STUDIES IN NITRATION, IV.[1] NITRATION OF *N*-ACYL COMPOUNDS OF ANILINE DERIVED FROM CERTAIN POLYBASIC, ALIPHATIC AND AROMATIC ACIDS.

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In the present paper we describe our work on the nitration of anilides of various aliphatic and aromatic polybasic acids. Our experiments have been carried out under the same general conditions as those described previously.[2] Unless otherwise stated we used, with each molecule of the aniline compound, 1.25 molecules of nitric acid and 4 molecules of glacial acetic, anhydrous oxalic, trichloracetic, or sulphuric acid, respectively. The nitric acid had sp. gr. = 1.46 and contained 80 per cent. of HNO_3; the sulphuric acid had sp. gr. = 1.83 and contained about 92 per cent. of H_2SO_4. For convenience of reference the experiments are numbered consecutively with those in our earlier papers.[3] A list of the aniline compounds which we have employed has been given previously.[3] A general discussion of our results is given on page 1594 in the present communication.

Experimental.

III. Derivatives of Dibasic Acids.

1. *Experiments with Oxanilic Acid* (Nos. 98–102).—The ortho-[4] and paranitro[5] derivatives of this compound are known and L. Weiss[6] has prepared the ethyl ester of the meta isomer.

98. *Oxanilic Acid, Nitric Acid (excess over 1.25 mols.) and Oxalic Acid.* Oxanilic and oxalic acids were ground together and added gradually to a large excess of nitric acid. On pouring into water, a yellowish white precipitate came down. This was filtered off and boiled with water, from which, on cooling, yellow crystals of *p*-nitroxanilic acid were deposited, melting at 209–210°. *p*-Nitroxanilic acid is soluble with difficulty in cold water but more easily in hot; it is soluble also in alcohol.

99. *The direct nitration of oxanilic acid* yields *p*-nitroxanilic acid.[7]

100. *Oxanilic Acid, Nitric Acid and Sulphuric Acid (excess over 4 mols.).* The oxanilic acid was dissolved in sulphuric acid, and nitric acid added gradually. After standing for a time, the reaction product was poured into water and an orange-red precipitate came down. This dissolved completely in boiling water, from which, on cooling, a yellow, amorphous compound separated out. It melted at 123–126°.

101. *Oxanilic Acid, Nitric Acid, and Acetic Acid (excess over 4 mols.).* Oxanilic acid was dissolved in a large excess of acetic acid. After the addition of the nitric acid the

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[1] Previous papers have appeared as follows: Bishop Tingle and Blanck, *Am. Chem. J.*, **36**, 607 (1906); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 822; Bishop Tingle and Blanck, *Ibid.*, **30**, 1395 (1908).

[2] THIS JOURNAL, **30**, 1395 (1908).

[3] *Loc. cit.*

[4] *Ann.*, **209**, 367; *Ber.*, **18**, 2937.

[5] *Ibid.*, **18**, 2936.

[6] *N. Handw. d. Chemie* (Beilstein), **4**, 265.

[7] *Ber.*, **18**, 2936.

liquid was allowed to stand and, on pouring into water, a brown precipitate was obtained. This dissolved in boiling water, except for a small amount of tarry matter. Brownish crystals, melting at 145–150°, separated from the aqueous liquid.

102. *Oxanilic acid, Nitric Acid and Trichloracetic Acid.* Oxanilic acid and trichloracetic acid were ground together, and the mixture added to nitric acid, at the room temperature. On each addition of the mixture there was a reddening of the nitric acid, which, after being stirred, became yellow again. The reaction product was poured into water and gave a heavy, flocculent, yellowish-white precipitate.

2. *Experiments with Oxanilide* (Nos. 103–107).—Of the mononitro derivatives of this compound, only the meta isomer[1] appears to have been prepared. No unsymmetrical dinitro compounds are known, but descriptions of the ortho-,[2] meta-,[3] and parasymmetrical[4] dinitroanilides are to be found in the literature.

3. *Oxanilide, Nitric Acid (2.5 mols.) and Sulphuric Acid.*—Oxanilide was dissolved in sulphuric acid, and nitric acid added drop by drop, the liquid being well cooled. On pouring the reaction-product into water, filtering and drying, a yellowish-white powder was obtained. It was evidently a meta isomer because, when hydrolyzed, it gave *m*-nitraniline, m. p. 109–113°.

104. *Nitration of oxanilide in the presence of acetic acid* yields *p*-dinitroxanilide.[5]

105. *Oxanilide, Nitric Acid (2.5 mols.) and Trichloracetic Acid.* The materials were mixed in the usual manner, allowed to stand, then heated on the water bath for an hour and finally allowed to remain at the room temperature for several days. On pouring into water, a yellow precipitate came down. Glacial acetic acid extracted from this a white powder melting at 235–237°.

106. *Oxanilide and Nitric Acid (large excess over 2.5 mols.).* The anilide was added to the nitric acid at the room temperature. After standing for a few minutes, the whole mass solidified, the temperature rose, and nitrogen peroxide was evolved. After remaining over-night it was poured into water, which precipitated a yellow compound. This was filtered off, dried and extracted with glacial acetic acid. From this solution, a white powder separated m. p. 232–240°.

107. *Oxanilide, Nitric Acid (excess over 2.5 mols.) and Oxalic Acid.* The anilide and oxalic acid were ground together and added to the nitric acid at the room temperature. In a few minutes the mass solidified, the temperature rose and nitrogen peroxide was evolved. After standing over-night, water was added to the mixture, and a yellow precipitate separated.

3. *Experiments with Succinanilic Acid* (Nos. 108–112).—The ortho-,[6] meta-,[7] and paranitro[8] derivatives of this compound have all been prepared.

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[1] *Bull. soc. chim.*, **81**, 1569; *Zentr.*, **1903**, I, 157.

[2] *Ann.*, **209**, 369.

[3] *N. Handw. d. Chem.* (Beilstein), **4**, 956.

[4] *Ann.*, **209**, 366; *Ber.*, **8**, 473.

[5] *Ann.*, **209**, 366.

[6] *Ann.*, **292**, 190; **327**, 54; *Zentralbl.*, **1903**, I, 1336.

[7] *Ann.*, **327**, 54.

[8] *Ibid.*, **292**, 191; **327**, 55; *Zentralbl.*, **1903**, I, 1336.

108. *Succinanilic Acid, Nitric Acid and Sulphuric Acid (excess over 4 mols.).* Succinanilic acid was dissolved in sulphuric acid on the water bath and then nitric acid added, the mixture being well cooled. After standing for several hours, the reaction product was poured into water, which gave a yellow precipitate. This was filtered off, dried and then extracted with hot water. On cooling, an orange-yellow compound melting at 149–164° was deposited. When hydrolyzed, it yielded *m*-nitraniline, m. p. 112–114°.

109. *Succinanilic Acid, Nitric Acid and Acetic Acid (excess over 4 mols.).* Succinanilic acid was dissolved in an excess of hot acetic acid, and nitric acid added to the solution, at the room temperature. After standing for twenty-four hours, the reaction mixture was colored brownish-red, and a brownish-yellow precipitate was obtained on pouring it into water. The crude nitration product was dissolved in boiling water, from which brown needles separated on cooling; they melted at 153–154.5°.

110. *Succinanilic Acid, Nitric Acid (excess over 1.25 mols.) and Oxalic Acid.* Succinanilic acid and oxalic acid were ground together and then gradually added to a large excess of well cooled nitric acid. If the addition is too rapid decomposition takes place. On standing over-night and pouring into water, a yellow precipitate was obtained. This was filtered off, dried and washed with a little chloroform. The residue, insoluble in chloroform, melted at 196–197° and gave *p*-nitraniline, m. p. 146–147°, on being hydrolyzed with hydrochloric acid. *p*-Nitrosuccinanilic acid is soluble in alcohol. ethyl acetate, chloroform and acetic acid; less soluble in hot water; soluble with difficulty in ether, benzene, and ligroin.

111. *Succinanilic Acid, and Nitric Acid (excess over 1.25 mols.).* Succinanilic acid was added to nitric acid at the room temperature. There was a slight decomposition of the nitric acid, and the whole mass was at once poured into water, giving a yellow precipitate.

112. *Succinanilic Acid, Nitric Acid and Trichloracetic Acid.* Succinanilic acid and trichloracetic acid were ground together, and then nitric acid thoroughly mixed with them at the room temperature. The mixture was poured into water at once and gave a small amount of an orange precipitate, together with some red, tarry matter.

4. *Experiments with Succinanil* (Nos. 113–117).—A number of chemists have investigated the ortho-[1] and para-nitro[2] derivatives of this compound, but the meta isomer does not appear to have been prepared.

113. *By direct nitration of succinanil,* ortho- and paranitrosuccinanil are obtained.[3]

114. *Succinanil. Nitric Acid and Trichloracetic Acid.* Succinanil and trichloracetic acid were ground together, then nitric acid ground with the mixture at the room temperature, and the whole allowed to stand several hours. On pouring into water, a faintly yellow precipitate was obtained, which, after being filtered and dried, melted at 156–158°. Hydrolysis with hydrochloric acid gave no nitraniline.

115. *Succinanil, Nitric Acid (excess over 1.25 mols.) and Oxalic Acid.* Succinanil and oxalic acid were ground together and added to a large excess of nitric acid. The mixture was heated on the water bath for fifteen minutes and then poured into water, when a yellow, flocculent precipitate came down. On boiling this precipitate with water and then cooling, red-brown needles melting at 150–152° were obtained. The residue, insoluble in boiling water, was dissolved in boiling alcohol, from which a

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[1] *Ber.*, **8,** 1225; *Ann.*, **209,** 374; **292,** 191.

[2] *Ber.*, **8,** 1225; **29,** 2679; *Ann.*, **209,** 375; **292,** 191; **327,** 49 *Ann.*; *Zentr.*, **1903,** I, 1336.

[3] *Ann.*, **209,** 374, 375; **292,** 191.

brownish-yellow material deposited. It proved to be p-nitrosuccinanil, m. p. 205–207°. It is insoluble in water, slightly soluble in cold alcohol, soluble with difficulty in chloroform and boiling alcohol, ether and ligroin, but it dissolves easily in hot chloroform.

116. *Succinanil, Nitric Acid and Acetic Acid.* Succinanil was dissolved in acetic acid, nitric acid added, and the mixture heated for several hours on the water bath. On pouring into water, a chocolate-brown precipitate was deposited. Reddish-brown needles, which melted at 154–156°, separated from the filtrate.

117. *Succinanil, Nitric Acid and Sulphuric Acid.* Succinanil was dissolved in sulphuric acid and nitric acid added gradually. On pouring into water, a heavy, yellow, amorphous precipitate came down. This was boiled with water to remove unchanged succinanil. On hydrolyzing the reaction product with hydrochloric acid and neutralizing with sodium carbonate, yellow crystals of p-nitraniline (m. p. 146–148°) were obtained.

5. *Experiments with Succinanilide* (Nos. 118–120).—We have been unable to find a reference of any mononitro derivatives of this compound. The only known dinitro product appears to be the disymmetrical para isomer.[1]

118. *Succinanilide, Nitric Acid and Sulphuric Acid* (*excess over 4 mols.*). Succinanilide was dissolved in sulphuric acid on the water bath, nitric acid was added, and the mixture allowed to stand several days at the room temperature. On pouring into water a small quantity of a yellow-red precipitate was obtained. The crude precipitate was extracted with boiling water, from which a red, tarry compound separated on cooling. It melted at 118–136°.

119. *Succinanilide, Nitric Acid* (*excess over 1.25 mols.*) *and Oxalic Acid.* Succinanilide and oxalic acid were ground together and the mixture added gradually to an excess of cooled nitric acid. After standing for a time, the liquid was poured into water. This gave a reddish-brown precipitate.

120. *The direct nitration of succinanilide* yields succin-p-dinitranilide.[1]

6. *Experiments with Tartranilide* (Nos. 121–125).—We have been unable to find description of any nitro derivative of this compound.

121. *Tartranilide, Nitric Acid* (*2.5 mols.*) *and Sulphuric Acid.* Tartranilide and sulphuric acid were mixed, and nitric acid added to the mixture. On pouring into water, a yellow precipitate came down. It was boiled with water. After filtering and cooling the filtrate, a yellow product was obtained which had an indefinite melting point, but was completely melted at 191°. The portion of the nitration product insoluble in water was boiled with alcohol and filtered. On cooling, the filtrate deposited a white substance which melted at 220–240°. The residue insoluble in alcohol was dissolved in acetone. It crystallized out as a gray powder melting at 258–261°.

122. *Tartranilide, Nitric Acid* (*2.5 mols.*) *and Acetic Acid.* Tartranilide was heated with acetic acid on the water bath, and nitric acid added, after which the mixture was heated on the water bath for six hours. The solution was colored dark-red and there was a yellow, insoluble solid. On pouring into water, a yellowish-brown precipitate was obtained. This precipitate was extracted with boiling water from which a yellow compound separated on cooling. It melted and decomposed at 255–256°. At 230–235° a small amount of volatile matter sublimed from it. The residue, insoluble in boiling water, was extracted with boiling alcohol, from which a flocculent, white powder crystal-

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[1] *Ann.*, **209**, 377.

lized. This melted at 250–256°. The residue insoluble in boiling alcohol consisted of a fine, white powder melting at 269–271°.

123. *Tartranilide, Nitric Acid (excess over 2.5 mols.) and Oxalic Acid.* Tartranilide and oxalic acid were ground together and added gradually to a well-cooled excess of nitric acid. After a few minutes' standing, the reaction product was poured into water, which gave a yellow precipitate. This crude precipitate was extracted with boiling water, from which, on cooling, a fine, yellow compound melting at 181–185°, separated. The residue insoluble in boiling water was then extracted with boiling alcohol, from which also a yellow product crystallized out. It melted at 233–235°. The portion insoluble in boiling alcohol melted at 249–251°.

124. *Tartranilide, Nitric Acid (2.5 mols.) and Trichloracetic Acid.* Tartranilide and trichloracetic acid were ground together, and nitric acid added at the room temperature. After standing several days, the reaction product was poured into water and a brown precipitate separated out.

125. *Tartranilide and Nitric Acid (excess over 2.5 mols.).* Tartranilide was added gradually to an excess of well-cooled nitric acid. After standing a *few* minutes, the reaction product was poured into water, producing a yellow precipitate. On boiling this precipitate with water, filtering. and cooling the solution, yellow crystals, melting at 164–184°, were obtained. The residue insoluble in boiling water was boiled with alcohol, from which a voluminous compound separated on cooling; it melted and decomposed at 218–225°. The residue insoluble in boiling alcohol melted and decomposed at 236–241°. The crude nitration product was hydrolyzed by means of hydrochloric acid; the yellow crystals which separated on neutralizing the hydrochloric acid with sodium carbonate were recrystallized from methyl alcohol. They consisted of *p*-nitraniline, m. p. 144–146°.

IV. Derivatives of Tribasic Acids.

1. *Experiments with Citranilide* (Nos. 126–130).—We have failed to find any record of the preparation of nitro derivatives of this compound.

126.

Nitric and sulphuric acids gave a yellowish-brown precipitate, from which boiling water extracted a yellow, amorphous substance, melting and decomposing at 140–150°. From the residue alcohol dissolved a red tar.

127.

Nitric and acetic acids yielded a pink-white precipitate from which boiling water extracted a yellow tar. Treatment of the residue with alcohol yielded a yellowish-white substance, m. p. 193–195°.

128.

Nitric and oxalic acids gave a yellow precipitate.

129.

Nitric and trichloracetic acids formed a greenish-brown oil solidifying to yellowish-pink mass.

130. *The direct nitration of citranilide* yields trinitrocitranilide.[1]

2. *Experiments with Citrobianil* (Nos. 131–133).—

131.

Nitric acid alone gave lemon-yellow precipitate.

132.

Nitric and sulphuric acids yielded a reddish-orange or flocculent yellow precipitate.

133.

Nitric and oxalic acids gave a yellow precipitate.

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[1] *Ber.*, 21, 666.

C. Aromatic Compounds.

III. Derivatives of Dibasic Acids.

1. *Experiments with Phthalanilic Acid* (Nos. 134–138).—The ortho-,[1] meta-,[1] and paranitranilides[1] of phthalic acid have all been prepared.

134. *Nitric and sulphuric acids* gave a brownish-red precipitate.

135. *Nitric and acetic acids* yielded a greenish precipitate.

136. *Nitric and oxalic acids* formed a yellowish-white crystalline substance.

137. *Nitric and trichloracetic acids* gave a white precipitate.

138. *Nitric acid alone* yielded brownish-red and pale-yellow crystals.

2. *Experiments with Phthalanil* (Nos. 139–143).—The ortho-,[2] meta-,[3] and paranitranils[4] of phthalic acid have all been prepared.

139. *Phthalanil and Nitric Acid (excess over 1.25 mols.).* Phthalanil was added gradually to the nitric acid, a white, powdery precipitate being thrown down. After a few moments' standing, the mixture solidified. It was treated with water, which gave a white compound. This was filtered, dried and extracted with alcohol, from which a flocculent, white substance was deposited. It melted at 183–185°.

The residue insoluble in alcohol was washed, successively, with boiling xylene and boiling acetic acid. The xylene extract, on cooling, gave a white, flocculent compound melting at 256–258°. From the acetic acid separated fine, white crystals melting at 264–266°. The residue, after treatment with the alcohol, xylene and acetic acid, consisted of a fine, white powder melting at 258–260°. The product from the acetic acid solution was identified as being *p*-nitrophthalanil.

140. *Phthalanil, Nitric Acid and Sulphuric Acid (excess over 4 mols.).* Phthalanil was dissolved in an excess of sulphuric acid, and nitric acid added carefully, the liquid being well cooled. After standing over-night, the reaction mixture was poured into water. A yellow precipitate was formed. A hot alcoholic extract of this crude material gave, on cooling, spherical aggregates of small, red crystals which melted and decomposed at 165–175°.

141. *Phthalanil, Nitric Acid (excess over 1.25 mols.) and Oxalic Acid.* Phthalanil and oxalic acid were ground together and added to well-cooled nitric acid. The mixture speedily changed to a white solid. This was poured into water, filtered, dried and washed, successively, with boiling xylene, boiling alcohol and boiling acetic acid. The residue was then dried; it melted at 262–264°, showing that it was the paranitro derivative. The precipitate from the alcoholic extract was colored brownish-yellow, and melted at 152–154°. White crystals melting at 262–265°, were obtained from the acetic acid solution. From the xylene, a white compound, melting at 200–205°, separated.

142. *Phthalanil, Nitric Acid and Acetic Acid (excess over 4 mols.).* Phthalanil was dissolved in acetic acid and nitric acid added at the temperature of the boiling water bath. The mixture was heated until it gave a precipitate on adding a little of it to water. The compound so obtained was yellowish-white; it was extracted with alcohol,

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[1] *Ann.*, **327,** 55; *Zentr.*, **1903,** I, 1336.

[2] *Ber.*, **28,** 1210.

[3] *Ibid.*, **11,** 2261; **27,** 3430; **28,** 941; **28,** 1119.

[4] *Ibid.*, **27,** 3430; **28,** 1119; *Zentralbl.*, **1903,** 1325.

from which a flocculent, white substance, melting at 205–208°, separated. The residue insoluble in alcohol consisted of beautiful, white crystals melting at 205–208°.

143. *Phthalanil, Nitric Acid and Trichloracetic Acid.* Phthalanil and trichloracetic acid were ground together, and the nitric acid added at the room temperature. The reaction mixture was then poured immediately into water. A white precipitate was formed.

Summary of the Results of the Present Paper.

Derivatives of Aliphatic Dibasic Acids.

By direct nitration (Exp. 99) and also in the presence of oxalic acid (Exp. 98), oxanilic acid gave the *paranitro* derivative.

Oxanilide gave the *metanitro* derivative by nitration in the presence of sulphuric acid (Exp. 103) and the *paranitro* derivative by nitration in the presence of acetic acid (Exp. 104). Succinanilic acid, by nitration in the presence of sulphuric acid (Exp. 108), yielded *metanitrosuccinanilic* acid, whereas nitration in the presence of oxalic acid gave the *paranitro* derivative (Exp. 110). Direct nitration of succinanil gave a mixture of *ortho-* and *paranitro* derivatives (Exp. 113). With sulphuric acid (Exp. 117), the *paranitro* derivative was obtained. Oxalic acid nitration of succinanil (Exp. 115) gave the *paranitro* derivative. The symmetrical *paradinitro* derivative of succinanilide was obtained by direct nitration (Exp. 120). Tartranilide gave the *paranitro* derivative by direct nitration (Exp. 125). The products obtained from the remaining nitrations have not, as yet, been identified.

Derivatives of Aromatic Dibasic Acids.

Phthalanil, both by direct nitration (Exp. 139) and by nitration in the presence of oxalic acid (Exp. 141), yields *paranitro*phthalanil. The other nitration products of phthalanil and those of phthalanilic acid have not, hitherto, been identified.

Derivatives of Aliphatic Tribasic Acids.

The direct nitration of citranilide gave a trinitro derivative (Exp. 130). The other new nitration products have not been identified.

For convenience of reference, we have embodied our results in the following table, but we have not included in it the work comprised in the large number of experiments in which we obtained unidentified compounds.

Substance.	Direct nitration.	Nitric and oxalic acids.	Nitric and acetic acids.	Nitric and sulphuric acids.	Nitric and trichloracetic acids.
Methylaniline	..	..	..	*m-*	..
Ethylaniline	..	..	..	*m-* and little *p-*	..
Dimethylaniline	..	*p-*[1]	*p-*	*m-*	..
Diethylaniline	..	..	..	*m-* and *p-*	..
Benzalaniline	Hydrolyzed to benzaldehyde and aniline.				
Formanilide	*p-*	..	..	*p-*	..
Acetanilide	*p-* and *o-*	*p-*	No reaction	*m-*	*p-*

[1] Formed with oxalic, acetic and nitric acids.

Substance.	Direct nitration.	Nitric and oxalic acids.	Nitric and acetic acids.	Nitric and sulphuric acids.	Nitric and trichloracetic acids.
Benzanilide	*o*-, *m*- and *p*-	*p*-[1]	*m*-	*p*-	. .
Oxanilic acid	*p*-	*p*-	. .	. .	. .
Oxanilide	. .	. .	*p*-	*m*-	. .
Succinanilic acid	. .	*p*-	. .	*m*-	. .
Succinanil	*o*- and *p*-	*p*-	. .	*p*-	. .
Succinanilide	*p*-	. .	. .	. .	. .
Tartranilide	*p*-	. .	. .	. .	. .
Citranilide	*m*-	. .	. .	. .	. .
Phthalanil	*p*-	*p*-	. .	. .	. .

It should be pointed out that the products mentioned in the table are the *chief* substances formed during the experiments, but not necessarily the only ones. We have not attempted to detect *traces* of isomers, but, in so far as time has permitted, we have isolated the essential products of the reactions.

General Discussion of Results.

Until the constitution of the numerous new compounds which we have prepared has been worked out more fully, it would be premature to offer any dogmatic statements regarding the influence of the nature of the *N*-substituent on the course of nitration. We desire, however, to consider briefly the question of the influence of the admixed acids. *Direct* nitration, in all cases in which the products were identified, yielded either the *paranitro* derivative or a mixture of *ortho*- and *paranitro* derivatives, except in the case of benzanilide, which also yielded some *metanitro* derivative.

Nitration in the presence of sulphuric acid yields either the *metanitro* derivative exclusively, or a greater percentage of the *meta* product.

Oxalic acid seems to exert no influence on the course of the nitration, because in all cases except, perhaps, succinanil, the products were the same as those obtained from direct nitration. This, as already suggested, is probably due to the sparing solubility of oxalic acid in nitric acid, in consequence of which the active mass of the former was evidently too small for it to exert any appreciable influence. This suggestion is confirmed by the fact that in the case of benzanilide, when the oxalic acid was dissolved in acetic acid, *benzparanitranilide* is produced, whereas acetic acid without the oxalic acid leads to the formation of the *meta* compound, and nitric acid alone yields all three isomers.

The products from the trichloracetic acid nitrations have not, as yet, been identified. Reactions, however, seem to take place even more readily in the presence of this acid than in the case of sulphuric acid. It is hoped to study later the influence of these acids and, possibly, of other substances on the formation of such compounds as nitramines, *i. e.*, to

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[1] Formed with oxalic, acetic and nitric acids.

ascertain whether their presence favors the nitration of the NHRR′ group rather than that of the benzene nucleus. It is quite evident, however, that the nature of the acid which is mixed with the nitric acid exerts a definite directive influence on the *position assumed by the entrant nitro group.*[1]

As will be evident from the foregoing pages, a considerable number of products have been obtained which could not be identified with known compounds because only a rather limited number of *N*-substituted anilines have been prepared. The simplest way that suggested itself was to hydrolyze our new substances with acids or alkalies and purify and isolate the resulting nitraniline or mixture of nitranilines. Concentrated hydrochloric acid, alcoholic hydrochloric acid, aqueous and alcoholic solutions of alkali hydroxides, sulphuric acid, and also barium hydroxide were used as the hydrolyzing agents, the experiments being carried out at the temperature of the boiling water bath. In a few cases, where the hydrolyses were not successful, attempts were made to reduce the substances with tin and hydrochloric acid and also with zinc dust and acetic acid. These experiments were essentially of a preliminary nature and were not completed.

It appears to us desirable to discuss, at this point, two subjects which have naturally been thrust very much on our attention during the progress of our work. The first concerns the correct representation of disubstitution products of benzene; the second, the mechanism of substitution.

The various plane formulae for benzene which have been proposed from time to time need not be referred to further, because benzene, like most other substances, exists in three, and not in one dimension! Of spatial formulae, the variety is not so great, but the fate of the ones brought forward has not been much happier than that of those existing in a single plane. The chief objection to the current formulae, from the point of view of substitution, is that the para positions are shown as being the most widely separated, whereas, as a matter of experimental fact, strongly negative groups take up the meta positions. We know, however, that bodies charged with electricity of the same sign tend to repel one another and that, in general, in chemistry, it is compounds of opposite electrical sign which combine most easily. Consequently, it would be expected that two strongly negative groups would tend to take up positions in the molecule as far apart as possible. The question is, therefore, can a formula for benzene be devised which will have the meta positions further removed from one another in space than are the para positions? To prevent misapprehension, it may be as well to state expressly that the above problem does not contain any suggestion opposed to the substituents in

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[1] Cf. Bishop Tingle and Blanck: *Am. Chem. J.*, 36, 607 (1906).

the meta position being separated by one carbon atom and those in the para by two; that these are the relative positions of the isomers in question is, of course, established by the firmest experimental evidence. This separation by one or two carbon atoms, however, is perfectly compatible with the closer proximity of the substituents in the latter than in the former case.

About two years ago Barlow and Pope[1] brought forward a new spatial conception of benzene, in which they represent its molecule as built up in layers.

According to this "the production of a monosubstitution derivative, C_6H_5X, necessitates the replacement of one hydrogen sphere in each alternate layer . . . . by the substituting group X; the introduction of a second group X to give the derivative $C_6H_4X_2$ may be brought about in two generally distinct ways: the second group X may enter the column in the same layers in which the first group was introduced, leaving the alternate layers still unsubstituted, and in this case a *metadi*-derivative alone will be found; or the second group X may be introduced into the alternate layers, into which the X group did not originally enter, and then an *ortho-* or *paradi*-derivative, or both, will be found. A complete geometrical difference in kind thus exists between the derivative of the 1 : 3-*di*-derivative and that of 1 : 2- and 1 : 4-isomers; this is wholly in harmony with the observed chemical facts."

The results obtained by us are fully and satisfactorily accounted for by this new formula of Barlow and Pope for benzene. Indeed, it may be said of it that, for the first time, a formula has been proposed which can account spatially for the formation, under the influence of *negative* groups, of metadisubstitution products instead of *para* derivatives. Should objections be raised to Barlow and Pope's formula on the ground that it is static, for instance (which we are far from wishing to do), we think that it might be possible to suggest a special formula which would be free from this objection and which would, at the same time, meet the requirements mentioned above. The conception of Barlow and Pope is, however, so valuable on account of its correlation of chemical and crystallographic properties, that it is sincerely to be hoped that it will be found fully adequate for all other purposes.

Turning now to the question of the mechanism of substitution and confining our attention to nitration, we have the well-known fact that dilute nitric acid oxidizes but does not nitrate, the action being essentially reversed in the case of concentrated acid. The former consists, of course, of nitric acid molecules and of the ions H^+ and NO_3^-, whereas these ions are relatively scarce in the highly concentrated acid which, in addition to

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[1] *J. Chem. Soc.*, **89**, 1697 (1906).

molecular nitric acid, contains its *ordinary—not electrolytic*—dissociation products, HO + NO_2. When the equilibrium is disturbed, the dissociated hydroxyl radicles doubtless combine to form water and oxygen. The question thus arises, does nitration occur essentially as the result of the action of —NO_2 radicles, or is it caused by molecular nitric acid? There is some evidence to show that the nitration of acetanilide, for example, is not retarded to any material extent by the presence of carbamide, a result which, we think, is in conflict with the idea that the —NO_2 radicles, or nitrous acid, are the active nitrating agents. We hope to throw further light on this question by the results of some work which is at present in progress.

Accepting, provisionally, the idea that nitration is the result of the action of molecular nitric acid, nitration must be preceded by addition, which might be thought of as taking place, in the case of benzene for instance, in the manner represented by one of the following expressions:

(1) $C_6H_5 - + -H + HNO_3 \longrightarrow ON(OH)_2C_6H_5 \longrightarrow H_2O + C_6H_5NO_2$.

(2) $C_6H_6 + HNO_3 \longrightarrow ON(OH)_2C_6H_5 \longrightarrow H_2O + C_6H_5NO_2$.

For the sake of simplicity the hypothetical intermediate compound is represented as being identical in the two cases; actually, it might not be so.

Of these rival views, we decidedly favor the second, because there is nothing at all strange in the suggestion of the direct combination of two such highly unsaturated molecules as those of benzene and nitric acid.

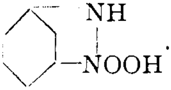
Against the idea represented in the first of the above expressions, that benzene is dissociated into phenyl and hydrogen, a number of considerations may be urged. What is the nature of this dissociation?

Obviously it is not electrolytic, because benzene is not a conductor of electricity. Obviously, also, it is not dissociation in the ordinary sense of the term, as applied to phosphorus pentachloride, for example, because, when boiled, benzene does not evolve hydrogen. The fact that benzene does yield a small proportion of diphenyl and hydrogen when passed through a tube heated to redness cannot be relied on as an argument, because of the difference in the physical conditions prevailing in the cases under consideration. Of course, it may be said that if there is appreciable dissociation at a red heat there must be *some* dissociation, however little, at the ordinary temperature. This statement, even if correct metaphysically, can have no practical importance until it is shown, by experiment, that the dissociation in question actually occurs at the temperature indicated. In other words, it relegates the question to the class occupied by "insoluble" substances, or by compounds which react with infinite slowness: they are of no practical importance so long as life itself is limited.

Finally, it may be pointed out that the recent well-known and brilliant work of Baly and his colleagues on the optical properties of benzene and allied compounds is entirely against there being such a dissociation. If, in spite of these considerations and of others which could be mentioned, the idea of dissociation is still retained for the reaction under consideration, we have a right to ask that it be named and defined, for it is evidently of an entirely new and strange variety.

We are led to make these remarks on account of the fanciful "dissociations" which have been so freely promulgated during the past few years by Professor Nef and his students. They are treated, in the most positive manner, as if actually occurring, although of course, at the best, they are only *possible* or more or less improbable modes of reaction, and a discreet vagueness is maintained as to their precise nature. Fortunately these views have not been taken very seriously by the majority of chemists.

If the considerations advanced in the preceding paragraphs are correct, we are driven to regard substitution as essentially an addition phenomenon, a view which has been discussed at some length by H. E. Armstrong in a series of papers.[1] Without committing ourselves to agreement with the details of his scheme of reactions, parts of which, indeed, are rather vague, yet, in general, we join him in regarding substitution as being preceded by addition.

With regard to the special case of aniline, the question arises, Does this addition occur in the nucleus, as in the nitration of benzene, or is the substituted amino group the point of attack? We believe that our experiments with aniline and nitric acid furnish ground for at least a tentative answer to this question. In these experiments, aniline nitrate is first formed; excess of concentrated nitric acid changes this into a colored, unstable compound which is reconverted into the nitrate on the addition of water. Here, then, the amino group is attacked first and, apparently, the next stage in the change is the dehydration of this nitrate, leading to the production of a deeply colored body. We believe that it is best to regard this latter substance as being a "nitramine," $C_6H_5NHNO_2$, or, possibly, a nitrate of this substance, such as $C_6H_5NH_2(NO_2)ONO_2$. Although such a representation may serve as a noncommittal formula for the compound, it is not satisfactory because it fails entirely to account for the color. In such substances as the one under consideration Hantzsch[2] has shown, very clearly, that color is associated with a cyclic structure. In analogy with the nitrophenols, we suggest the formula  as most probably representing the constitution of the

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[1] *Vide* especially *Proc. Chem. Soc.*, **7**, 89 (1891).

[2] *Ber.*, **39**, 1084, 3072; **40**, 1556.

colored compound. The choice of the meta linkage is, of course, purely arbitrary. The formula given accounts not only for the color of the substance, but explains the ease with which it passes into aniline nitrate by the addition of water, whereas, on the other hand, it also indicates that it should change readily into a nitraniline. Investigations regarding this last point are about to be made.

In the case of the *N*-substituted anilines where nitraniline derivatives are obtained with ease, we feel justified, at present, in regarding their formation as being due, primarily, to an addition of nitric acid to the nucleus. In cases where nitrosamines are the chief products, it is evident that the substituted amine group participates in the change. In all probability, in most cases, both reactions occur simultaneously, the experimental conditions, including the nitrating material, and the nature of the *N*-substituents determining which shall be the predominant reaction in any given instance. The question of the "protection" of the amino group has been already discussed in another connection in two of our earlier papers.[1]

The work is being continued at this university in the hope that it may throw further light on the very important and highly interesting questions referred to above. The present contribution can be regarded only as a preliminary survey of some of the ground which it will be necessary to explore before anything like positive conclusions can be reached.

The investigation described in the preceding pages was carried out at the Johns Hopkins University during 1906–07; it is being continued in this University by Mr. C. E. Burke under the direction of the senior author.

McMaster University, Toronto, Canada.
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THE ISOLATION OF DIHYDROXYSTEARIC ACID FROM SOILS.[2]

By Oswald Schreiner and Edmund C. Shorey.

Received August 8, 1908.

In the previous paper[3] dealing with the isolation of picoline carboxylic acid from soil it was pointed out that the productivity of a soil depends largely upon the condition of the organic matter in the soil and the processes which are at work in destroying plant remains. The great lack of knowledge, from a chemical point of view, concerning the organic matter of soils was also emphasized. It may not be out of place to remark that this chemical ignorance concerns an important soil ingredient,

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[1] *Am. Chem. J.*, **36**, 607 (1906); This Journal, **30**, 1395.

[2] Presented at the Chicago meeting, December, 1907, of the American Chemical Society by permission of the Secretary of Agriculture.

[3] This Journal, **30**, 1295.