[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 167.]

ON SOME AMINO AND NITROAMINO DERIVATIVES OF BENZOIC, METATOLUIC AND METAPHTHALIC ACIDS.

BY MARSTON TAYLOR BOGERT AND ALFRED H. KROPFF.[1]

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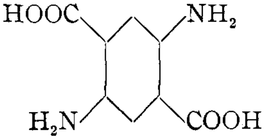
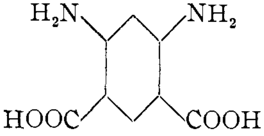
In previous papers from this laboratory,[2] the preparation and properties of *p*-diaminoterephthalic acid and several of its derivatives have been described. The results secured seemed to us of sufficient interest to justify the extension of the investigation to the analogous 4,6-diamino-*m*-phthalic acid. The similarity in the structure of these two acids is seen at once from a glance at their constitutional formulas:



(*p*-Diaminoterephthalic acid)



(4,6-Diamino-*m*-phthalic acid)

As will be noted, both contain the anthranilic acid grouping twice, and there was every reason to expect that the diamino-*m*-phthalic acid would yield ortho condensations as readily as the diamino-*p*-phthalic. This we found to be the case, and the 1,3,7,9-naphthotetrazines and other heterocycles thus produced will be described in a later paper.

The present article deals chiefly with the preparation and properties of the 4,6-diamino-*m*-phthalic acid and its derivatives. Five years ago, Errera and Maltese[3] endeavored to obtain this acid for the purpose of converting it into the corresponding dihydroxy acid and comparing the latter with the resorcinol dicarboxylic acids described in the literature. They first attempted the oxidation of 4,6-dinitro-*m*-xylene, but were unable to oxidize both methyl groups, and obtained only the dinitro-*m*-toluic acid. Turning then to the 4-amino-6-nitro-*m*-xylene (6-nitro-*m*-xylidine), they succeeded in oxidizing its acetyl derivative to the nitro acetamino-*m*-phthalic acid, and from this prepared the 4-amino-6-nitro-*m*-phthalic acid, but on attempting to reduce the latter, or its acetyl derivative, obtained only *m*-phenylenediamine,[4] and apparently abandoned further work in this direction. We have repeated their work and likewise failed to get any diamino-*m*-phthalic acid by the methods they employed.

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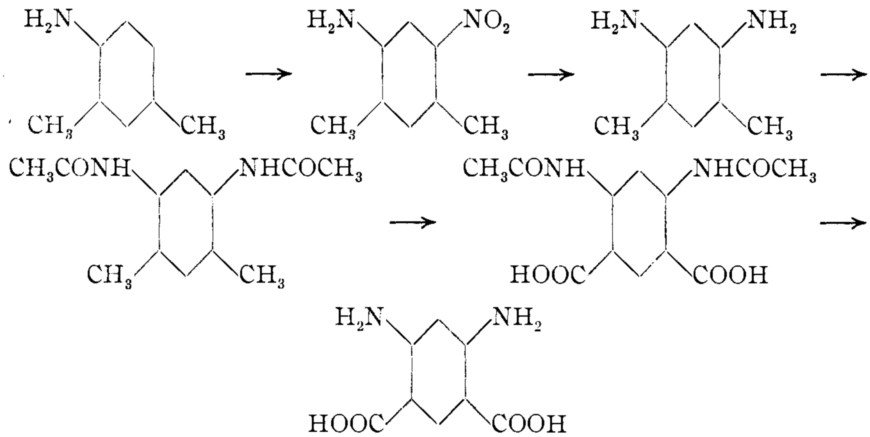
[1] Read at the meeting of the New York Section, March 5, 1909.

[2] Bogert and Dox, THIS JOURNAL, **27**, 1127 and 1302 (1905); Bogert and Nelson, *Ibid.*, **29**, 729 (1907).

[3] *Gazz. chim. ital.*, **33**, II, 277 (1904).

[4] *Ibid.*, **35**, II, 371 and 382 (1905).

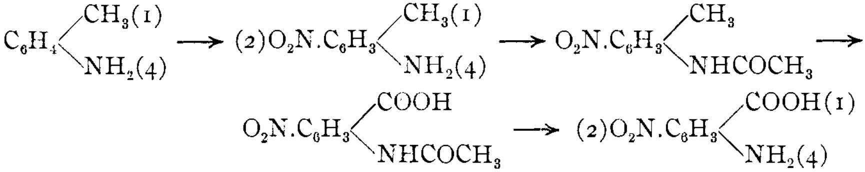
We have, however, prepared the diamino-*m*-phthalic acid from *m*-xylidine, easily and in large yield, by the following steps:



Various salts and esters were produced both from the diamino acid and from its diacetyl derivative, as well as the double acetanthranil (or *bis*-acetanthranil). The diformamino-, diphenyluramino-, and diphthalimido acids were also prepared.

As a by-product in this process, the diacetamino-*m*-toluic acid was isolated, and from it various derivatives were obtained and studied, including its acetanthranil.

The 4-amino-6-nitro-*m*-phthalic acid obtained in repeating the work of Errera and Maltese[1] was also found to yield an acetanthranil when heated with acetic anhydride. This aminonitro-*m*-phthalic acid loses one of its carboxyls quite readily, giving a mixture of 2-amino-4-nitro- and 4-amino-2-nitrobenzoic acids. As, at the time this investigation was in progress, the latter acid had not been described in the literature, we prepared it also from *p*-toluidine as follows:



$$C_6H_4\left\langle\begin{matrix}CH_3(1)\\NH_2(4)\end{matrix}\right. \longrightarrow (2)O_2N.C_6H_3\left\langle\begin{matrix}CH_3(1)\\NH_2(4)\end{matrix}\right. \longrightarrow O_2N.C_6H_3\left\langle\begin{matrix}CH_3\\NHCOCH_3\end{matrix}\right. \longrightarrow$$

$$O_2N.C_6H_3\left\langle\begin{matrix}COOH\\NHCOCH_3\end{matrix}\right. \longrightarrow (2)O_2N.C_6H_3\left\langle\begin{matrix}COOH(1)\\NH_2(4)\end{matrix}\right.$$

Since the completion of this part of the work, the Farbwerke vorm. Meister Lucius & Brüning have been granted a patent[2] for the production of this acid by partial reduction of 2,4-dinitrobenzoic acid. The acid and some of its derivatives are described in the following pages. No attempt

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[1] *Loc. cit.*

[2] D. R. P. 204884, *Chem. Zentralbl.*, 1909, I, 474.

was made to reduce it to the diaminobenzoic acid, as the latter is very unstable and can be more conveniently made by other methods.[1]

Experimental.

4-Amino-6-nitro-*m*-xylene, $(1,3)(CH_3)_2C_6H_2(NH_2)(4)(NO_2)(6)$, was prepared by nitrating 4-amino-*m*-xylene as described by Nölting and Collin.[2] It forms red prisms, m. p. 123°. Reduced with tin and hydrochloric acid,[3] the corresponding xylylene diamine (m. p. 105–105.5°) was obtained. In this reduction, after the removal of the tin as sulphide, the solution was concentrated, an equal volume of concentrated hydrochloric acid added, and the solution well cooled. The hydrochloride of the diamine crystallized out. It was dissolved in a small amount of water, and the base liberated by careful addition of ammonia. As there is some loss involved in this last step, the hydrochloride was generally used, instead of the free base, for the next step. By heating this hydrochloride with slightly more than the calculated amount of fused sodium acetate and excess of acetic anhydride, the diacetamino-*m*-xylene was secured. Morgan[4] gives its melting-point as "over 260°." Our product melted at 295.2° (corr.).

This diacetamino-*m*-xylene crystallizes well from glacial acetic acid. It is less readily soluble in alcohol. Another method by which it can be conveniently prepared is as follows: An aqueous solution of *m*-xylylene diamine hydrochloride (not too dilute) is made slightly alkaline with potassium hydroxide, then slightly acid with acetic acid. On adding to this slightly more than the calculated amount of acetic anhydride, considerable heat is developed, and on cooling the diacetamino-*m*-xylene crystallizes out. On concentrating the mother liquor and adding more acetic anhydride, another crop of crystals is secured. When this diacetamino compound is boiled with concentrated hydrochloric acid, the acetyl groups are split off and *m*-xylylene diamine hydrochloride obtained.

4,6-Diacetamino-1,3-phthalic acid, $(4,6)(CH_3CONH)_2C_6H_2(COOH)_2(1,3)$.—When the diacetamino-*m*-xylene was oxidized with potassium permanganate, in presence of magnesium sulphate, this acid resulted. From 250 grams *m*-xylidine, 130 grams pure diacetamino acid were obtained. The acid crystallizes from alcohol in fine, long, colorless needles, melting with decomposition at 276.2° (corr.).

Found: N, 9.87 and 10.12. Calculated for $C_{12}H_{12}O_6N_2$: N, 10.0.

It is practically insoluble in cold water, slightly soluble in hot; almost insoluble in ether, chloroform or benzene, moderately soluble in glacial acetic acid, less soluble in alcohol.

Dimethyl 4,6-diacetamino-1,3-phthalate, prepared from dimethyl 4,6-diamino-1,3-phthalate, crystallizes from methyl alcohol in colorless needles, m. p. 256° (corr.).

Found: N, 9.22. Calculated for $C_{14}H_{16}O_6N_2$: N, 9.09.

Diethyl 4,6-diacetamino-1,3-phthalate, prepared in similar manner, from the diamino ester and acetic anhydride, crystallizes from dilute alcohol in faintly yellowish, transparent needles, m. p. 230.4° (corr.).

Found: N, 8.56. Calculated for $C_{16}H_{20}O_6N_2$: N, 8.33.

It is insoluble in water, but easily soluble in alcohol or benzene. Its alcoholic solution shows a greenish fluorescence.

4,6-Diamino-1,3-phthalic Acid Hydrochloride.—Upon boiling the diacetamino acid for some time with concentrated hydrochloric acid, it suddenly dissolved and almost immediately yellow, transparent needles separated, m. p. 229–230° (corr.), which

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[1] Ullmann and Uzbachian, *Ber.*, **36**, 1803 (1903).

[2] *Ibid.*, **17**, 265 (1884).

[3] Witt, *Ibid.*, **21**, 2419 (1888).

[4] *J. Chem. Soc.* (London), **81**, 93 (1902).

proved to be the hydrochloride of the diamino acid. This hydrochloride is apparently insoluble in cold concentrated hydrochloric acid. Water hydrolyzes it to the free diamino acid.

4,6-Diamino-1,3-phthalic Acid, $(4,6)(NH_2)_2C_6H_2(COOH)_2(1,3)$.—The above hydrochloride was dissolved in dilute caustic alkali, the solution filtered, and the filtrate acidified with acetic acid. The diamino acid separated as a voluminous pink precipitate. It was purified by re-dissolving in alkali and re-precipitating with acetic acid. When dry, it formed a pinkish powder, m. p. 235° (corr.).

Found: C, 49.13; H, 4.4; N, 14.4. Calculated for $C_8H_8O_4N_2$: C, 48.99; H, 4.1; N, 14.28.

The acid is practically insoluble in all the ordinary neutral solvents, and is very unreactive. Its alkaline solutions are somewhat fluorescent. It exhibits triboelectric properties. With nitrous acid, colored compounds resulted, probably analogous to Bismarck brown. Boiled with excess of acetic anhydride, it gradually dissolved with formation first of the diacetamino acid and then of the bis-acetanthranil. Boiling glacial formic acid gradually dissolves it with production of the diformyl derivative.

Diethyl 4,6-Diamino-1,3-phthalate, $(4,6)(NH_2)_2C_6H_2(COOC_2H_5)_2(1,3)$.—In the preparation of this ester, the diacetyl acid was used instead of the free diamino acid, as the latter on esterification generally lost more or less CO_2. When the diacetamino *m*-phthalic acid was dissolved in a large amount of absolute alcohol and hydrochloric acid gas passed in, the hydrochloride of the diamino ester gradually (in three or four hours) separated. This was filtered out, the filtrate evaporated to dryness under diminished pressure, and the residue combined with the ester hydrochloride which was filtered out. This was treated with water, and sodium carbonate added to alkaline reaction, to dissolve any diaminophthalic acid or ester acids. The undissolved neutral ester was filtered out, washed with water, and crystallized from dilute alcohol. It was thus obtained in long, yellowish needles, m. p. 171.5° (corr.).

Found: N, 11.34. Calculated for $C_{12}H_{16}O_4N_2$: N, 11.11.

The ester is easily soluble in methyl or ethyl alcohol, and dissolves also in benzene or toluene, but is apparently insoluble in water, chloroform or ligroin. Its alcoholic solution shows a greenish fluorescence. Boiled with dilute potassium hydroxide solution, it gives the diamino acid again. Like the corresponding ester of 2,5-diamino-1,4-phthalic acid, it is apparently dimorphic, as in one case we obtained it in red crystals of the same m. p. as the yellow form.

Hydrochloride of the Ethyl Ester.—This precipitates in minute, shining, faintly yellowish needles, m. p. 245.4° (corr.), when dry hydrogen chloride is passed through an absolute alcohol solution of the ester. It is insoluble in concentrated hydrochloric acid or in absolute alcohol, and is partially hydrolyzed by water.

Monethyl Ester of 4,6-diamino-1,3-phthalic Acid, $(NH_2)_2C_6H_2(COOH)(COOC_2H_5)$.—As noted above, in the preparation of the neutral ester, the latter was purified by treatment with sodium carbonate solution. On acidifying this alkaline solution with acetic acid, a yellow amorphous precipitate separated, composed of the diamino acid and its acid ethyl ester. By extraction with boiling alcohol, and crystallization from the same solvent, the acid ester was obtained in short, flat, reddish-yellow prisms, melting with decomposition at 211.6° (corr.).

Found: N, 12.65. Calculated for $C_{10}H_{12}O_4N_2$: N, 12.5.

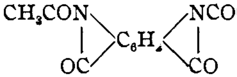
Although the neutral ester was prepared many times, this acid ester was found in but one case. It is easily soluble in alcohol. In caustic or carbonated alkalies, it dissolves, and is reprecipitated from such solutions by acetic or hydrochloric acid.

Dimethyl 4,6-diamino-1,3-phthalate, prepared in much the same way as the diethyl ester, crystallizes from dilute methyl alcohol in beautiful reddish needles, m. p. 204.6° (corr.). Esterification of the silver salt of the free diamino acid with methyl iodide, or of the potassium salt with dimethyl sulphate, proved unsatisfactory.

Found: N, 12.64. Calculated for $C_{10}H_{12}O_4N_2$: N, 12.5.

The alcoholic solutions of the ester show a greenish fluorescence. Its *hydrochloride* forms colorless, shining needles, melting with decomposition at 235.5° (corr.).

4,6-Diacetamino-1,3-phthalic Acid Di-lactam (*m-Bis-acetanthranil*),



.—On boiling the diamino-*m*-phthalic acid for some time with excess of acetic anhydride, it gradually dissolved, and on cooling colorless needles separated. These needles were washed with acetic anhydride, then with gasoline, dried and analyzed.

Found: N, 11.6. Calculated for $C_{12}H_8O_4N_2$: N, 11.47.

The pure substance melts at 282.3° (corr.). The same product resulted when the di-acetaminophthalic acid was boiled with excess of acetic anhydride. Boiling with water or alcohol hydrolyzes it to the diacetamino acid again. From acetic anhydride, or dry ethyl acetate, it can be re-crystallized unaltered. As it is structurally a *bis*-acetanthranil, we shall, for convenience, refer to it in the following pages as the "*bis*-acetanthranil." With ammonia or primary amines, it generally yields 1,3,7,9-naphthotetrazines. In some cases, the intermediate amide is obtained, as in the following.

4,6-Diacetamino-1,3-phthalisoamylamide, $(4,6)(CH_3CONH)_2C_6H_2(CONHC_5H_{11})_2(1,3)$.—When diethyl diacetamino *m*-phthalate was heated with isoamylamine and the clear solution concentrated, a colorless compound separated on cooling. Re-crystallized from dilute alcohol, this gave long, colorless, silky needles, m. p. 189.6° (corr.).

Found: N, 13.6. Calculated for $C_{22}H_{34}O_4N_4$: N, 13.4.

It is very difficultly soluble in water, but dissolves in alcohol or benzene. Boiling with solutions of caustic alkalies, apparently does not change this amide to the corresponding naphthotetrazine. The same amide resulted when the *bis*-acetanthranil was heated with isoamylamine.

4,6-Diformamino-1,3-phthalic Acid, $(HCONH)_2C_6H_2(COOH)_2$.—When the diamino-*m*-phthalic acid was boiled for several hours with a large excess of glacial formic acid, it gradually dissolved, and on cooling yellowish, minute needles crystallized out. Another crop of crystals (less pure) was obtained by concentrating the mother-liquor. The crystals were washed with glacial formic acid and with water, and re-crystallized from glacial formic acid.

Found: N, 11.27. Calculated for $C_{10}H_8O_6N_2$: N, 11.11.

The pure substance is colorless and microcrystalline. It melts above 360°, and is insoluble in water, but dissolves in alcohol. It is best crystallized from glacial formic acid. It dissolves in caustic or carbonated alkalies and is reprecipitated in an amorphous condition when such solutions are acidified with acetic or hydrochloric acid. Boiled with acetic anhydride, the formyl groups are displaced and the *bis*-acetanthranil results. When its ammonium salt is heated for an hour at 200°, decomposition occurs, apparently without formation of any naphthotetrazine.

Diethyl 4,6-Diphenyluramino-1,3-phthalate, $(4,6)(C_6H_5NHCONH)_2C_6H_2(COOC_2H_5)_2(1,3)$.—Diethyl diamino-*m*-phthalate and the calculated amount of phenyl isocyanate were dissolved in dry benzene and the solution boiled for an hour and a half. On cooling, colorless needles separated, which were washed with dry benzene, then with hot alcohol, and dried at 110°. An excess of isocyanate does not alter the result. Any carbanilide is readily eliminated through its solubility in alcohol.

Found: N, 11.7. Calculated for $C_{26}H_{26}O_6N_4$: N, 11.47.

The pure compound melts at 256.8° (corr.), and is triboelectric. It is practically insoluble, or very difficultly soluble, in water, alcohol, benzene, carbon tetrachloride or ethyl acetate. When boiled with excess of acetic anhydride, diethyl diacetamino-*m*-phthalate is produced. The 2,5-diphenyluramino-1,4-phthalate, when similarly treated, gives a tetracetyl derivative of diamino terephthalic acid.[1]

Diethyl 4,6-Diphthalimido-1,3-phthalate, $(C_6H_4(CO)_2N)_2C_6H_2(COOC_2H_5)_2$.—Diethyl diamino-*m*-phthalate was fused with excess of phthalic anhydride and the reddish melt when cold extracted repeatedly with boiling alcohol. There remained a cream-colored crystalline substance, melting at 251.8° (corr.).

Found: N, 5.71. Calculated for $C_{28}H_{20}O_8N_4$: N, 5.47.

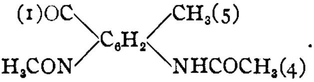
It is very slightly soluble in hot benzene, still less so in toluene or chloroform, and no satisfactory crystallizing medium was found.

4,6-Diacetamino-m-toluic Acid, $(4,6)(CH_3CONH)_2C_6H_2(CH_3)(1)COOH(3)$, was encountered as an occasional by-product in the oxidation of diacetamino-*m*-xylene to diacetamino-*m*-phthalic acid. As it is much more soluble than the phthalic acid, it was found in the mother-liquors from the latter.

Found: N, 11.3. Calculated for $C_{12}H_{14}O_4N_2$: N, 11.2.

Small, glassy, colorless needles (from water), m. p. 272.4° (corr.), difficultly soluble in water, soluble in alcohol or in dilute acetic acid; easily soluble in solutions of caustic or carbonated alkalies, and reprecipitated from such solutions in crystalline form on acidification with hydrochloric acid.

5-Methyl-4-acetaminoacetanthranil,



$$\begin{matrix}(1)\mathrm{OC} & & \mathrm{CH_3}(5)\\ & \mathrm{C_6H_2} & \\ (2)\mathrm{CH_3CON} & & \mathrm{NHCOCH_3}(4)\end{matrix}$$

.—This anthranil was obtained by boiling the above acetamino acid for fifteen minutes with excess of acetic anhydride. On strong concentration of the solution, it separated as a yellowish, crystalline compound which, on recrystallization from acetic anhydride, appeared in nearly colorless, small needles, m. p. 166.2° (corr.). These crystals carry half a molecule of acetic acid, which is not driven out at 120°.

Found: C, 59.6; H, 5.2; N, 10.8. Calculated for $2C_{12}H_{12}O_3N_2 + CH_3COOH$: C, 59.5; H, 5.3; N, 10.7.

It is hydrolyzed to the corresponding diacetamino-*m*-toluic acid when boiled with water or with alcohol. It can be crystallized from dry ethyl acetate. With ammonia, and with primary amines, it condenses to quinazolines.

4-Acetamino-6-nitro-1,3-phthalic Acid, $(4)CH_3CONH(6)(NO_2)C_6H_2(COOH)_2(1,3)$.—6-Nitro-4-amino-*m*-xylene was acetylated and the product oxidized by potassium permanganate, essentially as described by Errera and Maltese,[2] except that we used magnesium sulphate to maintain the neutrality of the solution. The acid forms opaque, nearly colorless, needles, melting with decomposition at 264°. It is very difficultly soluble in water or benzene, but can be crystallized from alcohol or glacial acetic acid. Saponified with 3 per cent. sulphuric acid, the amino-nitro-*m*-phthalic acid results, but if alkali, or 50 per cent. sulphuric acid be used, carbon dioxide is eliminated, and a mixture of 2-nitro-4-amino- and 2-amino-4-nitro-benzoic acids is obtained.

4-Amino-6-nitro-1,3-phthalic acid was prepared also by Errera and Maltese,[3] by saponifying the above acetyl derivative. It is a yellowish, crystalline compound, melting with decomposition at about 280°; difficultly soluble in water, and can be crystallized from dilute acetic acid. Errera and Maltese attempted in vain to reduce this nitroamino acid to the diamino acid. We also failed to accomplish the reduction.

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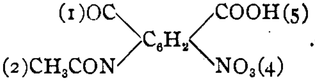
[1] Bogert and Nelson, THIS JOURNAL, 29, 729 (1907).

[2] *Gazz. chim. ital.*, 33, II, 286 (1903).

[3] *Loc. cit.*

Boiling this acid with concentrated mineral acids, tends to split out carbon dioxide and give the two nitroaminobenzoic acids noted above.

4-Nitroacetanthranil-5-carboxylic Acid,  $\begin{matrix}(1)OC\\(2)CH_3CON\end{matrix}\!\!>\!C_6H_2\!<\!\!\begin{matrix}COOH(5)\\NO_3(4)\end{matrix}$.—4-Amino-6-nitro-*m*-phthalic acid, or its acetyl derivative, was boiled for two hours with excess of acetic anhydride, and the solution concentrated. On cooling, yellowish crystals separated, which were washed with acetic anhydride, then with carbon tetrachloride, dried at 110° and analyzed.

Found: N, 11.23. Calculated for $C_{10}H_6O_6N_2$: N, 11.2.

This anthranil melts at 274.4° (corr.). Boiled with water, or with alcohol, the nitroacetaminophthalic acid is regenerated. It can be crystallized from acetic anhydride or dry ethyl acetate.

As already stated, 4-amino-6-nitro-*m*-phthalic acid loses carbon dioxide quite easily when heated with 50 per cent. sulphuric acid, giving a mixture of the two nitroaminobenzoic acids. Of the latter, the 2-amino-4-nitro acid is the less soluble in acetic acid, and a partial separation can be accomplished by crystallizing from this solvent. Some difficulty was encountered in getting a pure 2-nitro-4-amino acid from the mother-liquors of the 2-amino-4-nitro acid, so we prepared it from *p*-toluidine by the steps noted in the introductory portion of this paper.

p-Toluidine was nitrated by the method of Nölting and Collin,[1] the yield of pure 2-nitro-4-toluidine being nearly theoretical.

2-Nitro-4-acettoluidide, as prepared by the action of acetic anhydride upon 2-nitro-4-toluidine, crystallizes from dilute alcohol in yellowish crystals, m. p. 148.5° (corr.). Cunerth[2] gives the m. p. as 160°, while Wallach[3] gives it as 144.5°.

Found: N, 14.51. Calculated for $C_9H_{10}O_3N_2$: N, 14.45.

2-Nitro-4-acetaminobenzoic Acid.—The 2-nitro-*p*-acettoluidide was oxidized with potassium permanganate in presence of magnesium sulphate, the oxidation being completed in about two hours. The solution was filtered, strongly concentrated, allowed to cool, any of the unoxidized material filtered out, and the filtrate acidified with hydrochloric acid. The precipitated 2-nitro-4-acetaminobenzoic acid crystallized from alcohol in small, pale-yellow needles, m. p. 219° (corr.).

Found: N, 12.31. Calculated for $C_9H_8O_5N_2$: N, 12.5.

Dilute sulphuric acid, or, better, a 10 per cent. solution of potassium hydroxide, breaks off the acetyl group, giving the free *2-nitro-4-aminobenzoic acid,* which crystallizes from dilute acetic acid in bronze scales, m. p. 239.5° (corr.); slightly soluble in cold water, more readily in hot, easily soluble in glacial acetic acid or in alcohol. It possesses a very sweet taste.

Found: C, 46.3; H, 3.48; N, 15.5. Calculated for $C_9H_6O_4N_2$: C, 46.15; H, 3.29; N, 15.38.

As noted in the introductory part of this paper, a patent (D. R. P. No. 204,884) has recently been taken out for this acid by the Farbwerke vorm. Meister Lucius & Brüning, the method of preparation being the partial reduction of the 2,4-dinitrobenzoic acid.

On concentrating the mother-liquors from the recrystallization of ethyl diamino-*m*-phthalate and adding water, a dark red substance separated, melting roughly at about 102°. It was boiled with acetic anhydride, then water was added and the boiling continued for a short time longer. On cooling, pale yellow crystals separated which,

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[1] *Ber.*, **17**, 263 (1884).

[2] *Ann.*, **172**, 229.

[3] *Ibid.*, **234**, 354.

on recrystallization from water, melted at 189.4° (corr.). This compound is soluble also in alcohol or benzene.

Found: N, 10.9. Calculated for $C_{13}H_{16}O_4N_2$: N, 10.6.

The crystals have not been further examined, as only a small amount was obtained, but we believe them to be the *ethyl 2,4-diacetaminobenzoate*, $(CH_3CONH)_2C_6H_3COOC_2H_5$. If this assumption is correct, the dark-colored product (m. p. 102°) which first separated was probably the impure ethyl 2,4-diaminobenzoate. The free diaminobenzoic acid (m. p. about 140°) and its diacetyl derivative (m. p. 261°) have been described by Ullmann and Uzbachian.[1] The free acid is unstable.

NOTE.

The Action of Nitric Acid on Triphenylmethane.[2]—E. and O. Fischer[3] have shown that trinitrotriphenylmethane can readily be prepared by the action of strong nitric acid (sp. gr. 1.5) upon triphenylmethane, calling attention to the fact, however, that the best yield is obtained by slowly adding the finely ground substance to an excess of strong acid at a low temperature. In an attempt to repeat this work, E. S. Smith[4] obtained a white crystalline product closely resembling triphenylcarbinol. This substance had a melting point of 161° (uncorr.), did not contain nitrogen, and on combustion gave figures for carbon and hydrogen similar to those calculated for triphenylcarbinol (m. p. 159° corr.). In this test dilute acid (sp. gr. 1.34) was poured upon the triphenylmethane, some fuming nitric acid added, and the mixture finally heated on a water bath.

As Smith, however, was unable to duplicate his results, a number of experiments were undertaken by the writer to determine the conditions leading to the formation of the carbinol, and those giving the trinitrotriphenylmethane as a product.

For these tests a sample of triphenylmethane was recrystallized from alcohol until it was pure white and melted sharply at 92° (corr.). The acids used were:

I. Baker's brown fuming nitric acid, sp. gr.	1.58
II. Baker's yellow fuming " " " "	1.505
III.[5] A red fuming nitric acid, " "	1.48

The experiments are divided into two series. In the first, following the work of the Fischers, five grams of finely ground triphenylmethane were added in small portions to amounts of acids I, II, or III varying between 25 cc. and 60 cc., the temperature being kept at 0° by carrying on the reaction in a freezing mixture. When the triphenylmethane

[1] *Ber.*, 36, 1802 (1903).

[2] Read before the New York Section, April 9, 1909.

[3] *Ann.*, 194, 254.

[4] *Am. Chem. J.*, 19, 702.

[5] This was an old sample which had been standing in the laboratory and was rather dark from nitrogen peroxide.