STUDIES IN NITRATION, III. NITRATION OF ANILINE AND OF CERTAIN OF ITS *N*-ALKYL, *N*-ARYL AND *N*-ACYL DERIVATIVES.[1]

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Theoretical.

The fact that aniline cannot be directly nitrated and that, under ordinary conditions, nitric acid converts it into tarry matter, is usually accounted for by stating that the acid attacks the amino group more readily than the benzene nucleus.[2] Such an explanation cannot be accepted unreservedly, not only because it is devoid of experimental foundation, but also because of certain theoretical objections which may be urged against it. Among the latter may be mentioned the view, held by many chemists, that "substitution" in the nucleus is really preceded by addition or substitution in the side chain if one be present, or, addition in the nucleus itself, followed in each case by subsequent rearrangement. Further, the fact that, in general, the aromatic amine *nitrates* are usually stable, whereas, the *nitrites* are either highly unstable or altogether incapable of isolation suggests that nitrous acid may really be the active cause of the unfavorable result of direct nitration experiments. This view gains support from the well-known observations made in carrying out the diazo reaction; some resinous matter is always formed and it is apt to be the chief, or even the only tangible product of the experiment, unless the conditions are adjusted specially for each individual amine.

In view of these considerations, it appeared to us that it would be worth while to reinvestigate the direct nitration of aniline, employing conditions which should exclude nitrous acid as completely as possible from the materials employed, provision being also made for the speedy destruction or removal of any of this acid which might be formed during the course of the experiments.

Many careful and painstaking investigations have been carried out on the general phenomena of nitration. Much of this work has been done with the object of studying the effect of different atoms or complexes with respect to their influence on the position assumed by entering nitro groups. As the result of these researches many "rules" have been promulgated by different chemists at various times. The most important conclusions are, perhaps, best summarized by Brown and Gibson, as follows:[3] "When a monobenzene derivative, C_6H_5X, is so treated as to give a dibenzene derivative, C_6H_4XY, it is well known that, as a rule, this diben-

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[1] *Am Chem. Jour.*, 36, 607 (1906); This Journal, 30, 822 (1908).

[2] Vide, for example, Lassar-Cohn's "Application of Some General Organic Reactions," translated by J. Bishop Tingle, p. 3, *et. seq.*

[3] *J. Chem. Soc.*, 61, 367 (1892).

zene derivative is either (*a*) exclusively, or nearly so, a *meta* compound or (*b*) a mixture of *ortho* and *para* with none or very little *meta*; and that whether the case shall fall under (*a*) or (*b*) depends on the nature of the radicle X, and not at all, or only very slightly, on the nature of Y."

Blanksma explains the phenomena of nitration by supposing that there is "a direct and indirect introduction of the nitro group." In the former reaction the nitro group replaces hydrogen directly, whereas, in the latter a nitrate is formed primarily, which changes subsequently to the true nitro compound. Indirect substitution always gives *ortho* and *para* derivatives; direct substitution gives the three possible isomers with the *meta* derivative as the principal product. We shall refer to this point more fully later.

Although possessing some value, such rules are not very satisfactory, partly on account of vagueness and partly because they fail to take into account the formation of all three isomers in many cases. Moreover, on examining the literature carefully, it is found that many of the statements in it are contradictory. Instances of this will be found in the detailed references which we have made in connection with each compound studied by us.

Of the more recent work on the nitration of derivatives of benzene and aniline, it seems desirable to call attention to the investigations of Holleman,[1] who has attempted to determine, by careful and painstaking effort, the effect of relatively small quantities of water on the nature and quantity of the isomers formed. In subsequent papers[2] this author deals still further with the question of substitution in the benzene nucleus and the simultaneous formation of isomeric substitution products of benzene.

Other recent work which is of interest in this connection is that of Holdermann,[3] who has studied the influence of catalytic agents on substitution in the aromatic nucleus. The nitration of toluene yields a mixture of ortho and paramononitrotoluene, which, when the nitration is carried out in a mixture of nitric and sulphuric acids at 5°–10°, consists of 59–60 per cent. of the *ortho* derivative. This yield was not changed by the presence of various catalyzers, such as reduced copper, copper nitrate, mercury, mercurous nitrate, mercuric sulphate, reduced nickel, cobalt nitrate and ammonium vanadate.

Francis,[4] in an interesting paper, pointed out the possibility of using benzoyl nitrate, $C_6H_5COONO_2$, as a new nitrating agent. His experiments show that, when nitrating with benzoyl nitrate, more orthonitro

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[1] *Ber.*, **39**, 1607 (1906).

[2] *Centrabl.* 1906, I, 457; 1906, I, 770; 1906, I, 773; *Rec. trav. chim.*, **25**, 208.

[3] *Ber.*, **39**, 1250 (1906).

[4] *Ibid.*, **39**, 3798 (1906).

derivative is formed than para, the reactions in the case of anisole and phenetole yielding *theoretical* quantities of the orthonitro derivatives.

Experiments giving results similar to these were made by Pictet and Khotinsky,[1] who used acetyl nitrate, CH_3COONO_2, as their nitrating agent.

With this reagent almost theoretical yields of mononitro derivatives were obtained in all cases. In the substituted benzenes, the same tendency toward the formation of *o*-nitro derivatives, which Francis had previously pointed out, was noticed. Thus, toluene gave 88 per cent. of *o*-nitro and 12 per cent. of *p*-nitro derivative; phenol, 52 per cent. of *o*-nitro and 48 per cent. of *p*-nitro derivative; benzyl chloride, 60 per cent. of *o*-nitro and 40 per cent. of *p*-nitro derivative, while acetanilide gave 100 per cent. of *o*-nitro compound.

These results are of especial interest because the nitrating agents used by both Francis and Pictet necessarily insure the complete absence of water from the reacting substances at all stages of the experiments. Further reference will be made to them later.

In addition to our work on aniline itself, we desired to study, in a more detailed manner than had been done heretofore, the action of substituting groups on the process of nitration. With this, the further question was raised as to the influence of materials, other than nitric acid, which might be added to the reacting mixture. It has been shown, for example, that the use of a mixture of sulphuric and nitric acids does not simply act as a more powerful nitrating agent, by withdrawing the elements of water, but that the sulphuric acid exerts a directive[2] influence on the position assumed by the entering nitro group, in general; this position is the *meta* one. This is seen in the case of methylaniline,[3] ethylaniline[4] and dimethylaniline[5] and diethylaniline.[6] The results obtained by Reverdin[7] and his co-workers show, similarly, that, in the nitration of *p*-aminophenol and its derivatives in the presence of sulphuric acid, metanitro compounds are formed.

We thought it desirable to try to ascertain whether a similar directive influence could be established for other acids. A mixture of acetic and nitric acids has frequently been employed for nitrating purposes, the acetic acid having been regarded as an essentially indifferent solvent.

A few experiments have also been made by Orton[8] with nitric acid

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[1] *Ber.*, **40**, 1163 (1907).

[2] *Am. Chem. Jour.*, **36**, 607.

[3] *Centrabl.*, 1901 (I), 105.

[4] *Ber.*, **19**, 546 (1886).

[5] *Ibid.*, **19**, 198.

[6] *Ibid.*, **19**, 199.

[7] *Ibid.*, **39**, 125, 971, 2679, 3793.

[8] *J. Chem. Soc.*, **81**, 806.

and acetic anhydride in acetic acid solution. Witt published more recently[1] a remarkable paper entitled "A New Nitration Method," in which he states that he uses, as the nitrating agent, such a mixture of nitric acid, acetic acid and acetic anhydride. The curious feature of Witt's communication is that although he *professes* to use acetic anhydride, yet, in the only experiment which he describes, he omits entirely all reference to this substance. Moreover, at the end of his paper, he admits that other chemists have previously used the above mixture for nitration purposes. Hence, *by his own statement*, his "new method" *is not new and he does not use it.* Orton[2] has also shown that Witt's claim is quite unwarranted.

So far as we have been able to discover, no experiments have been carried out with nitrating mixtures of nitric acid and acids intermediate in strength between sulphuric and acetic acids, and we have, therefore, included this problem in our work. The choice of acids was necessarily rather limited. Obviously they had to be such as would not be acted on readily by nitric acid, and they had to be available in reasonably large quantity. We selected, eventually, anhydrous oxalic acid and trichloracetic acid. The former was chosen partly because it is dibasic, but chiefly because of its intermediate position in strength between the other two. It suffers from the disadvantage of sparing solubility in rather highly concentrated nitric acid, but it appeared to be worth while to carry out a sufficient number of experiments with it to discover if the quantity which did dissolve was sufficiently large to exert an appreciable influence on the nitration process. So far as our experiments permit of a conclusion being drawn, this does not appear to be the case. The results obtained by nitrating in the presence of oxalic acid appear to be essentially the same as those given by direct nitration.

Trichloracetic acid was chosen because it is, practically, the strongest acid which is available for use in any quantity. It may be convenient here to give the dissociation constants of these four acids, as the values afford an approximate indication of their relative strengths. For acetic acid, $K = 0.0018$; oxalic acid, $K = 10.00$; trichloracetic acid, $K = 121.00$; sulphuric acid, $K = 130.0$, approximately, by calculation.

A further point which influenced our choice of these acids was that they included a strong and a weak monobasic organic acid, a dibasic organic acid of medium strength, and a strong, dibasic, inorganic acid. It might be expected, therefore, that our results would throw light on the question as to whether the factors of the basicity or constitution of these admixed acids influenced the results of nitration, or whether the effect which they produced was due only to their strength. It will also

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[1] *Ber.*, **39**, 3901 (1906).

[2] *Ibid.*, 40, 370 (1907).

be noticed that, in so far as "strength" is concerned, sulphuric and trichloracetic acids are in the same class[1] and should, therefore, permit of a conclusion being drawn as to the influence, if any, of the mono- or dibasicity of the admixed acid and of its organic or inorganic composition, *i. e.*, as to the specific influence of a carboxyl group.

Regarding the nature of the aniline derivatives to be employed, an inspection of the literature revealed the fact that *N*-substituted derivatives had been less worked with than those where substitution had taken place in the nucleus. Our work will be extended later to this latter class of compounds, but, hitherto, it has been confined entirely to the *N*-substituted derivatives and to aniline itself.

The compounds employed may be divided into the following classes:

A. Experiments with Aniline.

a. Nitration experiments.
b. Formation of aniline nitrate.

B. Aliphatic Compounds.

I.—*Alkyl Derivatives.*
  a. Monalkyl: 1. Methylaniline; 2. Ethylaniline.
  b. Dialkyl: 1. Dimethylaniline; 2. Diethylaniline.
II.—*Derivatives of Monobasic Acids.*
  1. Formanilide; 2. Acetanilide; 3. Trichloracetanilide; 4. Propanilide; 5. Stearanilide.
III.—*Derivatives of Dibasic Acids.*
  1. Oxanilic acid; 2. Oxanilide; 3. Succinanilic acid; 4. Succinanil; 5. Succinanilide; 6. Tartranilide.
IV.—*Derivatives of Tribasic Acids.*
  1. Citranilide; 2. Citrobianil.

C. Aromatic Compounds.

I.—*Aryl Derivatives.*
  1. Benzanilide; 2. Metabrombenzanilide; 3. Phenylsulphanilide;
  1. Diphenylamine; 2. Benzalaniline.
II.—*Derivatives of Monobasic Acids.*
  4. Orthotolylsulphanilide; 5. Phenylacetanilide; 6. Picranilide.
III.—*Derivatives of Dibasic Acids.*
  1. Phthalanilic acid; 2. Phthalanil.

We desired to avoid, as far as possible, the formation of polynitro derivatives, consequently the experiments were usually carried out at room temperatures. In cases where there was a considerable evolution of heat on mixing the substances, cooling with ice was resorted to. Sometimes the mixtures were surrounded by ice and salt during the whole

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[1] Cf. Kastle, *Am. Chem. Jour.*, 33, 52 (1905).

time of an experiment. Occasionally, however, gentle warming was requisite to promote a reaction.

The experiments were carried out with the following reagents: 1. Nitric acid, sp. gr. = 1.46, containing 80 per cent. of HNO_3. 2. Nitric acid, sp. gr. = 1.46, with glacial acetic acid in the proportion 1.25 mols. of nitric acid to 4 mols. of acetic acid. 3. Nitric acid, sp. gr. = 1.46, and anhydrous oxalic acid in the proportion 1.25 mols. of nitric acid to 4 mols. of oxalic acid. 4. Nitric acid, sp. gr. = 1.46, and trichloracetic acid, in the proportion of 1.25 mols. of nitric acid to 4 mols. of trichloracetic acid. 5. Nitric acid, sp. gr. = 1.46, and concentrated sulphuric acid, sp. gr. = 1.83, containing about 92 per cent. of H_2SO_4, in the proportion of 1.25 mols. of nitric acid to 4 mols. of sulphuric acid. When the particular substance under investigation was soluble with difficulty, an excess over 4. mols. of sulphuric or acetic acid was employed. A few experiments were carried out with other solvents such, as acetic anhydride or carbon tetrachloride.

In all the experiments with aniline itself we used nitric acid which had been freed from dissolved oxides by means of a current of dry air. Oxidation during the experiment was avoided, as far as possible, by employing nitric acid of 99 per cent. concentration, made according to the method described by Morse.[1] Freshly distilled aniline was always used.

We carried out the experiments in platinum vessels, placed in a freezing mixture, so as to keep the temperature as low as possible, and took care that the reagents were gradually mixed and thoroughly stirred; moreover, we operated in the presence of urea, in the hope that any nitrous acid which might be produced by the possible reduction of some of the nitric acid would be instantly decomposed by this reagent.

In some experiments, aniline nitrate was employed in place of aniline, so as to eliminate the heat of formation of this salt. In every case, however, it was found to be impossible to keep the temperature sufficiently low and, as soon as it rose, tarry, or carbonaceous products were formed. The result was identical whether the acid was added to the aniline or *vice versa*.

This series of experiments, Nos. 1 to 7, was, therefore, discontinued and another series, Nos. 8 to 14, undertaken in order to determine at what concentration of nitric acid the formation of aniline nitrate ceases and nitration—or charring—begins. The results demonstrated that any strength of acid could be used up to at least 75.33 per cent. of HNO_3. provided, in the case of the more concentrated acids (above 50 per cent.), that the mixture was cooled and excess of acid was avoided. Acids of

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[1] "Quantitative Analysis," p. 247.

50.71 to 75.33 per cent. always gave, with aniline, the pink-colored solid compound described in our previous paper.[1]

With acids above 75.33 per cent. of HNO_3, charring took place rather quickly, although the aniline was in considerable excess. We believe, however, that this is due to the impossibility of preventing local superheating, *i. e.*, to the action of the concentrated acid, at a relatively high temperature, on aniline nitrate. Be this as it may, it is certain that. with acids containing up to 75.33 per cent. of HNO_3, any charring which may be brought about is due to an attack on aniline nitrate and not to one of free aniline. We emphasize this rather obvious fact in order to contrast it with the behavior of aniline towards a mixture of nitric and sulphuric acids, in which the latter is in considerable excess. In these circumstances, as is well known, nitration proceeds smoothly, because, as it is usually expressed, the sulphuric acid "protects" the amino group. Surely, however the amino group is equally well "protected" in the nitrate, $C_6H_5NH_3NO_3$, as in the sulphate, $C_6H_5NH_3SO_4H$, and the excess of concentrated sulphuric acid which is present must abstract so much water from the nitric acid as to make it of a higher concentration than 75.33 per cent. of HNO_3. The only very obvious difference in the conditions of the experiments, so far as we can see, is in that which governs the *temperature*. In the experiment with sulphuric acid all the materials are in solution and the "heat of nitration," as it may be termed, is instantaneously absorbed and diffused throughout the large volume of comparatively indifferent sulphuric acid, whereas, in our experiments with aniline nitrate and nitric acid, we had to rely on the relatively slow, inefficient and clumsy mechanical means of stirring and external cooling to neutralize this heat. We hope, later, to recur to this point, when more experimental data have been accumulated.

Of our experiments with the derivatives of aniline practically every one has been repeated three or four times; indeed, some of them have been carried out eight or ten times, in order to verify a result, to obtain a larger quantity of product, or for the purpose of determining the influence of some variable factor, such as temperature, concentration, etc.

We realize very fully the magnitude of the problems which we have attacked and we regard the present series of papers as constituting merely a preliminary survey of the field; there is a mass of detailed work which must necessarily be carried out before the subject can be regarded as being at all well known.

Experimental.

A. a. Experiments on the Nitration of Aniline. (Nos. 1–7). *Experiments with Aniline and Concentrated Nitric Acid in Presence of Urea.* 1. 23.2 grams aniline (1 mol.), 32 grams nitric acid (2 mols.) and 75 grams urea. The vessel containing the

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[1] *Am. Chem. Jour.*, **36**, 607 (1906).

aniline was kept immersed in a salt and ice bath and constantly stirred. A small quantity of the urea was added and then the nitric acid gradually, *drop by drop*, with further additions of small quantities of urea. It was found impossible to keep the temperature low, and there was consequently a violent decomposition of the nitric acid with a copious evolution of nitrogen peroxide; the aniline became tarry and, finally, only a charred mass remained in the vessel.

2. The procedure was the same as in the preceding experiment except that the nitric acid was stirred and aniline was added to the acid. Here, again, it was impossible to control the temperature, with the result that the nitric acid decomposed and the contents of the beaker took fire, burning fiercely even at the very low initial temperature.

Experiment with Aniline Nitrate. 3. 39 grams aniline nitrate (1 mol.), made by treating freshly distilled aniline with dilute nitric acid, 48 grams nitric acid (3 mols.), and 7.5 grams urea. The procedure was the same as in the preceding experiments. On the completion of the reaction, the mixture was poured into twice its volume of ice-water and filtered. This gave a red liquid and a black precipitate. Each was treated with sodium carbonate but in neither case could any definite compound be isolated.

The next experiments were taken with a view to study the possible effect of various solvents on the nitration. Carbon tetrachloride, acetic anhydride, and a mixture of the two were employed.

Experiments on the Use of Carbon Tetrachloride and Acetic Anhydride as Solvents.

4. 10 Grams aniline (1 mol.), 10.1 grams nitric acid (1.5 mols.) and 100 cc. carbon tetrachloride. The aniline was dissolved in the carbon tetrachloride, and the nitric acid added drop by drop to the cooled solution. A reddish precipitate was obtained and at the same time a bright blue coloration was noticed on the side of the vessel. Part of precipitate was taken out, washed with alcohol and dried over-night on a porous plate. It was colored reddish-white and melted and decomposed at 207–209°. After the mixture had stood twenty-four hours longer, the melting point of the product was 190–194° and the color had changed to green. Aniline nirate itself melts at 195–197° and the mixture of the reaction product with aniline nitrate melted at 192–195°, thus indicating that the substance was only aniline nitrate. The rest of the original precipitate was allowed to remain in the vessel in contact with the acid and after a time it charred. The carbon tetrachloride solution was filtered and evaporated, but nothing remained except a tar.

5. 10 Grams aniline (1 mol.), 10.11 grams nitric acid (1.5 mols.), and 109.1 grams acetic anhydride (10 mols.). Nitric acid and part of the acetic anhydride were carefully mixed and well cooled and the mixture added drop by drop to the solution of aniline in the rest of the anhydride. The product of the reaction was colored red and gave a red solution. It was stirred continually and allowed to remain in the ice bath 1¼ hours. On pouring into water a flocculent, yellow precipitate was obtained. This was extracted with benzene, from which a yellow product crystallized out, melting at 89–92°.

6. 10 Grams aniline (1 mol.), 10.11 grams nitric acid (1.5 mols.), 100 cc. carbon tetrachloride, and 19 grams acetic anhydride. The aniline was dissolved in carbon tetrachloride and the cold mixture of the nitric acid and acetic anhydride was added, drop by drop. A dark red, crystalline product was obtained. This was dissolved in water and neutralized with sodium carbonate. On standing, aniline, identified by testing with bleaching powder solution, separated out.

The next experiment was made to test the effect of *nascent nitric acid.*

7. 10 Grams aniline (1 mol.), 105 grams sulphuric acid (10 mols.), and 16.2 grams potassium nitrate (1.5 mols.). The aniline and sulphuric acid were mixed and powdered potassium nitrate was slowly added. The solution and precipitate obtained on pouring into ice-water were both colored dark green, which, on standing, changed to red, the precipitate then being colored greenish-black. This was filtered off and the filtrate extracted with ether, but on evaporation of the ethei nothing but a tar remained. The precipitate was insoluble in ether, but dissolved in alcohol, which, however, on evaporation left only a tarry residue.

(*b*) *Experiments on the Formation of Aniline Nitrate.* (Nos. 8–14).

8. 20 Grams of aniline were treated with nitric acid which contained 29.38 per cent. of HNO_3. Reaction took place readily on gentle heating. When the concentration of the solutions was sufficient, aniline nitrate crystallized out. In the later stages of the reaction, the addition of the nitric acid caused a pink coloration of the crystals, which disappeared after a time.

9. Nitric acid of sp. gr. 1.250, containing 39.82 per cent. of HNO_3, was used. The phenomena were identical with those described in Experiment 8.

10. Nitric acid, of sp. gr. 1.320, containing 50.71 per cent. of HNO_3, was used. The reaction took place more readily than in the preceding experiments and with an increase in the color phenomena. The crystals also were somewhat more finely divided. There was a slight fuming and darkening of the aniline with *almost immediate* formation of crystals. The liquid had a reddish-brown color which disappeared on standing.

11. Nitric acid of sp. gr. 1.350, containing 55.79 per cent. of HNO_3, was used. A reaction took place in the cold with immediate formation of crystals. The pink coloration assumed by crystals on each addition of nitric acid was especially noticeable. As in the preceding experiments, this color gradually disappeared.

12. Nitric acid of sp. gr. 1.375, containing 60.30 per cent. of HNO_3, was used. Here, again, aniline nitrate was formed with the accompanying color phenomena.

13. Nitric acid of sp. gr. 1.400, containing 65.30 per cent. of HNO_3, was used. The aniline was added to the acid, which was cooled in a salt and ice mixture. In this case the product was tarry. The experiment was repeated in a platinum dish, under the same conditions; no tar was found, the production of aniline nitrate being complete. On standing at the room temperature, decomposition set in after a time.

14. Aniline was treated with nitric acid of sp. gr. 1.4425, containing 75.33 per cent. of HNO_3, in a platinum vessel cooled by a salt and ice mixture. Here the color phenomena were again well marked. Exposure for a short time to the room temperature sufficed to cause the decomposition of the aniline nitrate.

B. I. Alkyl Compounds.

a. Monalkyl. 1. *Experiments with Methylaniline* (Nos. 15–19). As will be seen from the reference given below, a considerable amount of work has been done by many chemists, on the ortho-,[1] meta-,[2] and paramononitro[3] derivatives of this compound.

15. *Methylaniline, nitric acid and acetic acid.* In this and the following experiments unless otherwise stated, the nitrating reagents described on p. 1400 were used. For each molecule of the aniline derivative, 1.25 molecules of nitric acid and 4 molecules of glacial acetic, anhydrous oxalic, trichloracetic or sulphuric acid, respec tively, were employed.

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[1] *J. prakt. Chem.* [2], **41**, 164; [2], **46**, 565; *Ber.*, **27**, 369; **27**, 378; **31**, 2927. *Monatsh.* **19**, 634; *Rec. trav. chim.*, **21**, 272; *Centrabl.*, **1902**, II, 514.

[2] *Ber.*, **19**, 548; *Centrabl.*, **1901**, I, 105; *Ann.*, **327**, 112; *Centrabl.*, **1903**, I, 1213.

[3] *Bull. soc. chim.*, **53**, 775; *Ber.*, **27**, 370, 3791, 520; **31**, 2529, 2926; **33**, 113; *Rec. trav. chim.*, **21**, 270; *Centrabl.*, **1902**, II, 513.

The methylaniline and acetic acid were mixed while the latter was cooled. The nitric acid was then added, drop by drop. The solution became colored dark green. On pouring into water no precipitate was obtained and the aqueous solution was also colored green. It was extracted with ether; on evaporating the latter a tar remained. Experiments had previously been tried in which the reaction was allowed to take place at room temperature and others where the solution was warmed on the water bath; the time of standing was also varied, but in all cases tars were formed.

16. Nitric and oxalic acids.

17. Nitric and trichloracetic acids.

18. Nitric acid alone.

In all these experiments the products were tars.

19. Nitrating methylaniline in the presence of sulphuric acid gives *m*-nitromethylaniline.[1]

2. *Experiments with Ethylaniline* (Nos. 20–24). The ortho-,[2] meta-,[3] and paramononitro[4] derivatives of this compound have been far less extensively investigated than those of methylaniline.

Nitration in presence of acetic acid (Ex. 20), oxalic acid (Ex. 21), trichloracetic acid (Ex. 22) and with nitric acid alone (Ex. 23) gave only tars. Paranitroethylaniline is formed by the action of a mixture of nitric and sulphuric acids[5] (Ex. 24).

b. Dialkyl. 1. *Experiments with Dimethylaniline* (Nos. 25–30). As shown below, the ortho-,[6] meta-,[7] and paranitro[8] derivatives of this compound have all been investigated to some extent.

25. Nitrating dimethylaniline in the presence of sulphuric acid gives *m*-nitrodidimethylaniline.[9]

26. Nitrating dimethylaniline in the presence of glacial acetic acid yields *p*-nitrodimethylaniline.[10]

27. *Dimethylaniline and Nitric Acid.* No matter how the conditions of nitration were varied, a tar was always produced.

28. *Dimethylaniline, Nitric Acid and Trichloracetic Acid.* Resinous substances were formed.

29. *Dimethylaniline, Nitric Acid and Oxalic Acid.* The dimethylaniline and oxalic acid were added at a low temperature, which, however, could not be controlled by the rather primitive means at our command, consequently charring took place. The addition of the mixture of aniline and oxalic acid to cooled nitric acid gave similar results. Then a mixture of oxalic and nitric acids was used; it was carefully cooled and dimethylaniline was added to it *drop by drop*. It was found best to work in small quantities and to have both the aniline and acid mixture cooled. No tar was formed under these conditions.

Experiments were also tried with nitric acid of different concentrations. All of

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[1] *Centrabl.*, **1901**, I, 105.

[2] *J. pr. Chem.*, [2], **41**, 163.

[3] *Ber.*, **19**, 546.

[4] *Ibid.*, **16**, 31; **17**, 267; **19**, 149.

[5] *Ibid.*, **19**, 546.

[6] *Monatsh.*, **19**, 635.

[7] *Ber.*, **19**, 198, 1944; **27**, 1932; **30**, 2931; *Ann.*, **327**, 112; *Centrabl.*, **1903**, I, 1213; *Ber.*, **37**, 2616; *Centrabl.*, **1904**, II, 517.

[8] *Ber.*, 8, 620; **10**, 761; **12**, 529; **14**, 2176; **15**, 1234; **27**, 379; *Bull. soc. chim.* [3], **23**, 25; *Ber.*, **32**, 1896.

[9] *Ibid.*, **19**, 198.

[10] *Ibid.*, **10**, 761; **14**, 2176.

the higher concentration caused the production of tar, but this was not formed by the use of acid containing 21 per cent. HNO_3. On pouring the product of the reaction into water, filtering, and boiling the precipitate with alcohol and animal charcoal, beautiful yellow needles melting at 80–82° were obtained.

30. *Dimethylaniline (1 mol.), Nitric Acid (1.25 mols.), Oxalic Acid (4 mols.) and Acetic Acid (excess over 4 mols.).* The dimethylaniline and oxalic acid were ground together and dissolved in acetic acid. Then nitric acid was added and the product allowed to stand for a time. On pouring the acid liquid into water a greenish-yellow precipitate came down. This was filtered, dried, and then extracted with alcohol, from which *p*-nitrodimethylaniline crystallized out in beautiful yellowish-green needles melting at 162°–165°.

2. *Experiments with Diethylaniline* (Nos. 31–35). Only the meta-[1] and paranitro[2] derivatives of this compound appear to be known.

31. By nitrating diethylaniline in the presence of sulphuric acid, *m*-nitrodiethylaniline and some *p*-nitrodiethylaniline are obtained.[3] Nitration in the presence of acetic acid (Ex. 32), oxalic acid (Ex. 33), trichloracetic acid (Ex. 34) and nitric acid alone (Ex. 35) yielded only tarry or carbonaceous materials.

II. Aryl Compounds.

1. *Experiments with Diphenylamine* (Nos. 36–41). Considerable work has been carried out on the nitro derivatives of this substance but much still remains to be done. The ortho-[4] and paramononitro[5] derivatives have been prepared but, apparently, the meta compound is not known. Of the dinitro substitution products, the disymmetrical meta compound does not appear to have been isolated. On the other hand, several chemists have investigated the disymmetrical ortho-,[6] the disymmetrical-para,[7] and the 2,4-dinitro[8] derivatives.

36. *Diphenylamine, Nitric Acid (2.5 mols.) and Sulphuric Acid (excess over 4 mols.).* The sulphuric acid and diphenylamine were mixed and cooled; nitric acid was then added, drop by drop, which developed the well known blue-purple color. The nitric acid was partially decomposed and some tar was also formed. On pouring the reaction product into water, a brown precipitate was obtained.

37. *Diphenylamine, Nitric Acid (2.5 mols.) and Acetic Acid.* A small quantity of a brown precipitate was obtained. This was boiled with water. The residue insoluble in water was then extracted for some hours with alcohol in a Soxhlet apparatus. On standing, yellow-green crystals separated. They melted below 60°, thus indicating that they did not consist of a nitro derivative.

The experiment was then repeated at the temperature of the water bath. No precipitate was obtained on pouring the reaction product into water. The solution was colored red.

38. *Diphenylamine and Nitric Acid (excess over 2.5 mols.).* A reddish yellow precipitate was obtained. This was extracted with xylene, from which yellow crystals were deposited melting at 190°–194°.

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[1] *Ber.*, **19**, 199, 550.

[2] *Monatsh.*, 4, 293; *Ber.*, **19**, 199.

[3] *Ibid.*, **19**, 199.

[4] *Ber.*, **23**, 1840; **24**, 3796; *Centrabl.*, **1898**, II, 342; *Frdl.*, III, 46; *Centrabl.*, **1899**, II, 961.

[5] *Ber.*, **11**, 757; **15**, 827; **31**, 580; *Ann.*, **132**, 167; *Centrabl.*, **1899**, II, 961.

[6] *Ber.*, **11**, 759; **12**, 1400; **15**, 829; **28**, 2976; **31**, 580; *Ann.*, **132**, 167.

[7] *Ber.*, **11**, 759; **12**, 1400; **15**, 828; **31**, 580; **31**, 2535; *Ann.*, **132**, 167.

[8] *J. pr. Chem.* [1], **108**, 320; [2], **1**, 175; *Ber.*, **3**, 128; **9**, 977; **31**, 2536; *Bull. soc. chim.*, **30**, 5; *Ann.*, **215**, 363; *J. pr. Chem.* [2], **68**, 254; *Centrabl.*, **1903**, II, 1064.

39. *Diphenylamine, Nitric Acid (excess over 2.5 mols.) and Oxalic Acid.* A brownish yellow precipitate was obtained.

40. *Diphenylamine, Nitric Acid (2.5 mols.) and Trichloracetic Acid.* Diphenylamine and trichloracetic acid were ground together and nitric acid added, drop by drop, to the well-cooled mixture. After each addition of nitric acid there was a violent reaction with evolution of nitrogen peroxide. On pouring the product immediately into water a black tar separated out, leaving a brownish green solution.

41. *Diphenylamine, Nitric Acid (2.5 mols.) and Trichloacetic Acid.* Diphenylamine and trichloracetic acid were ground together and then acetic anhydride was added. This mixture was cooled and nitric acid gradually dropped in. On pouring the product into water, a tar separated.

2. *Experiments with Benzalaniline.* The meta-[1] and the paranitro[2] derivatives have been prepared from the corresponding nitranilines, but the ortho compound does not appear to have been obtained. Our own experiments with this substance were only of a preliminary nature. They resulted, always, in the production of benzaldehyde and aniline, consequently they were not carried further and it is unnecessary to give them in any detail.

The conditions employed in our experiments with *N*-acyl derivatives of aniline were similar to those described above (p. 1400). 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.

B. Aliphatic Compounds.

1. *Experiments with Formanilide* (Nos. 42–46).—The ortho-,[3] meta-[4] and paranitro[5] derivatives of this compound have all been prepared, although their investigation has been far from exhaustive.

42. *Formanilide, Nitric Acid and Sulphuric Acid.* The anilide was added to the sulphuric acid and the mixture then cooled before the addition of the nitric acid, which was added drop by drop. After standing at room temperature about ten minutes, the reaction product was poured into ice-water and gave a brown precipitate, which was filtered off and dried. It was dissolved in boiling water, from which an orange-yellow precipitate came down. It melted at 187–192°. The substance was treated with boiling ligroin and the insoluble portion was dissolved in alcohol. The ligroin extract, on cooling, deposited a yellow, amorphous product which, when hydrolyzed with aqueous potassium hydroxide, gave *p*-nitraniline (m. p. 146–147°). The alcoholic solution deposited beautiful, brown needles melting at 151–154°.

43. *Formanilide, Nitric Acid and Acetic Acid.* Formanilide was dissolved in acetic acid and nitric acid added gradually. After standing for 1½ hours the reaction product, was poured into water giving a red solution but no precipitate. This solution was then extracted with ether, which dissolved some of the red substance; on evaporating off the ether, no nitro derivative could be

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[1] *Jahres. d. Chem.*, **1870**, 760; *Monatsh.*, **9**, 697; *Ber.*, **31**, 2604.

[2] *Ber.*, **25**, 2503; *Monatsh.*, **9**, 697; *Ber.*, **34**, 833; **35**, 990; *Centrabl.*, **1902** (I), 870.

[3] *Ann.*, **209**, 369; *Z. physik. Chem.*, **23**, 459.

[4] *Am. Chem. J.*, 8, 346; *Z. physik. Chem.*, **23**, 460.

[5] *Am. Chem. J.*, 8, 346; *Z. physik. Chem.*, **23**, 460.

isolated from the residue. Our earlier experiments had failed on account of the mixtures being allowed to stand too long. An experiment was also tried, using monochloracetic acid instead of glacial acetic acid, but only a tar was formed.

44. *Formanilide, Nitric Acid (excess over 1.25 mols.), and Oxalic Acid.* Formanilide and oxalic acid were ground together and added carefully to well cooled nitric acid. After a few minutes' standing at room temperature the material was poured into water; a yellow precipitate came down and the solution was also colored yellow. On further standing of the water solution, its color and also that of the precipitate became dark brown.

45. *Formanilide, Nitric Acid (excess over 1.25 mols.), and Trichloracetic Acid.* Formanilide and trichloracetic acid were ground together and added gradually to a well cooled excess of nitric acid. After standing a few minutes at room temperature, the reaction product was poured into water; it gave a small quantity of oil which, on further standing, became tarry.

46. The direct nitration of formanilide yields *p*-nitroformanilide.[1]

2. *Experiments with Acetanilide* (Nos. 47–51).—The ortho-,[2] meta-[3] and paranitro[4] derivatives of this compound have, of course, been investigated by many chemists. Some of the more interesting recent work has been referred to above (p. 1397).

47. *Acetanilide, Nitric Acid and Sulphuric Acid.* The acetanilide was dissolved in a portion of the sulphuric acid. The nitric and the remainder of the sulphuric acid were carefully mixed and then added gradually to the solution of acetanilide. After standing several hours, the liquid was poured into ice-water; a yellow precipitate was obtained. This was recrystallized from hot water and proved to be *m*-nitracetanilide, m. p. 139–141°.

48. *Acetanilide, Nitric Acid and Trichloracetic Acid.* Acetanilide and trichloracetic acid were ground together in a mortar and nitric acid added to the mixture. It was allowed to remain an hour, after which time the reaction took place violently and the product decomposed. On repeating the experiment and cooling the vessel with water, a green-colored substance was obtained after seven hours' standing. It was poured into water, which caused the formation of a yellow precipitate and an oily green liquid. On filtering, the residue was colored brownish-black. This was partially soluble in hot water, from which an orange-colored compound separated out on cooling. It proved to be *p*-acetanilide, m. p. 205–207°.

49. *Acetanilide, Nitric Acid and Oxalic Acid.* Oxalic acid and acetanilide were ground together and added, little by little, to nitric acid cooled by means of salt and ice. When about two-fifths of the mixture had been added, decomposition took place. The reaction product was immediately poured into ice-water and a yellow precipitate was obtained which was recrystallized from hot water. It proved to be *p*-nitroacetanilide, m. p. 207–210°.

50. The direct nitration of acetanilide yields a mixture of ortho- and paranitroacetanilide.[5]

51. *Acetanilide, Nitric Acid and Acetic Acid.* Acetanilide was dissolved in acetic

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[1] *Am. Chem. J.*, **8,** 346.

[2] *Ber.*, **9,** 775; **19,** 336; *Jahres. d. Chem.*, **1875,** 344; *Ann.*, **209,** 352; **311,** 107.

[3] *Ann.*, **165,** 183; *J. prakt. Chem.* [2], **52,** 230; *Gazz. chim. ital.*, **24** (I), 446; *Am. Chem. J.*, **17,** 612; **18,** 87; **19,** 682; *Ber.*, **19,** 336; **31,** 661; *Bull. soc. chim.*, **53,** 778.

[4] *Z. Chem.*, **1871,** 202; *Ann.*, *Jahres. d. Chem.*, **1875,** 344; **1677,** 684; *Ann.*, **197,** 83; *Ber.*, **5,** 920; **9,** 775; **17,** 262; **19,** 336; *J. prakt. Chem.* [2], **52,** 233.

[5] *Ber.*, **9,** 775; *Jahres. d. chem.*, **1875,** 344; *Ann.*, **197,** 83.

acid and the nitric acid added gradually. The solution became colored green. After standing some time, it was poured into ice-water and a white precipitate was obtained. This was then filtered off and recrystallized from water. It proved to be unchanged acetanilide, m. p. 112°–114°.

3. *Experiments with Trichloracetanilide* (Nos. 52–56).—Only the ortho[1] and paranitro[2] derivatives of this compound appear to have been described in the literature, consequently it has not been possible, as yet, for us to identify the products which we have obtained. The reaction mixtures were allowed to stand for some time and poured into water. The results of the five experiments may be summarized as follows:

52. *Nitric and sulphuric acids* gave a dark yellow compound.

53. *Nitric and acetic acids* gave a yellowish white compound.

54. *Nitric and oxalic acids* gave a yellow amorphous substance.

55. *Nitric acid alone* gave a substance which was extracted with boiling water; a small quantity of a grayish-white material melting at 144.5–146.5° was obtained from the aqueous extract. The insoluble residue separated from alcohol in the form of a white, amorphous product, melting at 137–142°.

56. *Nitric and trichloracetic acids* yielded a light pink colored compound.

4. *Experiments with Propanilide* (Nos. 57–61).—The orthonitro derivative of this compound has been described,[3] but we have been unable to find any record of the preparation of the two isomers. Propanilide was prepared with great ease by treating propionyl chloride (1 mol.) with aniline (2.1 mols.) in benzene solution, at the ordinary temperature. The benzene was then evaporated off and the residue washed successively with water, dilute alkali and finally again with water. Subsequently it was recrystallized from alcohol.

57. *Nitric and sulphuric acids* gave a yellow flocculent product. The portion of it soluble in water was yellow and amorphous and melted at 150–160°. Alcohol extracted from the residue a yellowish red compound, melting at 189–192°.

58. *Nitric and acetic acids* gave a light brown product. From boiling water a grayish white compound was deposited, melting at 110–112°. Alcohol extracted a crystalline substance with a mother-of-pearl luster, melting at 100–104°.

59. *Nitric acid alone* yielded a brownish yellow, amorphous material. From boiling water a yellowish white substance was deposited melting at 100–101.5°

60. *Nitric and oxalic acids* formed a yellow product.

61. *Nitric and trichloracetic acids* yielded a brown oil.

5. *Experiments with Stearanilide* (Nos. 62–66).—A careful search through the literature has failed to show us a record of the preparation of any mononitro derivative of this compound.

62. *Nitric and sulphuric acids* gave a yellow oil.

63. *Nitric and acetic acids* yielded a white soapy mass.

64. *Nitric and oxalic acids* formed a greenish white, soapy material, which became yellow when dry.

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[1] *Ber.*, 40, 1735 (1907).

[2] *Ibid.*, 27, 1250; 40, 1735.

[3] *Am. Chem. J.*, 6, 172.

65. *Nitric acid alone* gave a greenish white precipitate which was yellow when dry.

66. *Nitric and trichloracetic acids* gave a product similar to that obtained in 65.

C. Aromatic Compounds.

II. Derivatives of Monobasic Acids.

1. *Experiments with Benzanilide* (Nos. 67–72).—As would be expected, a considerable number of chemists have investigated the ortho-,[1] meta-[2] and paranitro[3] derivatives of this compound.

67. *Benzanilide, Nitric Acid and Sulphuric Acid.* Benzanilide was dissolved in sulphuric acid, and nitric acid added to the well cooled mixture. After standing twenty-four hours, the reaction product was poured into water. At first, an oily layer separated, but this changed, later, to a green, flocculent precipitate. It was filtered off, dried and dissolved in hot alcohol. On cooling, a greenish white material was deposited. After being again recrystallized from hot alcohol it melted at 196–197°, thus proving to be *p*-nitrobenzanilide.

68. *Benzanilide, Nitric Acid and Acetic Acids (excess over 4 mols.).* Benzanilide was dissolved in an excess of acetic acid, and nitric acid added in the usual manner. After standing over night, reaction did not seem to have taken place, so the temperature was gradually raised. At about 90°, the action appeared to be complete. On pouring into ice-water, a yellow, flocculent precipitate came down and also some blackish brown product. The yellow precipitate was dried and dissolved in alcohol, and the crystals obtained from alcohol were recrystallized from chloroform. They melted at 151–155°, which proved them to be *m*-nitrobenzanilide.

69. *Benzanilide, Nitric Acid and Oxalic Acid.* Benzanilide and oxalic acid were ground together and then dissolved in the least possible quantity of acetic acid. This solution was now treated with nitric acid at the room temperature. The mixture was then heated for a time and afterwards allowed to stand over-night, the reaction product being finally poured into water. A greenish-white precipitate separated out. This precipitate was extracted with ether and the residue insoluble in ether was dissolved in alcohol, from which a slate-colored compound came down. It melted at 154–155.5°, which proved it to be *m*-nitrobenzanilide.

70. *Nitric and oxalic acids* gave a greenish white precipitate.

71. *Nitric and trichloracetic acids* yielded a green precipitate.

72. The direct nitration of benzanilide forms a mixture of ortho-, meta- and paranitrobenzanilide.[4]

2. *Experiments with Metabrombenzanilide* (Nos. 73–77).—We have failed to find a record of the preparation of any nitranilide of *m*-brombenzoic acid.

73. *Nitric and sulphuric acids* gave a yellow substance.
74. *Nitric and acetic acids* yielded a pale yellow compound melting at 128–134°.
75. *Nitric acid alone* gave a yellow material.
76. *Nitric and oxalic acids* formed a bright yellow substance.
77. *Nitric and trichloracetic acids* gave a yellowish white compound.

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[1] *Ann.*, **208**, 301; *Z. physik. Chem.*, 30, 539.
[2] *Ber.*, **7**, 498; 10, 1078; **10**, 1716; *Ann.*, 208, 297.
[3] *Ber.*, **7**, 463; **7**, 1315; **9**, 774; **10**, 1708; *Ann.*, 208, 294.
[4] *Ann.*, 208, 292.

3. *Experiments with Phenylsulphanilide* (Nos. 78-82).—The ortho-,[1] meta.,[2] and paranitroanilides[3] of phenylsulphonic acids are all known.

78. *Nitric and acetic acids* gave a yellow precipitate.

79. *Nitric and oxalic acids* yielded a tar.

80. *Nitric acid alone* also gave a tar.

81. *Nitric and trichloracetic acids* gave an orange-yellow precipitate.

82. *Nitric and sulphuric acids* formed a substance which produced a red solution when the acid liquid was poured into water.

4. *Experiments with o-Tolylsulphanilide* (Nos. 83-87).—None of the nitranilides of *o*-tolylsulphanilides appear to have been prepared.

83. *o-Tolylsulphanilide, Nitric Acid and Sulphuric Acid* (*excess over 4 mols.*). The anilide was dissolved in an excess of sulphuric acid and nitric acid was added. After standing 24 hours, the reaction product was heated on the water bath for 6 hours. On pouring into water, the solution was colored yellowish red and the precipitate brownish yellow. The latter was boiled with water, and the insoluble residue boiled with alcohol and filtered. On cooling, fine, reddish yellow needles which melted at 117-131°, separated out. The residue, insoluble in alcohol, was boiled with benzene and the portion insoluble in this solvent was dissolved in nitrobenzene from which a white, amorphous substance was deposited. It softened at 180° and melted completely at 228°.

84. *Nitric and acetic acids* gave a yellow material. From this boiling water extracted a tar. The residue, when treated with alcohol, gave yellow crystals melting at 89-93°.

85. *Nitric and oxalic acids* yielded a yellow substance.

86. *Nitric acid alone* gave results similar to 8.5.

87. *Nitric and trichloracetic acids* formed a brown tar.

5. *Experiments with Phenylacetanilide* (Nos. 88-92).—There appears to be no record of the preparation of any nitranilide of phenylacetic acid.

88. *Nitric and sulphuric acids* gave a yellow amorphous material.

89. *Nitric and oxalic acids* yielded a brownish yellow substance and a red tar.

90. *Nitric acid alone* gave a yellowish white compound.

91 *Nitric and acetic acids* formed a white flocculent substance.

92. *Nitric and trichloracetic acids* gave a yellow compound.

6. *Experiments with Picranilide* (Nos. 93-97).—The ortho-,[4] meta-,[5] and paranitranilides[6] of picric acid have been investigated by several chemists.

93. *Picranilide, Nitric Acid and Sulphuric Acid* (*excess over 4 mols.*). Picranilide was dissolved in sulphuric acid, and nitric acid added at the room temperature. After standing over-night and pouring into water, a brown precipitate was obtained. This was filtered off and the filtrate extracted with ether. On evaporating the ether, a red, tarry mass remained. The crude precipitate was boiled with water, from which a very small amount of a greenish-yellow precipitate was extracted. It softens at 170° then melts completely and chars at 198°.

[1] *Ber.*, **16**, 594; *Ann.*, **221**, 16.

[2] *Ber.*, **16**, 595.

[3] *Ibid.*, **16**, 595.

[4] *Ibid.*, **33**, 431.

[5] *Ibid.*, **7**, 1249; **33**, 431.

[6] *Ibid.*, **7**, 1249; **33**, 432.

94. *Picranilide, Nitric Acid and Acetic Acid (excess over 4 mols.).* Picranilide was dissolved in acetic acid on the water bath. Nitric acid was added, and the mixture heated several hours. On pouring into water, a bright yellow precipitate came down. The crude precipitate was boiled with water and the residue was extracted with alcohol. A small amount of a red precipitate separated from the latter solution. It melted at 144–147°. The residue, insoluble in alcohol, was then extracted with benzene, from which a yellow compound melting at 155–159° was deposited. The residue, insoluble in benzene, was colored lemon-yellow and melted at 176–179°.

95. *Picranilide, Nitric Acid and Trichloracetic Acid.* Picranilide and trichloracetic acid were ground together and nitric acid added at the room temperature. After standing over-night, the solution was poured into water; this produced a reddish yellow precipitate. It was boiled with water, and the residue was extracted with alcohol, from which crystals separated. They melted and decomposed at 155–157°. The residue, insoluble in boiling alcohol, was completely soluble in benzene; from this solution a product was obtained which melted and charred at 151–158°.

96. *Picranilide, Nitric Acid (excess over 1.25 mols.), and Oxalic Acid.* Picranilide and oxalic acid were ground together and added gradually to nitric acid at the room temperature. There was a slight warming and a small evolution of nitrogen peroxide. After standing for a few minutes the solution became red and thick. On adding it to water, a bright yellow compound was precipitated.

97. *Picranilide and Nitric Acid (excess over 1.25 mols.).* Picranilide was added to the nitric acid gradually at the room temperature. After standing some time it was poured into water, when a yellow precipitate came down. The crude precipitate was boiled with water, from which, on cooling, a small amount of yellowish red, tarry matter was deposited. The residue, insoluble in boiling water, was then extracted with alcohol, from which solution a voluminous orange-red compound was obtained. It melted and decomposed at 160–162°. The residue, insoluble in boiling alcohol, was then extracted with benzene. This solution deposited slender, yellow crystals melting at 165–168°. The residue, insoluble in boiling benzene, consisted of a fine, yellow powder which melted and decomposed at 193–203°.

Summary.

We desire to reserve for a later paper the full discussion of the results recorded in the preceding pages. The present portion of our work with the *N*-alkyl, *N*-aryl and *N*-acyl aniline derivatives may be briefly summarized as follows:

I. Monalkyl Derivatives.

All the nitration experiments with compounds of this class yielded tars. Metanitro derivatives had been obtained previously by other chemists from both methyl- and ethylaniline by nitrating in the presence of sulphuric acid (Expts. 20–24).

II. Dialkyl Derivatives.

The formation of tar was the general result of the nitration of the members of this class. However, in nitrating dimethyl- and diethylaniline in the presence of sulphuric acid, *metanitro* derivatives have been produced in both cases (Expts. 25 and 31).

The nitration of dimethylaniline in the presence of acetic acid has been found to yield *p*-nitromethylaniline (Expt. 26). In nitrating dimethylaniline in the presence of a mixture of oxalic and acetic acids, we obtained *p*-nitrodimethylaniline (Expt. 30).

We have also prepared several new compounds, notably one from diphenylamine, the nature of which it is hoped to elucidate later.

III. Derivatives of Monobasic Aliphatic Acids.

Formanilide, by direct nitration, gave the *paranitro* derivative (Exp. 46), which was also obtained in the presence of sulphuric acid (Exp. 42).

Acetanilide, by direct nitration, gave a mixture of *ortho-* and *paranitro derivatives* (Expt. 50). In the presence of sulphuric acid, *metanitroacetanilide* was obtained (Expt. 47). The oxalic and trichloracetic acid nitrations both gave *paranitro derivatives* (Expts. 48, 49).

The nitrations of trichloracetanilide, propanilide and stearanilide gave products which have not yet been identified.

IV. Derivatives of Monobasic Aromatic Acids.

Benzanilide yields a mixture of *ortho-*, *meta-*, and *paranitro derivatives* by direct nitration (Expt. 72). With sulphuric acid, *para*nitrobenzanilide was obtained (Expt. 67). Acetic acid nitration gave *meta*-nitrobenzanilide (Expt. 68). A mixture of oxalic and acetic acids gave the *para*nitro derivative (Expt. 69).

None of the nitration products of *m*-brombenzanilide, benzenesulphanilide, *o*-tolylsulphanilide, phenylacetanilide or picranilide have, as yet, been identified, owing to causes beyond our own control.

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McMaster University, Toronto, Can.,
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[Contribution from the Chemical Laboratory of the University of Texas.]

HYDANTOIN TETRAZONES.

By J. R. Bailey.

Received May 25, 1908.

Introduction.

In a paper published in this journal a few years ago, the author described some tetrazones, in which there is the group $N = N$ joined on either side to an hydantoin group.[1] To simplify the nomenclature, these substances were regarded as azohydantoins. Here an attempt is made to further establish the constitution of these compounds by showing the relation of dimethylphenylazohydantoin (I), to dimethylphenylhydantoin (II) and also to aminodimethylphenylhydantoin (III).

The analytical data, published in the first article, did not in all cases closely agree with the tetrazone formulae. At that time, these substances were prepared for analysis by precipitation from a chloroform

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[1] This Journal, **26**, 1006.