## XXVIII.—On Some New Coloring Matters, Produced by the Action of Diazo-Compounds on Phenols.

By Jas. H. Stebbins, Jr., B.S.

The study of the action of diazo-compounds on phenols dates back a good many years, but it is only within the last few years that it has met with any practical success, and I will now take the opportunity to give a brief sketch of some of the most interesting and valuable compounds, before entering on the description of my own results.

In 1875, P. Griess made the discovery that diazobenzolesulpho acid (from sulphanilic acid), acting on phenols, produced a series of interesting compounds, which were characterized by more or less tinctorial power.

In the spring of the following year, he sent a communication to the *German Chemical Society*,[*] describing this reaction. The great tinctorial power of these new compounds lead him to believe that they might be used with advantage in dyeing and printing, and several samples sent to an expert on colors, proved that his theory was correct, as may now be seen by the great demand for Poirrier's oranges, Nos. 1 and 2, chrysoine, tropaeoline, aecht-roth, roccelline, etc. Among this group the following compounds[†] deserve special attention, viz :

Parazosulphoxylbenzolephenol, $C_6H_4(HSO_3) - \overset{1}{N} = \overset{1}{N} - C_6H_4\overset{4}{OH}.$
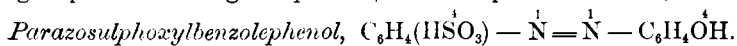
This is prepared by the action of diazosulphanilic acid on an alkaline solution of phenol, these two being taken in equal molecules. The yellow-red liquid thus produced, is allowed to rest for a short time, then heated to boiling, and saturated with acetic acid. On cooling, a large number of little yellow leaflets crystallize out, and constitute the acid potassium salt. These are then collected on a filter, dissolved in water, and purified by boiling a short time with a little animal black.

The free acid may be obtained by treating a hot and concentrated solution of the acid potash salt with a large excess of strong hydrochloric acid. It is purified by washing with dilute HCl, and finally crystallized from an acidified aqueous solution. It crystallizes from its concentrated aqueous solution in yellow-red prisms, with a strong violet lustre. It is pretty soluble in alcohol, but nearly insoluble in ether or hydrochloric acid.

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[*] Ber. d. d. chem. Gesell., **9**, 627.

[†] Ber. d. d. chem. Gesell., **11**, 2192.

Nitric acid, even diluted with 3–4 times its bulk of water, decomposes it, with formation of yellow, oily drops, which, after a while, crystallize. This acid has the property of forming acid and neutral salts, with bases.

The acid potassium salt, $C_{12}H_9N_2SO_4K$, may be prepared, besides the already mentioned method, by treating a hot solution of the acid with chloride of potassium.

The following compounds are prepared in exactly the same manner as the previous one, and in their description I will only call your attention to some of the more particular differences.

Metazosulphoxylbenzolephenol, $C_6H_4(H\overset{3}{S}O_3) - \overset{1}{N} = \overset{1}{N} - C_6H_4(\overset{4}{O}H)$. This is prepared by the action of metadiazobenzolesulpho acid on an alkaline solution of phenol. It is easily soluble in water and alcohol, but insoluble in ether.

Azobenzolesulphoxylphenol, $C_6H_5 - N = \overset{1}{N} - C_6H_3(H\overset{3}{S}O_3)(\overset{4}{O}H)$, prepared by the action of diazobenzole nitrate on an alkaline solution of orthophenolsulpho acid. The free acid is easily soluble in water and alcohol, but nearly insoluble in ether.

Parazosulphoxylbenzoleorthonitrophenol, $C_6H_4(H\overset{4}{S}O_3) - \overset{1}{N} = N$ $- C_6H_3(\overset{2}{N}O_2)(\overset{4}{O}H)$, prepared by the action of paradiazobenzolesulpho acid on orthonitrophenol ; crystallizes from alcohol in pretty, yellow needles.

Parazosulphoxylbenzoleresorcine, $C_6H_4(H\overset{4}{S}O_3) - \overset{1}{N} = N - C_6H_3(OH)_2$, prepared from paradiazobenzolesulpho acid and an alkaline solution of resorcine. The free acid crystallizes in pointed leaflets.

Metazosulphoxylbenzoleresorcine, $C_6H_4(H\overset{3}{S}O_3) - \overset{1}{N} = N - C_6H_3(OH)_2$, prepared in the same way as the previous compound.

Parazosulphoxylbenzoleorcine, $C_6H_4(H\overset{4}{S}O_3) - \overset{1}{N} = N - C_7H_5(OH)_2$, crystallizes in small yellow-red needles.

Parazosulphoxylbenzolesalicylic acid, $C_6H_4(H\overset{4}{S}O_3) - \overset{1}{N} = N - C_6H_3$ $(\overset{2}{O}H)(\overset{1}{C}OOH)$, pretty, yellow needles, soluble in alcohol.

I should like to call your attention here, to the fact, that this is the compound I mentioned in my last paper and which is so similar to the body I described as azobenzoleoxycarboxylbenzole (JOURNAL AMERICAN CHEMICAL SOCIETY, I, 466).

Azosulphoxylxyloleresorcine, $C_8H_8(HSO_3) - N = N - C_6H_3(OH)_2$, pretty, yellow-red needles, soluble in alcohol.

Metazosulphoxylbenzole-α-naphthol, $C_6H_4(\overset{3}{HSO_3})$ — $\overset{1}{N}$ = N — α-$C_{10}H_6OH$, dark green leaflets, with a golden green lustre, pretty soluble in warm water.

Metazosulphoxylbenzole-β-naphthol, $C_6H_4(\overset{3}{HSO_3})$ — $\overset{1}{N}$ = N — β-$C_{10}H_6OH$, similar to the previons compound.

Azobenzole-β-sulphoxylnaphthol, C_6H_5 — N = N — β-$C_{10}H_5(HSO_3)$. (OH), prepared by the action of diazobenzole nitrate on an alkaline solution of β-naphtholsulpho acid; red-brown needles, difficultly soluble in water. Besides the three last mentioned naphthol dyes, there are three more similar ones, two being discovered by Poirrier, of Paris, and known as :

Orange No. 1, $C_6H_4(\overset{4}{HSO_3})$ — $\overset{1}{N}$ = N — α-$C_{10}H_6(OH)$.

Orange No. 2, $C_6H_4(\overset{4}{HSO_3})$ — $\overset{1}{N}$ = N — β-$C_{10}H_6(OH)$, and thirdly, one discovered by A. W. Hofmann, of the following composition : C_6H_5 — N = N — α-$C_{10}H_5(HSO_3)$(OH), and prepared by the action of diazobenzole, on alphanaphtholsulpho acid.

Parazosulphoxylbenzole-β-naphtholsulpho acid, $C_6H_4(\overset{4}{HSO_3})$ — $\overset{1}{N}$ = N — β-$C_{10}H_5(HSO_3)$(OH), acid barium salt crystallizes in deep orange-red microscopic needles.

Azonaphthalenesulphoxyl-β-naphthol, $C_{10}H_6(HSO_3)$ — N = N — β-$C_{10}H_6OH$. This pretty, red dye was first discovered by Caro, and is prepared by the action of diazonaphthionic acid on β-naphthol. I should here like to remark that Poirier claims to have discovered the same dye, which he calls roccelline, and that a controversy is now going on as to the priority of the invention.

Azosulphobenzoic acid—α-oxynaphthoic acid, $C_6H_3(HSO_3)$. COOH — N = N — α-$C_{10}H_5(OH)(COOH)$, microscopic needles of a brown color.

Azodibromsulphoxylbenzoledioxynaphthalene, $C_6H_2Br_2(HSO_3)$— N = N — $C_{10}H_5(OH)_2$, violet-brown microscopic needles, soluble in water with a yellow color.

Besides the compounds I have just described, Griess has discovered quite a number of others, several of which he has patented. Among the prettiest of these may be mentioned anisole red and crimson.

Anisole red is prepared by the action of diazoanisole hydrochlorate on an alkaline solution of β-naphtholsulpho acid. The coloring matter, so obtained, is thrown upon a filter, washed, and dissolved in

water, from which it is reprecipitated with NaCl, in the form of a soda salt. This is very soluble in hot and cold water, and in an acid bath dyes animal fibre of a beautiful red.

Anisole crimson is prepared in the same manner as the foregoing compound, with the exception that β-naphtholdisulpho acid is used, instead of the monosulpho acid.

From what I have described, you will clearly see how neatly diazo compounds react upon phenols, and it will therefore not be necessary for me to give you any more illustrations ; and, with your permission, I will now describe a few compounds belonging to this group, and which are, perhaps, not quite as pretty as some of Griess', yet still are interesting enough to deserve your attention.

In my last paper, on the azo colors, I mentioned several bodies, which I will now briefly review, and add certain facts which I at first omitted.

Azobenzoletrinitroxybenzole, $C_6H_5 — N = N — C_6H(NO_2)_3OH$. This was prepared by the action of diazobenzole nitrate on an alcoholic solution of picric acid, taking equal molecules of each. The mixture, thus obtained, soon became filled with long, brown needles. These were thrown upon a filter, washed, and dried under the air pump. This compound is quite explosive, and the melting point could not be obtained on this account. It is soluble in alcohol, with a yellow color, but, on being boiled, it is decomposed, leaving a tarry mass behind. If this compound be treated with reducing agents (as tin and HCl), it should yield aniline and amidotrinitrophenol, according to the following equation :

$$C_6H_5 — N = N — C_6H(NO_2)_3.OH + 2H_2 = C_6H_5NH_2 + C_6H(NH_2)(NO_2)_3OH.$$
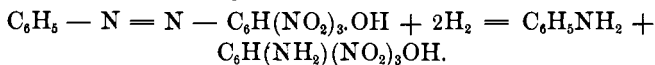
But, owing to the great difficulty of obtaining pure reduction products, I have not been able to verify this subject.

Several tests made to obtain this compound by the usual methods, namely, by treating diazobenzole nitrate (prepared by Victor Meyer's method), with an alkaline solution of picrate of potash, have remained fruitless, for the two compounds will not combine, and picric acid was regenerated in each instance. Therefore, it would seem that potash must interfere with their combining, and that the above named compounds can only be formed by treating pure diazobenzole nitrate with an alcoholic solution of picric acid.

Azobenzolepyrogallol, $C_6H_5 — N = N — C_6H_2(OH)_3$. This was obtained by allowing equal molecules of diazobenzole nitrate and an

alkaline solution of pyrogallol to react on one another.   Immediately a brick red precipitate is formed, which increases on standing.   It was then collected on a filter, washed with water, afterwards with alcohol, and then dried.   It dissolves readily in nitrobenzole and glacial acetic acid, at a gentle heat, and crystallizes from them in small, dark red-brown needles.   It likewise dissolves slightly in alcohol, and in this shape it is best adapted for dyeing.

Treated with tin and hydrochloric acid, it yields aniline and amidotrioxybenzole.

The positions held by the OH groups in this compound are respectively $1 : 2 : 4$.

Parazosulphoxylbenzolephloroglucine, $C_6H_4(H\overset{4}{S}O_3) -- \overset{1}{N} = N - C_6H_2(OH)_3$. If equal molecules of diazosulphanilic acid and phloroglucine are allowed to react on one another, the result is a heavy orange colored precipitate, which is collected on a filter, dissolved in boiling water, and precipitated with common salt, in the form of a soda salt. The soda salt is crystallized several times from hot water, and is then in a pretty pure state.

Soda salt, $C_6H_4(Na\overset{4}{S}O_3) - \overset{1}{N} = N - C_6H_2(OH)_3$, fine orange crystalline powder, easily soluble in water.   The free acid may be obtained from this by treating the concentrated aqueous solution with an excess of strong hydrochloric acid.

Free acid, $C_6H_4(H\overset{4}{S}O_3)-\overset{1}{N}=N-C_6H_2(OH)_3$. Thin orange colored tables or leaflets, with a strong beetle green lustre.   Pretty soluble in water.

Acid barium salt, $(C_{12}H_9N_2SO_6)Ba$, obtained by treating a concentrated aqueous solution of the free acid with a strong solution of baric chloride.   Orange colored leaflets, less soluble in water than the soda salt.

If we look back a few steps and demand the structure of this compound, the answer will be found in its reduction products ; for, if the free acid be treated with tin and hydrochloric acid, and the solution thus obtained is freed from tin by means of sulphuretted hydrogen, sulphanilic acid and amidophloroglucine may be extracted from the mixture.

The reaction that takes place here is as follows :

$$C_6H_4(H\overset{4}{S}O_3) - \overset{1}{N} = N - C_6H_2(OH)_3 + 2H_2 =$$
$$C_6H_4(HSO_3)NH_2 + C_6H_2(NH_2)(OH)_3.$$
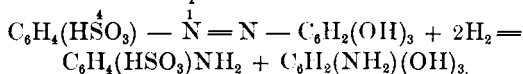
Therefore, as the HSO_3 group in sulphanilic acid is in the para

position, it is evident that it must hold the same position in parazo-sulphoxylbenzolephloroglucine.

This compound is of particular interest, as it is very similar to, and moreover, an isomere of azobenzolepyrogallol, the only difference being that the latter does not contain the HSO_3 group, while the former does.

Azobenzolesulphocresole, $C_6H_5 — N = N — C_6H_2(HSO_3)CH_3(OH)$. If an alkaline solution of cresolesulpho acid be treated with an aqueous solution of diazobenzole nitrate, the result is a deep orange colored oily liquid. If this be allowed to stand for a short time, and then be treated with an excess of strong hydrochloric acid, the acid is by this means set free, and will after a short time crystallize in long brown needles, with a strong metallic lustre. It is quite soluble in alcohol, less so in hot water, to which it imparts an orange color. When treated with reducing agents, it splits up into aniline and amidosulphocresole, viz :

$$C_6H_5 — N = N — C_6H_2(HSO_3)CH_3OH + 2H_2 =$$
$$C_6H_5NH_2 + C_6H_2NH_2(HSO_3)(CH_3)(OH).$$
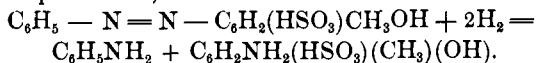
I have perhaps dwelt too long in the repetition of the compounds mentioned in my last paper, but there were certain points which I had omitted at first, and I therefore take this occasion of making them known.

We now come to some of my new dyes, and among the first may be mentioned

Dinitroxyazobenzoleorthoxysulphoxylbenzole, $C_6H_2(NO_2)_2(OH) —$ $\overset{1}{N}=\overset{2}{N}—C_6H_3(HSO_3)(OH)$. This compound lies intermediate between Griess' azosulphoxylbenzoleorthonitrophenol and my azobenzoletri-nitroxybenzole, and may be obtained by treating one molecule of diazodinitrophenol with an alkaline solution of one molecule of phenolorthosulpho acid.

The proportions used in the experiment were : 10 grms of dinitro-amidophenol were treated with 5 grms of strong HCl, and a solution of 3.5 grms of KNO_2 in 100 c.c. of water were added. The solution thus obtained is stirred for a short time, and then poured, little by little, into a solution consisting of about 5 grms of phenolsulpho acid, 2.5 grms of KOH, and 100 c.c. of water.

The mixture thus produced is allowed to rest for an hour, and the deep yellow-brown liquid is heated to boiling, and then saturated with strong hydrochloric acid. On cooling, the free acid crystallizes out in the shape of yellow-brown needles, with a metallic lustre. These are only sparingly soluble in hot and cold water.

The soda salt, $C_6H_3(NO_2)_2(OH) - N = N - C_6H_3(NaSO_3)OH$, may be obtained from the free acid by treating it with carbonate or hydrate of soda. It is somewhat more soluble in water than the free acid.

By reduction with strong reducing agents (as tin and hydrochloric acid), dinitroamidophenol and orthoamidosulphophenol are obtained, according to the following equation :

$$C_6H_3(NO_2)_2OH - N = N - C_6H_3(NaSO_3)OH + 2H_2 =$$
$$C_6H_3(NO_2)_2(OH)NH_2 + C_6H_3(NaSO_3)(NH_2)OH.$$
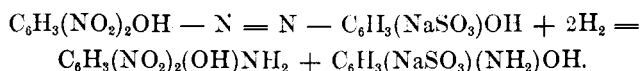
In this reaction, as, in fact, in all the others of this kind, the azo-group, $-N = N-$, is split in two, each nitrogen atom taking up two atoms of hydrogen, to form the amido compound. The compounds obtained in this reaction are of particular interest, as they clearly demonstrate the positions they hold.

Thus, we found that by reduction of dinitroxyazobenzoleortho-oxysulphoxylbenzole, that orthoamidosulphophenol was obtained, this clearly showing that the sulpho group is in the ortho position.

We next come to a compound I described a short time ago, but will here again mention, viz:

Dimethylazobenzoledinitroamidooxylbenzole, $C_6H_3(CH_3)_2 - N = N - C_6H(NO_2)_2(NH_2)OH.$ If equal molecules of diazoxylolchloride and dinitroamidophenol are mixed together, and the solution be kept slightly alkaline, a deep red-brown liquid is thus obtained, which is then filtered to separate it from a black resinous substance formed at the same time. The filtrate is then slightly heated, and saturated with strong HCl + aq, which precipitates the coloring matter in the form of a red-brown crystalline powder. This is then collected on a filter ; washed and dried. It is sparingly soluble in cold, but more soluble in boiling water, and easily soluble in alcohol.

The aqueous solution is of a red-brown color, and the slightest trace of acid causes a marked change of color, namely, from red-brown to straw yellow. Owing to this phenomenon, I think the dye might be used to advantage as a test for acids. Its formation may be expressed according to the following equation :

$$C_6H_3(CH_3)_2 - N_2 - HCl + C_6H_2(NO_2)_2(NH_2)ONa =$$
$$C_6H_3(CH_3)_2 - N = N - C_6H(NO_2)_2(NH_2)OH + NaCl.$$
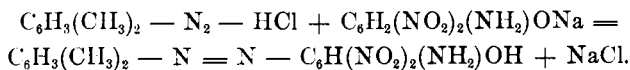
The free acid may be obtained by saturating the soda salt with a large excess of strong HCl.

Similar to Griess' azosulphoxylbenzoleorthonitrophenol is :

Azosulphoxylnaphthaleneorthonitroxybenzole, $C_{10}H_6(H\overset{1}{S}O_3)—\overset{1}{N} =$
$\overset{1}{N} — C_6H_3(\overset{2}{N}O_2)OH$. This compound was produced by treating one molecule of diazonaphthionic acid, with an equivalent amount of orthonitrophenol. The two substances were mixed slowly, under constant stirring, and care was taken to keep the solution slightly alkaline until the end of the reaction. The deep red-brown solution, so obtained, was allowed to rest for a few hours ; then heated to boiling, and saturated with strong HCl, which threw down the free acid in a crystalline state.

Free acid. Red-brown microscopical needles, very soluble in water, with a red-brown color.

Soda salt, $C_{10}H_6(Na\overset{4}{S}O_3) — \overset{1}{N} = \overset{1}{N} — C_6H_3(\overset{2}{N}O_2) — OH$. Brown crystalline powder, easily soluble in water, and obtained from the foregoing by treating with NaOH + aq.

If we demand the constitution of this compound, the answer can readily be found in its reduction products ; for, if the dye be treated with reducing agents, as tin and hydrochloric acid, it splits up into paraamidosulphonaphthalene and orthoamidonitrophenol, thus showing that the sulpho group in the naphthalene nucleus, and the nitro group in the benzole nucleus, hold respectively the para (1 : 4) and the ortho (1 : 2) positions.

Up to the present time no attempts had been made to combine more than two sulpho groups in one compound, and these were either joined to three nuclei, as in $C_6H_4(HSO_3) — N = N — C_6H_3(HSO_3)OH$, or, they were bound to one nucleus, as in

$$C_{10}H_7 — N = N — C_{10}H_4(HSO_3)_2OH.$$
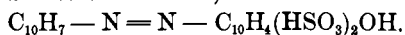
Now, it occurred to me that possibly three HSO_3 groups might be combined, and thus afford a new field for investigation.

With this point in view, the following compound was produced :

Paraazosulphoxylbenzole-β-oxydisulphoxylnaphthalene,

$$C_6H_4(H\overset{4}{S}O_3) — \overset{1}{N} = N — β\text{-}C_{10}H_4(HSO_3)_2OH.$$
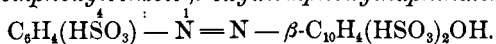
This compound can be produced by several methods, giving compounds isomeric with one another. For instance, it might be prepared by combining diazosulphanilic acid with betanaphtholdisulpho acid ; or, by treating diazodisulphobenzole with betanaphtholmonosulpho acid ; or, by treating diazobenzole nitrate with betanaphtholdisulpho acid, and then sulpho conjugating, or *vice versa.*

All these methods would probably yield compounds similar to one another, as already stated, but the simplest method seemed to be the

first one mentioned, namely, the combining of diazosulphanilic acid with betanaphtholdisulpho acid.

If one molecule of diazosulphanilic acid be treated with an equivalent amount of betanaphtholdisulpho acid (made slightly alkaline), and allowed to rest for a few hours, the result is a deep orange-red solution. It is then slightly heated and saturated with strong HCl. On cooling, the free acid crystallizes out in pretty, orange leaflets, with a beetle green lustre. These are very soluble in water with a fine orange color.

The soda salt, $C_6H_4(NaSO_3) - \overset{1}{N} = N - \beta\text{-}C_{10}H_4(NaSO_3)OH$, is an orange colored powder and exceedingly soluble in water. It can be obtained from the free acid by treating it with sodic carbonate.

A lead salt was likewise produced by treating the free acid with plumbic acetate. Yellow powder, soluble in water with an orange color.

Tin and hydrochloric acid reduce this compound to paraamido-benzolesulpho acid and amidodisulphonaphthol, thus showing the position held by the benzolesulpho group in the formula. This compound then goes to prove that what we at first stated is possible, namely, the combination of three sulpho groups in one compound.

Isomeric with Griess' parazosulphoxylbenzole-β-naphtholsulpho-acid, $C_6H_4(HSO_3) - N = N - C_{10}H_5(HSO_3)OH$, is *azobenzole disulpho-naphthol*, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4(HSO_3)_2OH$. This was obtained by treating an alkaline solution of the soda salt of β-naphtholdisulpho acid with one molecule of diazobenzole nitrate.

These two solutions were mixed under constant stirring, and the heavy orange colored precipitate thus formed, was collected on a filter, washed, dissolved in hot water, then precipitated with common salt, in the form of a soda salt, and finally dried.

The soda salt, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4(NaSO_3)_2OH$, consists of little, orange colored leaflets, with strong green metallic lustre, and very soluble in water.

The free acid, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4(HSO_3)_2OH$, is obtained from the soda salt by saturating an aqueous solution of the latter with an excess of strong HCl. Crystallizes in fern shaped leaflets, with strong metallic lustre; is very soluble in water and alcohol.

The barium salt, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4Ba(SO_3)_2OH$, is obtained by treating a hot concentrated solution of the free acid with $BaCl_2$; orange colored leaves, sparingly soluble in water.

Reducing agents, as tin and hydrochloric acid, yield aniline and amidodisulphonaphthol.

Parazotoluole-β-naphtholdisulpho acid, $C_6H_4(CH_3) \overset{1}{-} \overset{:}{N} = N \overset{4}{-}$
$\beta\text{-}C_{10}H_4(HSO_3)_2OH$. This pretty, scarlet dye was produced by combining equal molecules of diazotoluole nitrate and β-naphtholdisulpho acid together, the solution being kept slightly alkaline until the end of the reaction. The heavy red precipitate thus formed was collected on a filter, washed, dissolved in water, and precipitated again with common salt, in the form of a soda salt.

The soda salt, $C_6H_4(CH_3) - N = N - \beta\text{-}C_{10}H_4(NaSO_3)_2OH$, is produced as already stated. Red-brown crystalline powder, soluble in water with a fine scarlet color.

The free acid is obtained from this by treating with an excess of strong HCl. Red colored leaves, with strong beetle green lustre, and very soluble in H_2O.

The barium salt, $C_6H_4(CH_3) - N = N - \beta\text{-}C_{10}H_4(SO_3)_2BaOH$, is obtained from the free acid by treating with $BaCl_2$. Red crystalline powder, sparingly soluble in water.

Treated with reducing agents, paratoluidine and amidodisulphonaphthol are formed.

I have likewise produced the ortho (1 : 2) and meta (1 : 3) azotoluole-β-naphtholdisulpho acid in the same way as the previous compound, and it will not be necessary to describe the method of preparation.

They all resemble the para compound, more or less, and differ mostly in their shades ; one being yellower and the other redder. They are, likewise, pretty, scarlet dyes, and are easily soluble in water. On reduction, they yield respectively ortho and meta-toluidine and amidodisulphonaphthol. Similar in nature to Griess' parazo-sulphoxylbenzoleresorcine, and differing only in the color, is:

Parazosulphoxylnaphthaleneresorcine, $C_{10}H_6(HSO_3) \overset{4}{-} \overset{:}{N} = N \overset{1}{-}$
$C_6H_3\diagup_{OH}^{OH}$ This is produced by treating one molecule of diazo-naphthionic acid with an equivalent amount of an alkaline solution of resorcine. The mixture thus obtained is allowed to stand for an hour, then heated to boiling and saturated with strong HCl. On cooling, the free acid crystallizes out, and may be purified by re-crystallizing from water.

The free acid, $C_{10}H_6(HSO_3) \overset{4}{-} \overset{1}{N} = N - C_6H_3\diagup_{OH}^{OH}$, crystallizes in dark brown needles, with metallic lustre, and is very soluble in water, with a fine red-brown color.

The soda salt, $C_{10}H_6(NaSO_3) - N = N - C_6H_3 {\diagdown}^{\diagup OH}_{\diagdown OH}$, is prepared from the foregoing by treating with NaOH. Brown crystalline powder, soluble in water. The constitution of the above named compound can be found in its reduction products, which are naphthionic acid and amidoresorcine.

Parazodibromsulphoxylbenzole-β-naphthol, $C_6H_2Br_2(H\overset{1}{S}O_3) - \overset{1}{N}$ $= N - \beta\text{-}C_{10}H_6OH.$ This interesting compound was obtained by allowing equal molecules of paradiazobibrombenzolesulpho acid and β-naphthol to react on one another ; the solution being kept slightly alkaline until the end of the reaction. The mixture thus obtained was then heated slightly and saturated with HCl, which precipitated the free acid in the shape of an amorphous, orange-red mass. This was then washed, and crystallized from water.

The free acid is pretty soluble in hot water, less so in cold.

The soda salt can be obtained from the acid by treating with NaOH.

Reducing agents form amidotribrombenzolesulpho acid and amidonaphthol.

In concluding, I would say, that I hope next fall to be able to give a much fuller account of these compounds, with the analytical data.

XXIX.—On the Action of Light and Darkness on Standard Ammonium Chloride and Tannin Solutions.

By A. R. Leeds, Ph.D.

In the December number of the Proceedings of the American Chemical Society, for 1878, in a paper " On the Alteration of Standard Ammonium Chloride Solution, when kept in the Dark," I have given a brief resumé of the labors of MM. Schloesing and Muntz on the dependence of nitrification upon the presence of an organized ferment, and of the researches of Mr. R. Warington upon the necessity of darkness to the development of the nitrifying body. A standard ammonium chloride, kept in the dark, was found to contain a determinable amount of nitrites, and the titre of the solution to have diminished by an amount sufficient to unfit it for employment in Nesslerizing. These results were connected, by the author, with the transformation of the elements of ammonia into nitrous acid, under influence of fungoid growth in the dark. At the close of this article, it was stated that two methods of avoiding the change were naturally suggested : " 1st. Keeping the ammonium solutions, not in