, Basle, (1897).

[4] *Loc. cit.*

carbon bisulphide, benzene, and nitrobenzene ; glacial acetic acid, at 26°, takes up 7.5 per cent. (Aguiar,[1] Diehl and Merz).[2] It is much less soluble in all ordinary solvents than the corresponding 4,nitro-*o*-phthalic acid.

Derivatives of 3,Nitro-o-phthalic Acid.

Acid Aniline Salt,

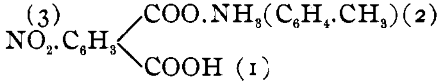


$$\overset{(3)}{\mathrm{NO_2}}.\mathrm{C_6H_3}\left\langle\begin{matrix}\mathrm{COO.NH_3(C_6H_5)}(2)\\ \mathrm{COOH}\ (1)\end{matrix}\right.$$

—The strong tendency of 3,nitro-*o*-phthalic acid to form acid salts with the ammonium bases, rather than neutral salts, was commented upon by Laurent[3] as early as 1842. This peculiarity is still more marked in the case of the aromatic amines, of which no neutral salts with the nitrophthalic acids are known. By adding aniline to the alcoholic solution of 3,nitro-*o*-phthalic acid and then concentrating upon the water-bath, colorless needles of the acid aniline salt separate, melting at 185°–187°, with loss of water and production of the anil. Only the acid salt could be obtained, no matter how large the excess of aniline employed. Several months after the completion of this experiment an article by Graebe and Buenzod[4] appeared, in which they record similar results.

As the carboxyl adjacent to the nitro group is the stronger of the two, it seems most likely that this acid salt has the formula given above.

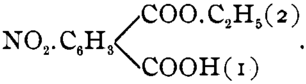
Acid o-Toluidine Salt,



$$\overset{(3)}{\mathrm{NO_2}}.\mathrm{C_6H_3}\left\langle\begin{matrix}\mathrm{COO.NH_3(C_6H_4.CH_3)}(2)\\ \mathrm{COOH}\ (1)\end{matrix}\right.$$

— Prepared in a similar manner, this acid salt forms fine white needles melting at 181°, a few degrees above which point it breaks up into water and the *o*-tolil. Its aqueous solution is acid to carbonates and to litmus.

Acid Ethyl Ester,



$$\mathrm{NO_2}.\mathrm{C_6H_3}\left\langle\begin{matrix}\mathrm{COO.C_2H_5}(2)\\ \mathrm{COOH}(1)\end{matrix}\right.$$

.—3,Nitrophthalic anhydride was dissolved in absolute alcohol in a flask carrying a reflux condenser, and the solution heated for five hours upon the water-bath. Upon distilling off the alcohol, a yellow oil remained, which was dissolved in strong sodium carbonate solution and the mixture extracted with ether, to remove any neutral

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[1] *Ber. d. chem. Ges.*, **5**, 899 (1872).

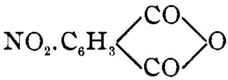
[2] *Ibid.*, **11**, 1667 (1878).

[3] *Ann. Chem.* (Liebig), **41**, 110 (1842).

[4] *Ber. d. chem. Ges.*, **32**, 1992 (1899).

ester (none was found). The addition of hydrochloric acid to the sodium carbonate solution caused the separation of a white crystalline precipitate, melting at 157°, soluble in alcohol or ether, but insoluble in cold water. Its solutions decompose carbonates and are acid to litmus. The substance was dissolved in alcohol and titrated with tenth-normal sodium hydroxide solution. 0.807 gram of the substance took 33.3 cc. of the tenth-normal sodium hydroxide; theory requires 33.7 cc. The silver salt forms nearly colorless crystals.

The isomeric acid ethyl ester, with the ester group meta to the nitro, and melting at 110°, was first obtained (in the impure state) by Faust,[1] and, subsequently described by Baeyer,[2] Miller,[3] Nerking,[4] and Edinger.[5]

Anhydride,  $NO_2.C_6H_3{<}\begin{matrix}CO\\CO\end{matrix}{>}O$.—Laurent,[6] Faust,[7] and Miller[8] all state that the anhydride is formed by the action of heat upon the acid. Recently, however, Lipschitz[9] reported that by careful heating of the acid at 220°, even in a stream of carbon dioxide, he obtained only a brown melt containing decomposition products with the odor of nitrogen dioxide and benzaldehyde. Our experience has been more in accord with that of the earlier investigators. The 3,nitro acid, in a small flask, was heated in an oil-bath at 235°–240° until water vapor ceased to be given off (six to eight hours' heating necessary). On cooling, a yellow crystalline solid appeared, which was nearly pure anhydride, and, after a single crystallization from glacial acetic acid or acetone, formed colorless needles melting sharply at 163°. If there should be any indication of unchanged acid in the product, it may be crystallized from acetyl chloride, which likewise converts the acid to the anhydride.[10] The anhydride is easily soluble in acetyl chloride or hot glacial acetic acid, moderately in acetone or hot alcohol, and very difficultly soluble in benzene.

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[1] *Ann. Chem.* (Liebig), **160**, 57 (1871).

[2] *Ber. d. chem. Ges.*, **10**, 125, 1079 (1877).

[3] *Ann. Chem.* (Liebig), **208**, 223 (1881).

[4] Inaug. Dissertation, Heidelberg, (1896).

[5] *J. prakt. Chem.*, (2), **53**, 382 (1896).

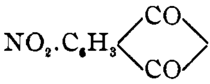
[6] *Ann. Chem.* (Liebig), **41**, 110 (1842).

[7] *Ztschr. Chem.* 1869, 108; *Ann. Chem.* (Liebig), **160**, 57 (1871).

[8] *Ann. Chem.* (Liebig), **208**, 223 (1881).

[9] *Monatsh. Chem.*, **21**, 787 (1900).

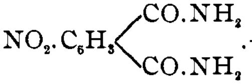
[10] Leupold: *Loc. cit.*; Lipschitz: *Loc. cit.*

Imide,  $NO_2.C_6H_3\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle NH$.—Laurent[1] states that when the ammonium salt of 3,nitro-*o*-phthalic acid is distilled the free acid is regenerated and no imide is formed; also, that when the anhydride is treated with dry ammonia gas a new compound is obtained, but he gives none of the properties of this "new compound." We have, therefore, prepared this imide by the action of heat upon the acid ammonium salt. The salt begins to decompose at about 225°, and the heating is continued until no more water vapor is evolved and the melt remains in quiet fusion. On cooling, a yellow crystalline solid is obtained, easily soluble in acetone, moderately in hot alcohol or hot glacial acetic acid, and very difficultly in water. It crystallizes from alcohol in pale yellow lustrous needles melting at 215°–216°.

I. 0.1513 gram substance gave 20 cc. nitrogen at 22° and 753 mm.
II. 0.1694 gram substance gave 22.1 cc. nitrogen at 22° and 751.5 mm.

	Calculated for $C_8H_4O_4N_2$.	Found. I.	Found. II.
Nitrogen	14.62	14.82	14.51

By dissolving the imide in a mixture of alcohol and acetone and adding exactly one molecule of potassium hydroxide dissolved in alcohol, a white crystalline precipitate of the potassium salt of the imide results.

Amide,  $NO_2.C_6H_3\left\langle\begin{matrix}CO.NH_2\\ CO.NH_2\end{matrix}\right.$.—Strong ammonium hydroxide is added to the imide and the mixture warmed slightly. The lustrous flaky crystals of the imide gradually disappear and in their place a sandy crystalline precipitate appears, the reaction being complete at the end of about one hour. Dried to constant weight over sulphuric acid *in vacuo*, the following analytical results were obtained from the substance:

0.1452 gram substance gave 26.1 cc. nitrogen at 22° and 758 mm.

	Calculated for $C_8H_7O_4N_3$.	Found.
Nitrogen	20.1	20.3

When heated in an open tube, the amide melts at 200°–201° with evolution of ammonia, remelting, after cooling, at 215°, the melting-point of the imide.

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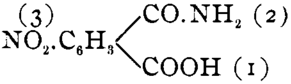
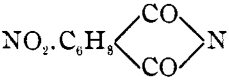
[1] *Loc. cit.*

Amidic Acid,  $\overset{(3)}{NO_2}.C_6H_3\left\langle\begin{array}{l}CO.NH_2\ (2)\\ COOH\ (1)\end{array}\right.$.—Baryta water is added to the imide and the mixture heated for an hour at 80°, and then allowed to stand for twenty-four hours at the ordinary temperature. Upon acidifying with sulphuric acid, the barium sulphate precipitate carries down with it some of the amic acid, which may be recovered by extraction with cold strong alcohol. Concentration of the filtrate from the barium sulphate precipitation, or of the alcoholic extracts, yields white needles of the amidic acid. This concentration must be carried out cold, by blowing a stream of dry air through the liquid, as hot concentration appears to destroy the amic acid, probably causing hydration. The crystals of amic acid were washed with ether, and dried *in vacuo* over sulphuric acid. They melt at 156°, with evolution of water, and, after solidifying, remelt at 213°, showing the production of the imide. The amidic acid is but sparingly soluble in cold water, easily in alcohol, and apparently insoluble in ether. Its solutions are acid to litmus and decompose carbonates.

0.1509 gram substance gave 17.6 cc. nitrogen at 22° and 755 mm.

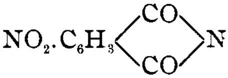
	Calculated for $C_8H_6O_5N_2$.	Found.
Nitrogen	13.3	13.13

Ethylimide,  $NO_2.C_6H_3\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle N.C_2H_5$.—When the acid ethylamine salt is heated at 125°–165° for some time there results a greenish crystalline solid, sparingly soluble in hot water, but easily in hot alcohol. From the latter solvent it crystallizes in long lustrous needles of yellowish cast, melting at 105°.

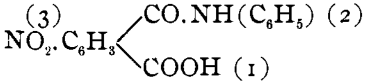
0.1747 gram substance gave 20.4 cc. nitrogen at 27.5° and 760 mm.

	Calculated for $C_{10}H_8O_4N_2$.	Found.
Nitrogen	12.7	12.85

Attempts to prepare the same compound by the action of ethyl iodide upon the potassium salt of the imide, in sealed tubes, all resulted unsatisfactorily.

Anil,  $NO_2.C_6H_3\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle N.C_6H_5$.—Aniline and 3,nitro-*o*-phthalic anhydride are heated together at about 190°, or, better, the acid aniline salt is carefully heated. In the latter case, an amber colored solid is obtained, soluble in acetone, difficultly soluble in cold alcohol, moderately in hot. Crystallized from a mixture of alcohol and acetone, it forms yellowish needles, melting at 136°–137°. Graebe and Buenzod,[1] whose article, as already explained, appeared subsequent to the completion of this part of the work, give 134° as the melting-point of the anil.

Anilic Acid,



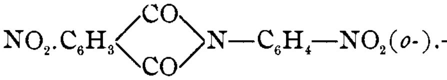
$\overset{(3)}{NO_2}.C_6H_3\left\langle\begin{array}{l}CO.NH(C_6H_5)\ (2)\\ COOH\ (1)\end{array}\right.$

.—This compound may be prepared from the anil in a manner entirely analogous to that for the preparation of the amic acid from the imide, except that when the baryta solution is acidified by sulphuric acid most of the anilic acid separates with the barium sulphate as a flocculent precipitate, which must be dissolved out by cold alcohol, and the solution concentrated cold as already described. Pale yellow needles are thus obtained, which can be washed with ether and dried. These needles melt at 180°, and, after resolidifying, the melting-point sinks to 135°, showing conversion of the anilic acid to the anil (m. p. 136°). The anilic acid is easily soluble in alcohol, difficultly in cold water, and apparently insoluble in ether. Its solutions are acid to litmus but do not seem to decompose carbonates.

0.1962 gram substance gave 17.4 cc. nitrogen at 23° and 758 mm.

	Calculated for $C_{14}H_{10}O_5N_2$.	Found.
Nitrogen	9.8	9.96

o-Nitranil,



$NO_2.C_6H_3\left\langle\begin{array}{l}CO\\ CO\end{array}\right\rangle N—C_6H_4—NO_2(o\text{-})$

.—When the acid *o*-nitraniline salt is heated it begins to decompose at 150° with loss of water, and at 200° the last portions of water are removed. The yellowish mass resulting, when crystallized from a mixture of alcohol and acetone, gives yellow crystals of the *o*-nitranil, melting at 167°.

0.1619 gram substance gave 20 cc. nitrogen at 25° and 759 mm.

	Calculated for $C_{14}H_7O_6N_3$.	Found.
Nitrogen	13.4	13.7

m-Nitranil is prepared by heating the acid *m*-nitraniline salt at 170°–200°. The product is less soluble in alcohol or acetone than the corresponding ortho compound, and, when crystallized from a mixture of these solvents, forms pale brown, microscopic crystals, melting at 219°.

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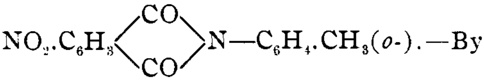
[1] *Loc. cit.*

p-Nitranil.—The acid *p*-nitraniline salt was heated at 200°–250° until water ceased to be evolved. The brown crystalline mass resulting was purified by crystallization from acetone, in which it was only moderately soluble, small yellow crystals of the *p*-nitranil being thus obtained, of a melting-point of 249°.

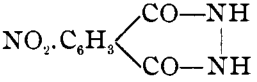
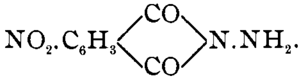
o-Tolil,  .—By heating the acid *o*-toluidine salt at 160°–190°, and crystallizing the product from a mixture of alcohol and acetone, pale yellow needles of the *o*-tolil result, melting at 145°. These are easily soluble in acetone, and only sparingly in alcohol.

m-Tolil is prepared in a similar manner, the acid *m*-toluidine salt losing its water at about the same temperature as the ortho compound. From a mixture of alcohol and acetone, it crystallizes in long yellow needles, melting at 129°.

p-Tolil.—Equal molecules of *p*-toluidine and 3,nitro-*o*-phthalic anhydride were heated together at 170°–180° until the evolution of water ceased. The *p*-tolil thus obtained crystallizes from a mixture of alcohol and acetone in pale yellow needles (m. p. 154°).

0.2003 gram substance gave 18.3 cc. nitrogen at 23° and 752 mm.

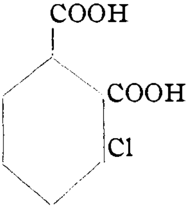
	Calculated for $C_{15}H_{10}O_4N_2$.	Found.
Nitrogen	9.93	10.17

Hydrazide,  or 

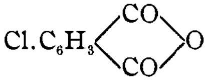
—3,Nitro-*o*-phthalic acid was dissolved in alcohol, one molecule of hydrazine hydroxide (in 50 per cent. aqueous solution) added, and the solution evaporated to dryness. The residue was then carefully heated in an oil-bath. At 150° the evolution of water began and continued until the temperature reached 250°. Even at this latter temperature the material did not melt, but remained a pale brown, porous solid. It dissolved readily in a warm sodium carbonate solution, with effervescence, forming a yellowish red liquid. Acidification with hydrochloric acid caused the precipitation of a yellow powder, which crystallized from glacial acetic acid in pale yellow, microscopic crystals, melting with decomposition at about 320°. These crystals are likewise decomposed by caustic alkali.

0.1510 gram substance gave 27.4 cc. nitrogen at 24° and 761 mm.

	Calculated for $C_8H_5O_4N_3$.	Found.
Nitrogen	20.3	20.36

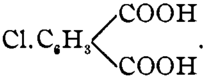


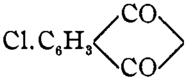
3, Chlor-o-phthalic Acid.

Anhydride,  $Cl.C_6H_3\langle{}^{CO}_{CO}\rangle O$.—Ten grams of 3,nitro-*o*-phthalic anhydride and 11 grams phosphorus pentachloride were heated together in a sealed tube for six hours at 175°. From the contents of the tube pale yellow crystals were separated, which, after recrystallization from a mixture of benzene and naphtha, formed nearly colorless needles, melting at 122°, corresponding to that recorded by Krüger[1] for 3,chlor-*o*-phthalic anhydride.

0.1763 gram substance gave 0.1415 gram silver chloride.

	Calculated for $C_8H_3O_3Cl$.	Found.
Chlorine	19.4	19.8

Acid,  $Cl.C_6H_3\langle{}^{COOH}_{COOH}$.—By boiling the anhydride obtained above for several hours with dilute hydrochloric acid, the corresponding chlorphthalic acid was obtained. This crystallized from water in colorless needles (m. p. 186°). Guareschi[2] found the melting-point of 3,chlor-*o*-phthalic acid to be 184°.

Imide,  $Cl.C_6H_3\langle{}^{CO}_{CO}\rangle NH$.—The 3,chlor-*o*-phthalic anhydride was dissolved in strong ammonium hydroxide, the solution evaporated to dryness, and the residue carefully heated. A sublimate of white needles resulted. In an open tube, these needles sublime before melting; in a closed tube they melt at 118°–120°. The substance appears to be the 3,chlorphthalimide, which has

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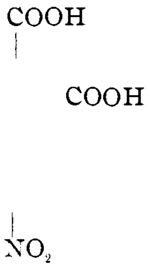
[1] *Ber. d. chem. Ges.*, **18**, 1759 (1885).

[2] *Gaz. chim. ital.*, **17**, 120.

not been previously described, but not sufficient of the substance was prepared for an analysis.



β, OR 4,NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

Method of Miller.[1]—As has been stated, the action of a mixture of concentrated sulphuric acid and fuming nitric acid upon phthalic acid produces about equal amounts of the two nitro-*o*-phthalic acids. Of these, the 3,nitro acid is readily separated in the pure state by virtue of its sparing solubility in water. The isolation of the 4,nitro acid, however, is a matter of much greater difficulty, not only on account of its great solubility, but also from the fact that the picric acid present tends to follow it through and to combine with it or its salts in crystallization, so that even by the recrystallization of its difficultly soluble barium salt only about 15 per cent. pure 4,nitro acid can be recovered from the original precipitate of crude acids. A much better method of separation depends upon the fact that when a mixture of these two acids is esterified by the action of hydrochloric acid gas upon their alcoholic solution the 3,nitro acid yields mainly the acid ester, while the 4,nitro acid is converted into the neutral ester. By treating the product of this esterification with strong sodium carbonate solution, the acid ester (together with picric acid) is dissolved out, leaving the neutral ester of the 4,nitro acid as an insoluble oil.

In applying this process, we usually crystallized out as much of the 3,nitro acid as possible from the crude nitro acids, then evaporated the mother-liquors to dryness, dissolved the residue in absolute alcohol and esterified with dry hydrochloric acid gas. Upon the addition of water, then, the esters separate as an oily layer, which is washed repeatedly with strong sodium carbonate

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[1] *Ber. d. chem. Ges.*, **11**, 393 (1878); *Ann. Chem.* (Liebig), **208**, 223 (1881).

solution. The neutral ester of the 4,nitro acid is thereby left as an oil, which gradually solidifies, and is purified by crystallization from ether and then from alcohol, forming large pale yellow plates, melting at 34°–35°. From this neutral ester the free acid may be prepared by saponifying with alcoholic potassium hydroxide, dissolving the precipitated potassium salt in water, acidifying the solution with hydrochloric acid and extracting with ether. Evaporation of the ether leaves the 4,nitro-*o*-phthalic acid as a crystalline crust, melting at 162°.

Although the yield by this process is good, the purification of the neutral ester is rather troublesome, as it is apt to contain small amounts of the neutral esters of 3,nitro-*o*-phthalic acid and of phthalic acid itself, the presence of the latter preventing the solidification of the oily ester.

Preparation of the Acid from p-Nitrophthalide.—Hoenig[1] was the first to prepare the 4,nitro-*o*-phthalic acid from the nitrophthalide (m. p. 141°) by oxidation. He found the best oxidizing agents to be a mixture of glacial acetic acid and chromic anhydride, or, better, dilute nitric acid in a sealed tube.

Oxidation by glacial acetic acid and chromic anhydride is far from satisfactory, and much the same may be said concerning the use of dilute nitric acid. The latter method is also open to the objection that it is not convenient for the preparation of large amounts of material.

Hoenig[2] further states that oxidation of the nitrophthalide by means of alkaline potassium permanganate gave no result. We have found, on the contrary, that this is much the best oxidizing agent for the purpose, 90 per cent. of the theoretical yield of 4,nitro-*o*-phthalic acid being thereby readily and rapidly obtained, the ease and rapidity of the method rendering it by far the best method of preparing the 4,nitro-*o*-phthalic acid pure and absolutely free from its isomer.

The oxidation is carried out as follows: *p*-nitrophthalide is dissolved in dilute alkali, the solution placed in a large evaporating dish on the water-bath, and potassium permanganate solution added gradually until the oxidation is completed. Excess of permanganate is then destroyed by the addition of a little alcohol, the manganese dioxide filtered off and the precipitate washed

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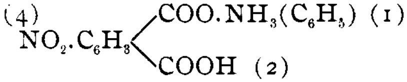
[1] *Ber. d. chem. Ges.*, **18**, 3447 (1885).

[2] *Loc. cit.*

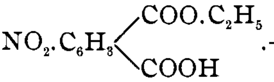
once or twice with hot water. The filtrate and washings are combined, concentrated to about 150 cc., acidified with hydrochloric acid, and repeatedly extracted with ether. The ether extracts are combined, dried with calcium chloride, and the ether evaporated, leaving the pure 4,nitro-*o*-phthalic acid as a pale yellow crystalline mass (m. p. 163°).

The 4,nitro acid loses water a few degrees above its melting-point, being thereby changed to the anhydride. The acid is easily soluble in water, methyl or ethyl alcohols, and acetone; moderately in ether or ethyl acetate; sparingly in cold isoamyl alcohol or glacial acetic acid, easily in hot; apparently insoluble in petroleum ether, benzine, chloroform, carbon tetrachloride, ethyl nitrate, carbon disulphide, benzene, and cold nitrobenzene; moderately soluble in hot nitrobenzene.

Derivatives of 4,Nitro-o-phthalic Acid.



Acid Aniline Salt, $\overset{(4)}{NO_2.C_6H_3}\left\langle\begin{array}{l}COO.NH_3(C_6H_5)\ (1)\\ COOH\ (2)\end{array}\right.$.—Like the 3.nitro acid, the 4,nitro-*o*-phthalic acid appears incapable of forming neutral salts with the aromatic amines. As prepared by us, this acid aniline salt melts at 181°–182° with production of the anil. It has also been described by Graebe and Buenzod.[1] It seems probable that in these acid salts the para carboxyl carries the base.



Acid Ethyl Ester, $NO_2.C_6H_3\left\langle\begin{array}{l}COO.C_2H_5\\ COOH\end{array}\right.$.—Miller,[2] by evaporating an absolute alcohol solution of the 4,nitro-*o*-phthalic anhydride, reports the production of an acid ester different from the ordinary one (m. p. 127°–128°), but does not describe any of its properties. We have, therefore, repeated the experiment:

4,nitro-*o*-phthalic anhydride was dissolved in absolute alcohol in a flask fitted with a reflux condenser, the solution boiled for eight hours on the water-bath, and the alcohol then distilled off. A reddish brown oil remained. This oil dissolved, with effervescence, in sodium carbonate solution. The sodium carbonate solution was then extracted with ether, to remove any neutral ester which might have formed, the residual alkaline liquid acidified

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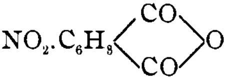
[1] *Loc. cit.*

[2] *Ann. Chem.* (Liebig), **208**, 223 (1881).

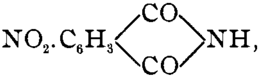
with hydrochloric acid, and the turbid acid solution again subjected to extraction with ether. This ether extract was dried with calcium chloride and the ether evaporated, leaving a yellow oil, which, after standing about eight hours over sulphuric acid in vacuo, solidified to a pale yellow, amorphous mass, melting at 141°–150°. Recrystallization failed to yield a substance with any sharper melting-point. The acid ethyl ester, produced by the action of dry hydrochloric acid gas upon the alcoholic solution of the 4,nitro acid, melts sharply at 127°–128°. The acid ethyl ester described above appears, therefore, to be an isomer (although probably impure).

This result is rather at variance with the investigations of Wegscheider and Lipschitz[1] in preparing the methyl esters of 4,nitro-*o*-phthalic acid, as they obtained the same acid ester by the action of methyl alcohol upon the anhydride as by the action of hydrochloric acid gas upon the methyl alcohol solution of the free acid.



Anhydride, $NO_2.C_6H_3\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$.—By heating the 4,nitro acid at 165° until no more water is evolved and then cooling, a sticky, yellow mass remains. Miller[2] heated this mass to 200° and sublimed the anhydride by passing a current of dry air through the melt. We have found it more convenient to dissolve this sticky mass in hot acetyl chloride and evaporate the solution to crystals. Pale yellow needles of the anhydride are thus obtained, melting sharply at 114°, which are easily soluble in acetyl chloride, hot glacial acetic acid or hot alcohol, and but sparingly in hot benzene.

Leupold[3] prepared this anhydride by heating the acid in sealed tubes with acetyl chloride.



Imide, $NO_2.C_6H_3\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$, is prepared by the action of heat upon the acid ammonium salt, in similar manner to the preparation of the imide of the 3,nitro acid. It crystallizes from a mixture of alcohol and acetone in pale yellowish brown flakes, melting at 197°. It is easily soluble in hot acetone, sparingly in hot alcohol or hot water.

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[1] *Monatsh. Chem.*, **21**, 787 (1900).

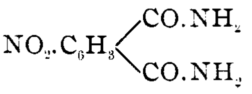
[2] *Ann. Chem.* (Liebig), **208**, 223 (1881).

[3] Inaug. Dissertation, Basle, 1897.

I. 0.1804 gram substance gave 24 cc. nitrogen at 23° and 755 mm.
II. 0.1494 gram substance gave 19.9 cc. nitrogen at 22° and 756 mm.

	Calculated for $C_8H_4O_4N_2$.	Found. I.	II.
Nitrogen	14.62	14.96	15.00

By dissolving the imide in a mixture of alcohol and acetone and adding one molecule of alcoholic potassium hydroxide, the potassium salt of the imide separates as a white precipitate, slightly soluble in cold strong alcohol easily soluble in water.

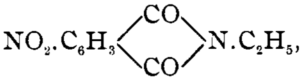


Amide, $NO_2.C_6H_3\left\langle\begin{array}{l}CO.NH_2\\CO.NH_2\end{array}\right.$ —The imide was mixed with strong ammonium hydroxide and dissolved by gentle warming. After standing for an hour at the temperature of the room, a heavy white crystalline precipitate appeared. This precipitate was filtered out, washed with a little cold water, and dried finally *in vacuo* over sulphuric acid. It then melted at 200° with evolution of ammonia, and when remelted, after solidifying, showed the melting-point of the imide (197°).

0.1430 gram substance gave 25.9 cc. nitrogen at 22.5° and 755 mm.

	Calculated for $C_8H_7O_4N_3$.	Found.
Nitrogen	20.1	20.3

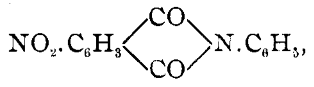
Amic Acid.—Attempts to prepare the aminic acid of the 4,nitro-*o*-phthalic acid by the same process that yielded the aminic acid of the 3,nitro-*o*-phthalic acid have so far been entirely unsatisfactory.



Ethylimide, $NO_2.C_6H_3\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle N.C_2H_5$, is prepared by the action of heat upon the acid ethylamine salt, or by heating the potassium salt of the imide in a sealed tube with ethyl iodide. Pale yellow scales (m. p. 111°–112°) are slightly soluble in hot water, readily in alcohol or ether.

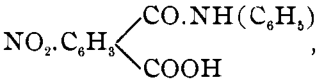
0.1805 gram substance gave 20.6 cc. nitrogen at 23° and 758 mm.

	Calculated for $C_{10}H_8O_4N_2$.	Found.
Nitrogen	12.7	12.83



Anil, $NO_2.C_6H_3\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle N.C_6H_5$, results when the acid aniline salt is heated above its melting-point. It crystallizes from a mixture of alcohol and acetone in yellow needles, melting at

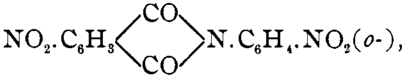
194°. It is moderately soluble in acetone, sparingly in alcohol. Graebe and Buenzod[1] give its melting-point as 192°.



Anilic Acid, $NO_2.C_6H_3<\begin{array}{l}CO.NH(C_6H_5)\\COOH\end{array}$, is prepared by the action of baryta water upon the anil. When the baryta solution is acidified with sulphuric acid the anilic acid precipitates with the barium sulphate, and must be extracted from it with cold alcohol. It forms pale yellow crystals, melting at 181° with formation of the anil. It is easily soluble in cold alcohol, nearly insoluble in ether, and apparently totally insoluble in cold water. Its solutions are acid to litmus but do not decompose carbonates.

0.1955 gram substance gave 17.2 cc. nitrogen at 25° and 761 mm.

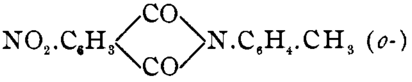
	Calculated for $C_{14}H_{10}O_5N_2$.	Found.
Nitrogen ························	9.8	9.83



o-Nitranil, $NO_2.C_6H_3<\begin{array}{c}CO\\CO\end{array}>N.C_6H_4.NO_2(o\text{-})$, is prepared by the action of heat upon the acid *o*-nitraniline salt. It crystallizes from nitrobenzene in pale yellow needles (m. p. 233°), difficultly soluble in acetone, very slightly in alcohol, and readily in hot nitrobenzene.

m-Nitranil is prepared in a similar manner from the acid *m*-nitraniline salt. It crystallizes from nitrobenzene in opaque yellow needles (m. p. 243°). It is sparingly soluble in alcohol or acetone, but readily in hot nitrobenzene.

p-Nitranil is prepared in a similar manner, crystallizes from nitrobenzene in small yellow crystals, melting at 251°–253°, difficultly soluble in acetone, apparently insoluble in alcohol, but easily soluble in hot nitrobenzene.



o-Tolil, $NO_2.C_6H_3<\begin{array}{c}CO\\CO\end{array}>N.C_6H_4.CH_3$ (*o*-), is obtained by the action of heat upon the acid *o*-toluidine salt, and forms a brownish crystalline powder (m. p. 160°). It is very slightly soluble in alcohol, moderately in acetone.

m-Tolil is prepared in a similar manner from the acid *m*-toluidine salt. Pale brownish crystals (from nitrobenzene, m. p. 197°) are practically insoluble in alcohol, difficultly soluble in acetone, easily in hot nitrobenzene.

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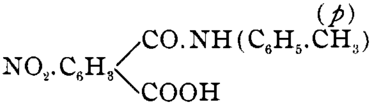
[1] *Loc. cit.*

p-Tolil is produced by heating together *p*-toluidine and 4,nitro-*o*-phthalic anhydride at 180°–190°. It crystallizes from a mixture of alcohol and acetone in yellow pearly flakes, melting at 165°, slightly soluble in alcohol, readily in acetone.

0.1935 gram substance gave 17.5 cc. nitrogen at 22.5° and 751 mm.

	Calculated for $C_{15}H_{10}O_4N_2$.	Found.
Nitrogen	9.93	10.14

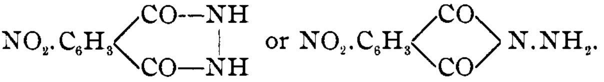
p-Tolilic Acid,



$$NO_2.C_6H_3\left\langle\begin{matrix}CO.NH(C_6H_5.\overset{(p)}{CH_3})\\ COOH\end{matrix}\right.$$

—*p*-Tolil is heated for fifteen minutes on the water-bath with baryta water, and the mixture then allowed to stand twenty-four hours at the room temperature, The flaky crystals of tolil are gradually replaced by long yellow needles of the barium salt of the tolilic acid. Upon the addition of sulphuric acid, the free tolilic acid precipitates with the barium sulphate and may be extracted from it by strong alcohol. On cold evaporation of the alcohol, the tolilic acid remains in white needles, melting at 172° (with formation of the tolil). The tolilic acid is insoluble in ether or cold water, does not decompose carbonates, but reacts acid to litmus.

Hydrazide,



$$NO_2.C_6H_3\left\langle\begin{matrix}CO-NH\\ |\\ CO-NH\end{matrix}\right. \text{ or } NO_2.C_6H_3\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle N.NH_2.$$

—A solution of 4,nitro-*o*-phthalic anhydride was treated with one molecule of hydrazine hydrate (in 50 per cent. aqueous solution), and the mixture warmed for several hours. No precipitate formed, but, upon evaporation, a red oil remained, which changed to a yellowish brown precipitate when water was added. This precipitate was boiled down repeatedly with water, and finally washed with water, alcohol, and ether. In warm sodium carbonate solution it dissolved with effervescence, and reprecipitated in pale yellow flocks when the solution was acidified. Recrystallized from water, it forms a microcrystalline powder.

0.1503 gram substance gave 27.4 cc. nitrogen at 24° and 750 mm.

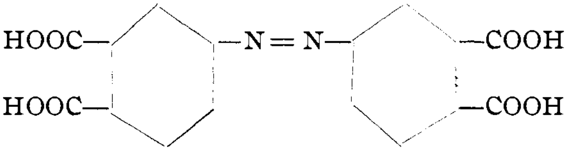
	Calculated for $C_8H_5O_4N_3$.	Found.
Nitrogen	20.3	20.16

4,Nitro-*o*-phthalic acid was dissolved in water, one molecule of hydrazine hydrate added, the liquid evaporated to dryness, and the residue carefully heated. At 150° the mass began to soften and evolve water, but the reaction did not appear completed until the temperature had reached about 250°. Even at this temperature the mass refused to melt, remaining hard and porous. It was purified by solution in sodium carbonate, reprecipitation, etc., as in the foregoing case, and yielded a similar product.

0.1733 gram substance gave 32 cc. nitrogen at 22° and 743 mm.

	Calculated for $C_8H_5O_4N_3$.	Found.
Nitrogen	20.3	20.45

The hydrazide forms small yellow crystals, slightly soluble in water or alcohol, difficultly soluble in glacial acetic acid. When heated to 270° it gives a white sublimate, then darkens at 280°, but does not melt even at 300°. Heated with acetic anhydride for several hours, no definite acetyl derivatives could be obtained.



4,4′,AZOPHTHALIC ACID.

Preparation from 4,Nitro-o-phthalic Acid.—4,Nitro-*o*-phthalic acid was dissolved in dilute caustic soda, and the solution reduced by the gradual addition of 2 per cent. sodium amalgam. After the requisite amount of amalgam had been added, the mixture was heated for an hour upon the water-bath, the red alkaline solution decanted from the mercury, concentrated, and acidified with hydrochloric acid. A yellowish red precipitate appeared, which was filtered off, dried, and crystallized from water. It then formed a salmon-colored crystalline powder, moderately soluble in hot water, slightly in alcohol or glacial acetic acid, and insoluble in ether. It refused to melt at 360°. Its aqueous solution was acid to litmus and decomposed carbonates.

0.2046 gram substance gave 14 cc. nitrogen at 23° and 762 mm.

	Calculated for $C_{16}H_{10}O_8N_2$.	Found.
Nitrogen	7.8	7.73

The compound was unchanged by boiling with glacial acetic acid and sodium nitrite, showing the absence of hydrazo combinations.

The silver salt was prepared by adding a solution of argentic nitrate to the solution of the neutral ammonium salt. It separated as a red precipitate, insoluble in hot water, and when dried to constant weight at 110°, appeared as a heavy red crystalline powder.

0.2039 gram substance yielded, upon ignition, 0.1085 gram silver.

	Calculated for $C_{16}H_6O_8N_2Ag_4$.	Found.
Silver	54.9	53.2

This low result is accounted for by the fact that the silver salt explodes when heated to a certain point, thus rendering the securing of accurate results a matter of considerable difficulty.

Preparation from Azophthalide.—An alkaline solution of 5,5',-azophthalide was oxidized by potassium permanganate in the manner already described for the conversion of nitrophthalide into 4,nitro-*o*-phthalic acid. By acidifying the filtrate from the manganese dioxide with hydrochloric acid, a reddish yellow precipitate separated, which was filtered off and dried. It then melted at 285°–300°, with decomposition, and was crystalline in appearance.

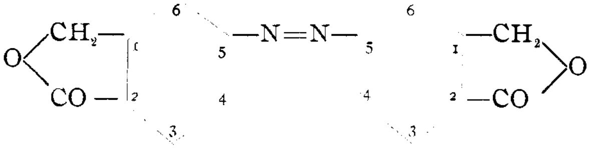
0.1946 gram substance gave 13 cc. nitrogen at 22° and 752 mm.

	Calculated for $C_{16}H_{10}O_8N_2$.	Found.
Nitrogen	7.8	7.8

The silver salt formed a heavy red crystalline powder, somewhat soluble in hot water, and exploded when heated.

It will be noted that the azophthalic acid obtained by this process melts, with decomposition, at a temperature somewhat below 300°, and gives a silver salt which is partly soluble in hot water, while that obtained by reduction of 4,nitrophthalic acid does not melt at 360°, and its silver salt appears to be insoluble in hot water. The cause of this difference has not as yet been determined. It will be made the subject of further investigation.

The corresponding 3,3',azophthalic acid has been prepared by Claus and May[1] by the reduction of the 3,nitro-*o*-phthalic acid with sodium amalgam, and forms golden yellow needles, decomposing at 220°–250°.



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[1] *Ber. d. chem. Ges.*, **11**, 762 (1878) ; **14**, 1330 (1881).

5,5′,Azophthalide.

This was obtained by the action of a 2 per cent. sodium amalgam upon the dilute alkaline solution of *p*-nitrophthalide. Hydrochloric acid is added to the resultant alkaline solution, and the red precipitate obtained is filtered off and dried. From dilute alcohol, it forms small red crystals, melting with decomposition at 260°–280°. It is sparingly soluble in hot water, moderately in hot alcohol or glacial acetic acid.

0.2000 gram substance gave 17.6 cc. nitrogen at 26° and 756 mm.

	Calculated for $C_{16}H_{10}O_4N_2$.	Found.
Nitrogen	9.5	9.6

This work is being continued and other papers upon the subject will be published.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY,
July 1, 1901.

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.[1]

By CHARLES BASKERVILLE.

Received August 15, 1901.

ALMOST five years ago I attempted to separate thorium quantitatively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium[2] and titanium.[3] The separation of thorium by this means was not quantitative. On resolution of the precipitated portion in hydrochloric acid and exact neutralization with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite[4] in the neutral menstruum. This was verified by many repetitions of the process using thorium chloride solutions of different strengths and varying amounts of ammonium chloride.

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[1] Presented at the Denver meeting of the American Chemical Society.

[2] *Chem. News*, **70**, 57 (1894); This Journal, **16**, 475 (1894).

[3] This Journal, **16**, 437 (1894).

[4] These basic sulphites are being investigated at present. It may be well to state that in addition to a flocculent basic sulphite there has been obtained a gelatinous compound, or hydrogele, similar in appearance to the zirconium sulphite described by Venable and Baskerville, this Journal, **17**, 448 (1895).