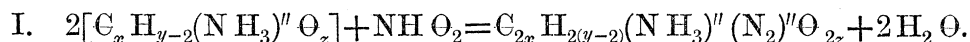XVIII. *On a New Series of Bodies in which Nitrogen is substituted for Hydrogen.*
By Peter Griess, *Esq.* *Communicated by* A. W. Hofmann.

In some former papers* I have had occasion to describe a peculiar class of nitrogen-compounds, obtained by the action of nitrous acid upon amido-compounds, by the exchange of some of the hydrogen of the latter for the nitrogen of the nitrous acid. This substitution may be effected in two different ways; accordingly every amido-compound may give rise to two distinctly different series of bodies. By viewing the amido-compounds as constructed according to the general formula $C_x H_{y-2}(N H_3)'' O_z$†, the changes may be expressed as follows:—

I. $2[C_x H_{y-2}(N H_3)'' O_z] + NH O_2 = C_{2x} H_{2(y-2)}(N H_3)'' (N_2)'' O_{2z} + 2 H_2 O.$

II. $C_x H_{(y-2)} (N H_3)'' O_z + NH O_2 = C_x H_{(y-2)}(N_2) O''_z + 2 H_2 O.$
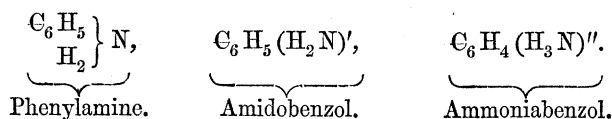
In the first equation one atom of nitrogen is substituted for three atoms of hydrogen contained in *two* atoms of the amido-compound, but in the second the substitution affects only *one* atom of the latter. I have hitherto directed my attention more particularly to the members of the first group, whether derived from amido-acids (such as diazo-amido-benzoic acid), or whether corresponding to amido-bases (diazo-amidobenzol). The bodies which I now shall have to describe in this communication are derived according to the second of the above general equations, and I have restricted myself almost entirely to the study of those which can thus be obtained from aniline and similar bases.

With regard to the chemical nature of these bodies, I may mention generally that they are capable of combining with acids and bases, but that their basic character preponderates. They are remarkable for the great variety of compounds which they

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* Ann. der Chem. und Pharm. Bd. cxiii. p. 201; Bd. cxvii. p. 1; Bd. cxxi. p. 257; Supplement I. 1861, p. 100. Proceedings of the Royal Society, vol. ix. p. 594; vol. x. p. 309.

† Chemists are not agreed upon the rational constitution of amido-compounds. They are frequently referred to the ammonia-type, and almost as frequently to the same type to which the nitro-compounds from which they are derived belong. In the latter case the group NH_2 is considered as replacing one atom, or NH_3 as taking the place of two atoms of hydrogen. Aniline can thus be written in three different ways, and expressed by the three formulæ,

$\left. \begin{array}{c} C_6 H_5 \\ H_2 \end{array} \right\} N,$ $C_6 H_5 (H_2 N)',$ $C_6 H_4 (H_3 N)''.$

Phenylamine.   Amidobenzol.   Ammoniabenzol.

The two latter formulæ appear to me to be capable of explaining in the most natural manner the formation of bodies in which nitrogen is substituted for hydrogen.
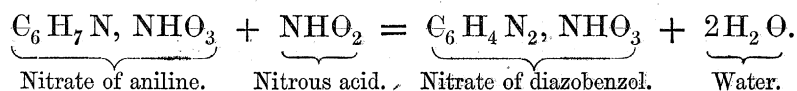
produce, such as is not met with in any other portion of the field of organic chemistry. When in the free state they are remarkable for their instability; their compounds, however, are somewhat more stable; and it is for that reason that the latter have chiefly engaged my attention, and have been employed in the experiments to be described hereafter. The very striking physical properties of these bodies, as well as the large number of products of decomposition to which they give rise, likewise deserve to be specially noticed. Altogether they may be looked upon as one of the most interesting groups of organic compounds. I have avoided, as much as possible, discussing their rational composition, and have abstained from theoretical speculation. I have, however, come to the conclusion that the two atoms (or the molecule) of nitrogen, N_2, they contain must be considered as equivalent to two atoms of hydrogen, and it is in accordance with this view that the names of the new compounds have been framed.

PART I.—COMPOUNDS OF DIAZOBENZOL.

Nitrate of Diabenzol, $C_6H_4N_2, NHO_3$.

This substance can be prepared in various ways; most readily, however, by acting with nitrous acid upon a solution of nitrate of aniline. This salt of aniline is not very soluble in cold water; therefore, in order to obtain a concentrated solution of the new compound, it is best to make a thick paste by grinding up a portion of the nitrate with water and submitting it to the action of the gas, when the undissolved portion of the aniline-salt rapidly disappears, and the whole is converted into the new body. The reaction being accompanied by considerable increase of temperature, it is necessary to keep the solution cool, and to guard against passing a too-rapid current of the gas. The temperature of the solution should not rise much above 30° C. The operation is interrupted as soon as the whole of the aniline has disappeared. This can be ascertained by adding a little strong solution of potassa to a portion of the liquid on a watch-glass, when, if no more aniline is liberated, it may safely be inferred that the reaction is complete. The nitrate of diazobenzol is almost insoluble in ether, and even in ether mixed with much dilute alcohol, in consequence of which it may readily be obtained in a crystalline state thus:—the solution is first filtered, to remove traces of a brown resin, then mixed with about three times its volume of strong alcohol, and ether added until the precipitation is complete. The crystals are allowed to subside, and then filtered from the mother-liquor. The small quantity of the new body which remains in the mother-liquor may be neglected altogether, as its recovery is accompanied with great difficulty. To remove the last traces of colouring matter, the crystals are taken up with cold dilute alcohol and reprecipitated by the addition of ether, when they are obtained as long white needles.

Analysis, as will be shown further, proves that the new compound has the formula $C_6H_4N_2, NHO_3$. Its formation may be explained by the following equation:—

$$\underbrace{C_6H_7N, NHO_3}_{\text{Nitrate of aniline.}} + \underbrace{NHO_2}_{\text{Nitrous acid.}} = \underbrace{C_6H_4N_2, NHO_3}_{\text{Nitrate of diazobenzol.}} + \underbrace{2H_2O}_{\text{Water.}}.$$

Another method of preparing nitrate of diazobenzol is based upon the action of nitrous acid upon diazo-amidobenzol, a body described in a previous communication to the Royal Society. On dissolving this latter compound in cold ether, and passing a current of nitrous acid gas through the solution, long acicular crystals of the new substance soon appear. The action should be continued as long as crystals form. The compound so obtained is collected on a filter and washed with ether. The reaction is expressed by the following equation:—

$$\underbrace{C_{12}H_{11}N_3}_{\text{Diazo-amidobenzol.}} + NHO_2 + 2NHO_3 = \underbrace{2(C_6H_4N_2, NHO_3)}_{\text{Nitrate of diazobenzol.}} + 2H_2O.$$
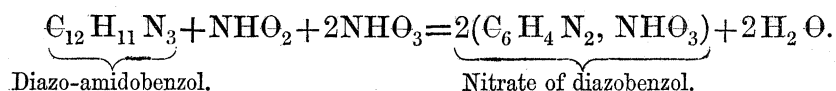
However elegant and simple this method of preparation of the nitrate of diazobenzol may appear, it will scarcely ever be employed, since it involves the previous preparation of diazo-amidobenzol, a body which it is rather troublesome to obtain in large quantities. Nitrate of diazobenzol can also be procured by the direct action of nitrous acid upon a mixture of aniline with about four times its volume of alcohol. The gas is passed into the alcoholic solution till, on the addition of ether to a small portion of it, a copious precipitation of white acicular crystals is produced. When this point is reached, the whole of the reddish-brown solution is mixed with ether, and the precipitate purified as already described.

This method of preparing the nitrate, however, is not suitable when large quantities have to be prepared. It is similar in principle to the preparation by means of diazo-amidobenzol, since to all appearance the aniline is first converted into this compound.

The methods just described, although simple, will only give favourable results when strict attention is paid to the directions given above; for it happens sometimes, and especially when the temperature of the solution is allowed to rise too high, that a copious evolution of nitrogen gas ensues, which cannot be stopped by any means before the whole of the substance has been destroyed.

By employing the first of the above processes, it is sometimes found that, on the addition of ether to the weak alcoholic solution of the crude compound, no crystals separate, but that an aqueous layer is deposited at the bottom of the vessel. This, however, only happens when an insufficient amount of alcohol has been originally added to the solution, because in this case the ether, not being able to mix with the liquor, causes no separation of crystals to take place. If this occurs, it is best to remove the ethereal liquor, and to dilute the residuary aqueous solution with strong alcohol, when, on the addition of ether, crystallization invariably ensues.

The nitrate of diazobenzol, by whatever method it may have been prepared, crystallizes in long white needles, which have been obtained several inches in length and are very soluble in water, less so in alcohol, and almost insoluble in ether and benzol. They can be dried over sulphuric acid without undergoing any change. Heated even below 100° C., they explode with unparalleled violence, far surpassing that of fulminating mer-

cury or iodide of nitrogen. About a gramme of this substance causes by its explosion a concussion like that produced by firing a pistol.

The destructive action of such an explosion is likewise extreme. Iron slabs of several lines in thickness were found smashed to atoms when a somewhat larger quantity was exploded upon them. Friction, pressure, and concussion also cause it to explode. The smallest particles of this substance, accidentally dropped upon the floor of a room, when trodden upon when dry, gave rise to a series of explosions attended with flashes of light. The properties of the nitrate of diazobenzol render it absolutely necessary that the greatest precaution should be observed when manipulating it. The portion of the substance required for analysis having been well washed with ether[*], was placed in a platinum crucible and dried over sulphuric acid. Concussion or pressure had to be carefully avoided, especially with the dry substance, on account of its great explosiveness.

For the above-mentioned reasons I abstained from analyzing this compound in the usual manner, especially as I had opportunities of ascertaining the composition of analogous but less dangerous compounds by the ordinary analytical method. I have, however, been enabled to arrive at a knowledge of the composition of nitrate of diazobenzol by the very interesting change which an aqueous solution undergoes by the action of heat. By ebullition the compound is transformed under the influence of the water into carbolic acid, nitrogen, and nitric acid; and by estimating the quantities of the two latter products I have arrived at the true composition of the explosive substance.

$$\underbrace{C_6 H_4 N_2, NHO_3} + H_2 O = \underbrace{C_6 H_6 O} + NHO_3 + N_2.$$

Nitrate of diazobenzol.   Carbolic acid.
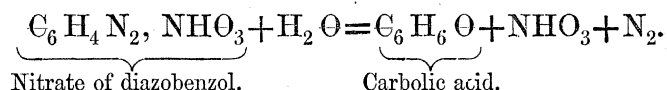
The method employed for the determination of the quantity of nitrogen evolved by the ebullition of the aqueous solution of the explosive compound is as follows:—The solution was introduced into a flask and a stream of carbonic acid gas passed through it. When the air was expelled, the delivery-tube was placed under a graduated cylinder containing solution of potassa, and the contents of the flask heated to ebullition[†].

[*] When it is intended to recover the ether employed in the preparation of nitrate of diazobenzol, it is advisable, in order to avoid explosions, to shake the ethereal mother-liquor first with a little water, so as to dissolve any traces of the diazo-compound suspended in it. I have had a most dangerous explosion by neglecting this simple precaution. A large quantity of ether, which had been employed for the precipitation of the new compound from its alcoholic solution, had accumulated. From this liquid a few crystals had been observed to have separated. Their number seemed, however, to be so small, that it was deemed unnecessary to remove them from the vessel containing the ethereal liquid for distillation. As soon as the vessel became warm in the water-bath, and before the boiling-point of the ether had been reached, a fearful explosion took place, shattering the whole of the distilling apparatus to pieces and setting fire to the ether, the flame of which spread most alarmingly through the laboratory. The gas-flames, which were burning at the time in the room, were suddenly extinguished by the violent pressure upon the atmosphere, and all those working in the laboratory (who fortunately escaped unhurt) were for a moment deprived of their breath. The explosive properties of the nitrate of diazobenzol may perhaps at a future period find practical application.

[†] In all analyses mentioned herein the analyzed substances are understood to be desiccated by sulphuric acid previously, unless the contrary is distinctly stated.

I. 0.605 grm. of the compound, treated as above, gave 80.4 cub. centims. of nitrogen at $0°$, and 760 millims. bar. pressure$=0.101$ grm. of nitrogen, or 16.70 per cent.

Theory.	Experiment.
$N=16.77$	16.70

II. $.492$ grm. of substance, dissolved in water and boiled, required for neutralization 29.5 cub. centims. of alkali solution, corresponding to 0.185 grm. of nitric acid, or 37.77 per cent.

	Calculated.		Found.
$C_6 H_4 N_2$	190	62·27	——
NHO_3	63	37·73	37·77
	253	100·00	

Sulphate of Diazobenzol, $C_6 H_4 N_2, SH_2 O_4$.

Acid sulphate of aniline, when treated with nitrous acid, is converted into sulphate of diazobenzol according to the equation

$$* C_6 H_7 N, S H_2 O_4 + NHO_2 = C_6 H_4 N_2, S H_2 O_4 + 2 H_2 O.$$

Acid sulphate of aniline.   Sulphate of diazobenzol.
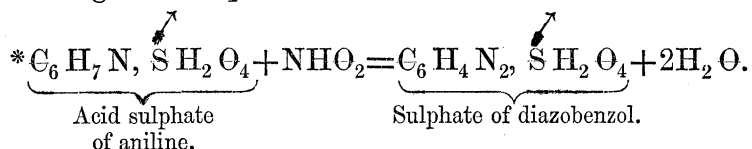
On account of the slight solubility of sulphate of aniline, and in order to avoid employing a large quantity of liquid, it becomes necessary to suspend the salt in water, and to expose it in this state to the action of nitrous acid. The reaction, however, is very slow, and the salt is only gradually converted into the diazo-compound. I found it therefore more convenient to prepare the sulphate from the nitrate of diazobenzol, by treating a concentrated aqueous solution† of the latter with a sufficient quantity of sulphuric acid, previously diluted to avoid rise of temperature upon addition.

The solution thus obtained is then mixed with three times its volume of absolute alcohol, and lastly with a sufficient amount of ether, which causes the sulphate of diazobenzol, together with some water, to separate in a layer at the bottom of the vessel, the liberated nitric acid, together with the excess of sulphuric acid, remaining mixed with the supernatant alcohol and ether. This latter is decanted, and the solution of the sulphate (with a view to the removal of a further quantity of water) is once more treated with absolute alcohol and reprecipitated by means of ether. The precipitated liquid is then placed in flat dishes over sulphuric acid, when it soon solidifies to a magma of white crystals. In order to purify these crystals completely, they are washed on a filter with a mixture of alcohol and ether, which removes any trace of sulphuric and carbolic acids which may have been produced by a partial decomposition of the sulphate of diazobenzol, then dissolved in weak cold alcohol, and precipitated by the addition of

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* Ordinary sulphate of aniline containing excess of free sulphuric acid is understood by this formula.

† The crude solution obtained by the action of nitrous acid upon nitrate of aniline may be employed.

ether. The crystals are separated without delay from the mother-liquor and dried over sulphuric acid.

0·4848 grm. of substance gave 0·6278 grm. of carbonic acid gas and 0·1397 grm. of water, corresponding to 35·32 per cent. of carbon and 3·20 per cent. of hydrogen.

0·4185 grm. gave, on boiling with water, 44·7 cub. centims. of nitrogen at 14° C. and 763 millims. bar. pressure =44·9 cub. centims., at 0° and 760 millims. bar. pressure =0·05642 grm., or 13·49 per cent.

		Calculated.	Found.
C_6	72	35·65	35·32
H_6	6	2·97	3·20
N_2	28	13·86	13·49
S	32	15·83	——
O_4	64	31·69	——
	202	100·00	

For the estimation of the sulphuric acid 0·558 grm. of substance, precipitated by chloride of barium, gave 0·647 grm. of sulphate of barium, corresponding to 48·76 per cent. of sulphuric acid.

		Calculated.	Found.
$C_6 H_4 N_2$	104	51·49	——
$S H_2 O_4$	98	48·51	48·76
	202	100·00	

Sulphate of diazobenzol crystallizes in prisms, which readily dissolve in water, but are soluble with difficulty in absolute alcohol and insoluble in ether. The aqueous as well as the alcoholic solution is decomposed on boiling with evolution of gas. Exposed to the air, this compound attracts moisture very rapidly and becomes liquid, and gradually decomposes. Heated alone, it deflagrates feebly at about 100° C.

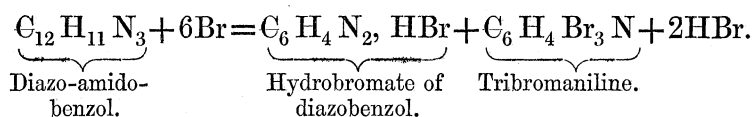### *Hydrobromate of Diazobenzol*, $C_6 H_4 N_2$, HBr.

This compound is prepared by the action of bromine upon diazo-amidobenzol. When an ethereal solution of bromine is gradually added to a rather concentrated solution of the diazo-amido-compound, each drop of the bromine-solution is seen to produce a precipitation of the hydrobromate of diazobenzol. When no more crystals are formed the precipitate is separated from the mother-liquor, washed with ether till quite white, and then dried over sulphuric acid. All these operations must be performed as speedily as possible, since the new compound is of a very unstable nature and rapidly decomposes.

Should it be found necessary to recrystallize the precipitate, it must be dissolved in the least possible quantity of cold alcohol, and ether added to the solution till no more precipitation takes place.

0·3025 grm. of the substance gave, on precipitation with nitrate of silver, 0·304 grm. of bromide of silver, corresponding to 43·3 per cent. of hydrobromic acid.

	Calculated.		Found.
$C_6 H_4 N_2$	104	56·22	——
HBr	81	43·78	43·30
	185	100·00	

Hydrobromate of diazobenzol crystallizes in white nacreous scales, which, like the compound previously described, are readily soluble in water, less so in alcohol, and insoluble in ether. The solution of this compound is distinguished by a strong acid reaction. Heat, friction, and pressure cause the crystals of the hydrobromate to explode with the same violence as the nitrate of diazobenzol. Even when in a perfectly dry state this compound can only be kept for a short time without undergoing decomposition (which is accompanied by the production of a peculiar aromatic odour), the decomposition being complete in a few days. It is formed according to the equation

$$C_{12} H_{11} N_3 + 6Br = C_6 H_4 N_2, HBr + C_6 H_4 Br_3 N + 2HBr.$$

Diazo-amido-   Hydrobromate of   Tribromaniline.
benzol.   diazobenzol.

Tribromaniline remains in the ethereal mother-liquor, from which it crystallizes on evaporation.

It is most likely that, by the action of chlorine upon diazo-amidobenzol, hydrochlorate of diazobenzol may be obtained. An aqueous solution of this latter compound, however, may also be prepared by treating a solution of the hydrobromate with moist chloride of silver.

Perbromide of Diazobenzol, $C_6 H_4 N_2, HBr, Br_2$.

On adding a small quantity of bromine-water to an aqueous solution of the nitrate of diazobenzol, a white crystalline precipitate of tribromophenylic acid is usually obtained, owing to the presence of a small quantity of phenylic acid formed by the spontaneous decomposition of the nitrate by water. On removing the tribromophenylic acid as quickly as possible by filtration, and on the addition of a large excess of bromine-water containing free hydrobromic acid to the filtrate, the new bromine-compound separates as a brownish-red oil, which solidifies to a crystalline mass soon after the supernatant liquor has been removed. The crystals are obtained pure for analysis by washing with a little ether.

I. 0·7154 grm. gave 0·5504 grm. CO_2, corresponding to 20·98 per cent. of carbon and 1·60 of hydrogen.

II. 0·4805 grm. of this substance, digested with excess of aqueous ammonia *, gave, on expulsion of the excess of ammonia and precipitation with nitrate of silver, 0·8005 grm. of bromide of silver, corresponding to 70·68 bromine per cent.

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* The transformation which this substance thus undergoes, and which renders it possible to determine the bromine in this manner, will be fully explained further on.

	Calculated.		Found.
C_6	72	20·87	20·98
H_5	5	1·45	1·60
N_2	28	8·12	——
Br_3	240	69·56	70·89
	345	100·00	

Perbromide of diazobenzol, which crystallizes in yellow plates, is insoluble in water, rather difficultly soluble in alcohol, and insoluble in ether. It is comparatively stable when in a dry state. Its alcoholic solution, on the other hand, rapidly decomposes, even in the cold, with evolution of gas. For this reason it is impossible to recrystallize it without loss. In order to purify this unstable perbromide, it is most advantageous to dissolve it in cold alcohol, and to allow the solvent to evaporate spontaneously in shallow vessels in the open air. Very fine crystals are usually obtained in this manner, but contaminated with trifling quantities of an oily product of decomposition, which, however, may be removed by washing with a little cold ether. On application of heat this compound deflagrates at a comparatively low temperature. The constitution of the perbromide of diazobenzol seems the same as the periodide of tetrethylammonium and similar compounds of other bases.

Platinum-salt of Hydrochlorate of Diazobenzol, $C_6 H_4 N_2$, HCl, $PtCl_2$,

is obtained by the addition of bichloride of platinum to a rather concentrated aqueous solution of the nitrate of diazobenzol. The fine yellow prisms which are precipitated are almost insoluble in alcohol and ether. They are rather stable; when kept for some time, however, they acquire a brownish colour, and are gradually but completely decomposed. On heating they deflagrate, hence it is impossible to estimate the platinum by simple ignition.

0·760 grm., ignited with carbonate of sodium, gave 0·241 grm. of platinum, corresponding to 31·71 per cent.

$$C_6 H_4 N_2, HCl, PtCl_2.$$

Theory.	Experiment.
Pt=31·82	31·71

Gold-salt of Hydrochlorate of Diazobenzol, $C_6 H_4 N_2$, HCl, $AuCl_3$.

By the addition of terchloride of gold to a dilute aqueous solution of the nitrate of diazobenzol, this compound is obtained in the form of a light-yellow crystalline precipitate, insoluble in water, but soluble in alcohol, especially when warm, from which, on cooling, it is deposited in the form of small golden-yellow plates. This salt cannot, however, be recrystallized without some loss, especially when the alcoholic solution is heated to boiling. The decomposition is indicated invariably by an evolution of gas; continued boiling with alcohol destroys it completely. 0·6965 grm. of this salt

gave, on precipitation with sulphuretted hydrogen and ignition of the tersulphide of gold, 0·309 grm. of gold, corresponding to 44·36 per cent. of that metal.

$$C_6 H_4 N_2, HCl, Au Cl_3.$$

	Theory.	Experiment.
Gold	44·37	44·36

It is well known that when bromine, chlorine, or hyponitric acid is substituted in organic compounds for certain hydrogen atoms, the product formed is distinguished from the original compound, if the latter be an acid, by stronger acid properties, or if a base, by less pronounced basic characters; and also that the contrary is observed in the case of substitution of potassium, NH_2, &c. for the same hydrogen atoms.

Nitrogen, however, exhibits in this respect a peculiar double nature, since it is found only slightly (or not at all) to affect the basic properties of a compound, whilst at the same time it exerts so decided an acidulating action as to impart to strong bases an acid nature. I have already clearly shown that diazobenzol has all the characters of an organic base, capable, like aniline, of forming with acids saline compounds. It possesses, at the same time, the property of combining with metallic hydrates, playing, to a certain extent, the part of an acid. These metallic derivatives are, as a rule, distinguished by the same instability as the compounds of diazobenzol with acids. They are less affected, however, by heat. Their aqueous or alcoholic solutions can be heated to boiling for some time without suffering complete decomposition. Heated alone they explode, although at a much higher temperature, and not with so great violence as the bodies previously described. The compounds which are soluble in water are mostly well crystallized, whilst the insoluble ones, such as those formed with silver and lead, are obtained as amorphous precipitates.

Compound of Hydrate of Potassium with Diazobenzol, $C_6 H_4 N_2, KHO.$

By introducing a very concentrated solution of nitrate of diazobenzol into an excess of an equally concentrated solution of caustic potash, drop by drop, a yellowish liquid is obtained possessing a peculiar aromatic odour, and solidifying, by evaporation in the water-bath, to a crystalline mass. This is a mixture of the compound of hydrate of potassium with diazobenzol and nitre, together with a brownish-red amorphous body— the result of a secondary reaction, which a portion of the original substance undergoes, and which is always indicated by the evolution of gas. In order to separate these bodies it is necessary to remove the excess of caustic potash. This is best done by putting the crystalline mass into a strong linen cloth and squeezing it powerfully between porous stones. The dry cake is then treated with absolute alcohol, which readily dissolves the compound of hydrate of potassium with diazobenzol, leaving the nitrate of potassium insoluble; it is then separated by filtration. The alcoholic filtrate (which, on account

of the above-mentioned secondary product of decomposition, possesses an intense reddish-brown colour) is then evaporated on the water-bath. The residue is once more pressed and washed with a mixture of alcohol and ether to remove the reddish-brown substance, when the compound is obtained nearly white. By again pressing and dissolving the dry cake in a small quantity of absolute alcohol, filtering, and adding a sufficient amount of ether, the substance is obtained in white plates, which must be dried at once over sulphuric acid.

0·735 grm. gave 0·3992 grm. of sulphate of potassium, corresponding to 35·00 per cent. of KHO.

	Calculated.		Found.
$C_6 H_4 N_2$	104	64·92	——
KHO	56·2	35·08	35·00
	160·2	100·00	

The compound of hydrate of potassium with diazobenzol crystallizes in small, white, soft plates, which become reddish by exposure to the air; they are very readily soluble in water and alcohol, but insoluble in ether. The solution has a strong alkaline reaction. A freshly prepared aqueous solution is but slightly coloured; but by keeping for a short time it rapidly acquires a yellow colour, and ultimately a reddish-yellow substance is precipitated. Ebullition does not seem to accelerate this decomposition materially. The dry substance is very stable, and can be kept a long time unchanged. Heated alone it explodes at a little above 130°; the explosion is accompanied by a slight report.

Compound of Hydrate of Silver with Diazobenzol, $C_6 H_4 N_2$, Ag HO*.

This is obtained as a white or slightly chocolate-coloured precipitate, by treating a freshly prepared solution of the previous compound with a solution of nitrate of silver. After removing the mother-liquor, the precipitate is thoroughly washed with water, dried by pressing between filter-paper, and finally over sulphuric acid.

0·5830 grm. gave 0·6772 grm. of CO and 0·126 grm. of water, corresponding to 31·68 per cent. of carbon and 2·40 per cent. of hydrogen.

0·9645 grm. gave 0·5955 grm. of chloride of silver, corresponding to 46·46 per cent. of silver.

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* It deserves notice that diazo-amidobenzol and the analogous double compounds likewise combine with bases. When speaking of these bodies (Ann. der Chem. und Pharm. Bd. cxxi, p. 362) I have pointed out that they all possess the property of forming insoluble precipitates with nitrate of silver. Without examining these precipitates more closely, I then came to the conclusion that (judging from the manner in which they were obtained, and taking a few silver-determinations into consideration), they were simply combinations of the respective diazo-amido-compound with nitrate of silver. This view has proved erroneous ; for, on closer examination, it was found that these bodies contain no nitric acid, but must be regarded as combinations of silver with diazo-amido-compounds, viz. $C_{12} H_{11} N_3$, Ag. I intend subsequently to refer to this subject.

	Theory.		Experiment.
C_6	72	31·44	31·68
H_5	5	2·19	2·40
N_2	28	12·23	——
Ag	108	47·16	46·46
O	16	6·98	——
	229	100·00	

The compound of hydrate of silver with diazobenzol is insoluble in all the ordinary neutral solvents. Nitric acid even when cold dissolves it with great facility. It is distinguished by great stability; for even after having been kept for weeks, not the least sign of decomposition could be discovered. Exposed to a higher temperature it explodes with some violence. Since the constitution of the two compounds just described affords sufficiently fixed data for establishing the composition of other combinations of metallic hydrates with diazobenzol, I have not thought it necessary to extend my analyses to the other salts.

Their preparation and constitution, moreover, present no important characteristics, and I will therefore describe them very briefly.

Compound of Hydrate of Barium with Diazobenzol

is obtained when a solution of a very soluble barium-salt is added to a rather concentrated solution of the potassium-compound. It is precipitated in the form of white, microscopic, indistinct needles or plates, which become yellowish in consequence of a gradual decomposition. It is difficultly soluble in water.

The compound of diazobenzol with hydrate of zinc is a white amorphous powder insoluble in water. The compound with hydrate of lead is also a white powder, but acquiring rapidly a yellow colour. With sulphate of copper a brown precipitate changing to green is obtained. Mercurial chloride gives no precipitate.

Diazobenzol, $C_6 H_4 N_2$.

This remarkable substance is obtained when an aqueous solution of the compound of hydrate of potassium with diazobenzol is treated with a sufficient quantity of acetic acid. A thick yellow oil is liberated, which possesses a peculiar odour, and is remarkable for its extraordinary instability. Its existence is very ephemeral, and after a short time nitrogen gas begins to be evolved, and the oil is rapidly converted into a brownish-red substance. The heat which is produced when larger quantities of the oil undergo this spontaneous decomposition is sufficient to give rise to dangerous explosions.

The addition of ether to the oil dissolves it instantaneously, producing a red solution, a tumultuous evolution of gas taking place. It combines with nitric and sulphuric acids, and with hydrate of potassa, terchloride of gold, &c., forming the compounds previously described.

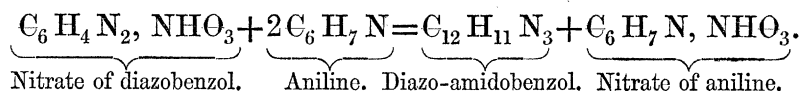COMPOUNDS OF DIAZOBENZOL WITH ORGANIC BASES.

Diazo-amidobenzol, as is well known, is formed by the action of nitrous acid upon an alcoholic solution of aniline, according to the equation

$$\underbrace{2C_6 H_7 N}_{\text{Aniline.}} + NHO_2 = \underbrace{C_{12} H_{11} N_3}_{\text{Diazo-amidobenzol.}} + 2H_2 O.$$
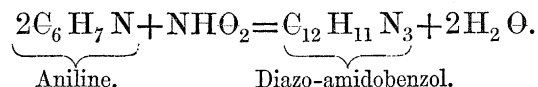
By viewing this body as a double compound of diazobenzol and aniline,

$$C_{12} H_{11} N_3 = \begin{cases} C_6 H_4 N_2, \\ C_6 H_7 N \end{cases}$$
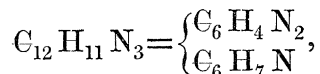
I was led to prepare it by the direct action of aniline upon compounds of diazobenzol. This reaction proceeds readily on mixing an aqueous solution of nitrate of diazobenzol with aniline, when a viscid yellow mass is speedily produced, which becomes crystalline after a short time, and which can be obtained in a perfectly pure state by several recrystallizations * from alcohol. The formation of the diazo-amidobenzol may be expressed as follows:—

$$\underbrace{C_6 H_4 N_2, NHO_3}_{\text{Nitrate of diazobenzol.}} + \underbrace{2 C_6 H_7 N}_{\text{Aniline.}} = \underbrace{C_{12} H_{11} N_3}_{\text{Diazo-amidobenzol.}} + \underbrace{C_6 H_7 N, NHO_3}_{\text{Nitrate of aniline.}}.$$

On referring to the equation given on page 669 for the formation of nitrate of diazobenzol from diazo-amidobenzol,

$$C_{12} H_{11} N_3 + NHO_2 + 2NHO_3 = 2(C_6 H_4 N_2, NHO_3) + 2H_2 O,$$
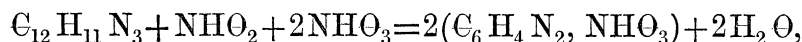
it is seen that these two bodies may be readily transformed into one another.

Many other bases deport themselves with nitrate of diazobenzol exactly like aniline, and we may therefore look forward to the discovery of a large number of double compounds analogous to diazo-amidobenzol.

It is not my intention to give a full history of these compounds, as a few short statements will show clearly how closely they are allied to their prototype diazo-amidobenzol.

Diazobenzol-amidobromobenzol, $\begin{cases} C_6 H_4 N_2 \\ C_6 H_6 Br N \end{cases}$.

This compound is obtained by the action of bromaniline upon nitrate of diazobenzol. It crystallizes in very fine small yellow plates or needles, which are rather difficultly soluble in alcohol, but readily soluble in ether. Its platinum-salt,

$$C_{12} H_{10} Br N_3, H_2 Cl_2, 2 Pt Cl_2,$$
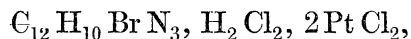
is obtained as a buff-coloured precipitate consisting of fine hair-like crystals. Nitrate of silver produces, in an alcoholic solution, a yellow precipitate similar to that of the compound previously described.

* Any excess of aniline must be removed by means of acetic acid before crystallization.

In the formation of the above bodies two atoms of base enter into chemical action with one atom of nitrate of diazobenzol, forming, together with the diazo-amido-compound, the nitrate of the base employed. Naphtalidine (amidonaphtol), however, combines directly in equal numbers of atoms with nitrate of diazobenzol, giving rise to a compound which has the formula

$$C_{16} H_{14} N_4 O_3,$$
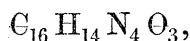
and which, as will be shown, must be viewed as nitrate of diazobenzol-amidonaphtol. This compound is obtained in an impure state as a violet crystalline precipitate on adding an aqueous solution of nitrate of diazobenzol to an alcoholic solution of naphtalidine. It is purified by repeated washings with cold alcohol and recrystallization from the same, forming beautiful green prisms.

0·2303 grm. gave 0·5235 grm. of carbonic acid and 0·0975 grm. of water, corresponding to 61·99 per cent. of carbon and 4·70 per cent. of hydrogen.

These numbers lead to the formula

$$C_{16} H_{14} N_4 O_3 = \left.\begin{array}{c} C_6 \ H_4 \ N_2 \\ C_{10} \ H_9 \ N \end{array}\right\} NHO_3.$$
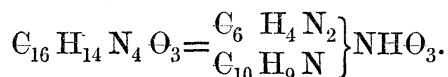
	Calculated.		Found.
C_{16}	192	61·94	61·99
H_{14}	14	4·52	4·70
N_4	56	18·06	——
O_3	48	15·48	——
	310	100·00	

The new compound is formed according to the equation

$$C_6 H_4 N_2, NHO_3 + C_{10} H_9 N = C_{16} H_{14} N_4 O_3.$$

Nitrate of diazo-benzol.   Naphtalidine.   Nitrate of diazo-benzol-amidonaphtol.
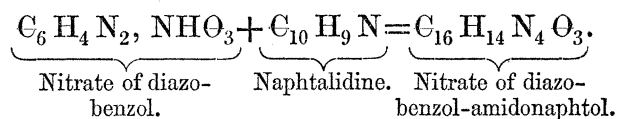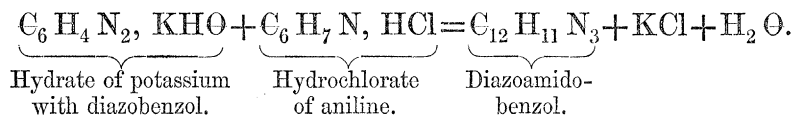
It is one of the finest bodies of which chemistry can boast. It crystallizes in well-defined prisms, which by reflected light are of a magnificent grass-green colour, but ruby-red by transmitted light. The crystals are almost insoluble in water and ether. Hot alcohol dissolves them freely, and redeposits them almost entirely on cooling.

$$\textit{Diazobenzol-amidonaphtol,} \left.\begin{array}{c} C_6 \ H_4 \ N_2 \\ C_{10} \ H_9 \ N \end{array}\right\}.$$
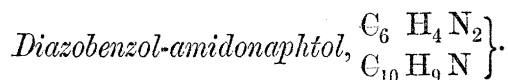
This compound is obtained from the previous substance by removing the nitric acid by means of ammonia or potassa. It crystallizes in very brilliant ruby-red prisms, readily soluble in alcohol and ether, forming yellow liquids. Acids impart a beautiful violet colour to these solutions. Bichloride of platinum produces a purple-blue crystalline precipitate; nitrate of silver a yellow precipitate, which consists of small fine needles.

It is worth mentioning that these diazobenzol-amido-compounds can also be obtained by acting with an aqueous solution of the salts of the respective bases upon the com-

pound of hydrate of potassium with diazobenzol. The reaction which takes place may be expressed by the following equation:—

$$C_6 H_4 N_2, KHO + C_6 H_7 N, HCl = C_{12} H_{11} N_3 + KCl + H_2 O.$$

Hydrate of potassium   Hydrochlorate   Diazoamido-
with diazobenzol.   of aniline.   benzol.

COMPOUNDS OF DIAZOBENZOL WITH AMIDO-ACIDS.

Amido-acids are likewise capable of entering into combination with diazobenzol. One would have expected that the compounds to which this reaction gives rise would deport themselves in an analogous manner to the sulphate or nitrate of diazobenzol, which, like the salts of organic bases, are capable of double decomposition. This, however, is not the case. The compounds of diazobenzol with amido-acids behave more like simple bodies, exhibiting much similarity to the diazo-amidobenzol, being capable, like the latter, of forming, with bichloride of platinum, double compounds of the nature of the potassio-bichloride of platinum. They possess, moreover, the property of combining with metals, giving rise to bodies which correspond entirely to the salts of simple acids.

$$\textit{Diazobenzol-amidobenzoic acid,} \begin{cases} C_6 H_4 N_2 \\ C_7 H_7 NO_2 \end{cases}.$$
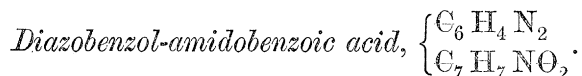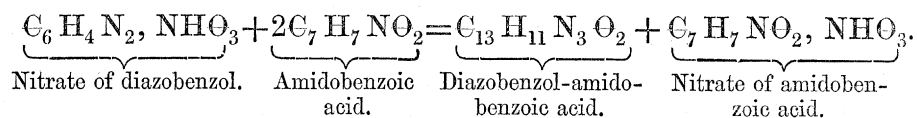
This compound is obtained by simply mixing an aqueous solution of the nitrate of diazobenzol (1 molecule) with a solution of amidobenzoic acid (2 molecules). It separates as a yellow crystalline precipitate which is readily freed from the mother-liquor, and when dry dissolved in ether and filtered. The ethereal solution deposits on evaporation yellow crystals, which are obtained pure for analysis by washing with cold alcohol.

0·3333 grm. of substance gave 0·785 grm. at CO_2 and 0·1458 grm. of water, corresponding to 64·23 per cent. of carbon and 4·86 per cent. of hydrogen.

0·49 grm. gave 68·8 cub. centims. of nitrogen at 0° C. and 760 millims. pressure, =17·4 per cent.

		Theory.	Experiment.
C_{13}	156	64·73	64·23
H_{11}	11	4·56	4·86
N_3	42	17·43	17·65
O_2	32	13·28	——
	241	100·00	

This body is formed according to the equation

$$C_6 H_4 N_2, NHO_3 + 2C_7 H_7 NO_2 = C_{13} H_{11} N_3 O_2 + C_7 H_7 NO_2, NHO_3.$$

Nitrate of diazobenzol.   Amidobenzoic   Diazobenzol-amido-   Nitrate of amidoben-
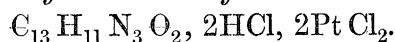   acid.   benzoic acid.   zoic acid.

Diazobenzol-amidobenzoic acid forms small indistinct plates or crystalline grains. It

is almost insoluble in water, very difficultly soluble in alcohol, and easily soluble in ether. Solutions of ammonia, potash, or carbonate of potassium dissolve the acid readily, the solution acquiring a yellow colour. On heating a little of the substance on platinum-foil, it fuses and is rapidly decomposed, the decomposition being accompanied by a violent evolution of gas.

Cold dilute mineral acids act upon it but slowly; on heating, however, speedy decomposition ensues. Acetic acid, even when highly concentrated, has no action in the cold, but on the application of heat destroys it.

Platinum-salt of the Hydrochlorate of Diazobenzol-amidobenzoic Acid,
$$C_{13} H_{11} N_3 O_2, 2HCl, 2Pt Cl_2.$$

This compound forms small yellowish-white indistinct plates, and is obtained by adding an alcoholic solution of bichloride of platinum to the ethereal solution of the diazo-benzol-amidobenzoic acid.

0·7455 grm. of the substance gave, on ignition with carbonate of sodium, 0·234 grm. of platinum.

$$C_{13} H_{11} N_3, H_2 Cl_2, 2Pt Cl_2.$$

Calculated.	Found.
Pt = 30·80	31·39

Diazobenzol-amidobenzoic acid in its behaviour with bases is similar to a bibasic acid, since it combines with metallic bodies in two ways. All the salts formed are comparatively stable; those, *e. g.*, which are soluble in water, as the potassium-salt, will even bear recrystallization. With the oxide of silver and barium it forms insoluble precipitates. A more minute description of these compounds I must defer to a future time.

Compounds analogous to the diazobenzol-amidobenzoic acid are formed when amido-dracylic acid (isoamidobenzoic acid), amidoanisic acid, &c. are made to react in the manner previously described upon nitrate of diazobenzol. It is my intention to investigate these compounds more specially, and I therefore abstain from entering further upon their description, only noticing that they possess a remarkable resemblance to diazobenzol-amidobenzoic acid.

IMIDOGEN COMPOUNDS OF DIAZOBENZOL.

By this name are designated a peculiar class of diazobenzol-compounds obtained by the action of ammonia, ethylamine, and analogous organic bases upon perbromide of diazobenzol ($C_4 H_4 N_2$, HBr, Br_2). All the compounds hitherto described exist in a solid state, and none of them can be volatilized without decomposition; the new compounds to be described, on the other hand, are liquors which can be distilled, and which possess the narcotic odour of some vegetable bases, such as conidine and nicotine. Beyond this odour, however, they have nothing in common with these natural bases. They are indifferent bodies, combining with neither acids nor bases.

$$\textit{Diazobenzolimide, } C_6H_5N_3 = \begin{array}{c} (C_6H_4N_2)'' \\ H \end{array} \Big\} N.$$
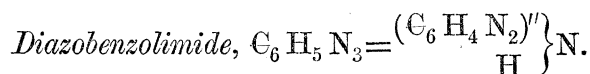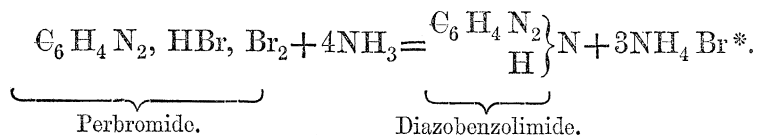
On treating perbromide of diazobenzol with aqueous ammonia, a speedy decomposition ensues with evolution of much heat. The products of the reaction are, first, bromide of ammonium, this passes into solution; secondly, diazobenzolimide, which separates as a heavy oil, rather highly coloured by a brown substance simultaneously produced in small quantity. By repeatedly distilling the oil with water it is obtained perfectly pure, and of a slightly yellowish colour; the substance which imparts to it the intense brownish colour, not being volatile, is left behind in the retort. The purified oil is separated from the water by means of a separating funnel, placed over chloride of calcium, and then distilled once more from a water-bath *in vacuo*.

0·1148 grm. gave 0·253 grm. carbonic acid and 0·0505 grm. of water.

		Calculated.	Found.
C_6	72	60·50	60·10
H_5	5	4·20	4·88
N_3	42	35·30	——
	119	100·00	

Its formation is explained by the following equation:—

$$C_6H_4N_2, HBr, Br_2 + 4NH_3 = \begin{array}{c} C_6H_4N_2 \\ H \end{array} \Big\} N + 3NH_4Br*.$$

$\underbrace{\qquad\qquad}_{\text{Perbromide.}}$ $\underbrace{\qquad\qquad}_{\text{Diazobenzolimide.}}$

Diazobenzolimide is remarkable for its narcotic, aromatic-ammoniacal odour. It is volatilized by distillation with water, and also when heated *in vacuo*, as shown above. Distilled at the ordinary atmospheric pressure, it is decomposed with explosive violence. Alcohol and ether dissolve it rather difficultly. I could not succeed in solidifying the oil by using a frigorific mixture of nitre and sal-ammoniac. Hydrochloric acid, even when concentrated, and aqueous potassa have no effect upon it. Strong nitric and sulphuric acids dissolve it with decomposition.

$$\textit{Ethyldiazobenzolimide} = \begin{array}{c} (C_6H_4N_2)'' \\ C_2H_5 \end{array} \Big\} N.$$
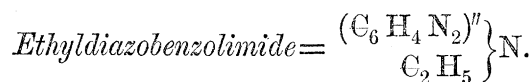
This body is obtained in a manner exactly similar to the one employed for the preparation of diazobenzolimide, viz. by acting with ethylamine upon the perbromide of diazobenzol. It is likewise a yellowish-coloured oil, having a deceptive resemblance to the previously described compound.
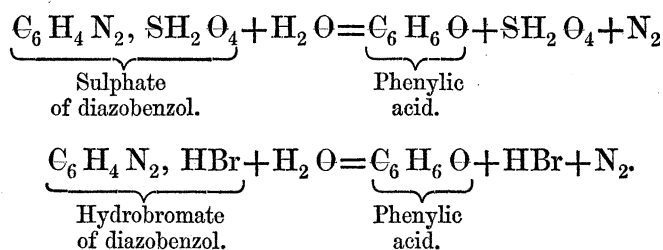
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* This decomposition of the perbromide explains the method of analysis adopted for the estimation of the bromine described in page 673.

PRODUCTS OF DECOMPOSITION OF THE DIAZOBENZOL COMPOUNDS.

The transformations which the molecule of diazobenzol undergoes through the influence of various reagents are numerous, and there is probably no other body to be met with in the large field of organic chemistry that surpasses it in this respect. The products of decomposition to which it gives rise frequently possess new and very distinctive features; more frequently, however, they belong to the benzol or phenyl group, in which latter case their formation depends upon the great inclination which the two nitrogen atoms of the diazobenzol exhibit to escape and to cede their place to other atomic groups of the same value (HH).

Deportment of Diazobenzol Compounds when boiled in an aqueous solution.

The transformation of nitrate of diazobenzol, under the influence of boiling water, has already been noticed. A similar change is observed with regard to its sulphate and hydrobromate, as will be seen from the following equations:—

$$\underbrace{C_6 H_4 N_2, SH_2 O_4}_{\substack{\text{Sulphate} \\ \text{of diazobenzol.}}} + H_2 O = \underbrace{C_6 H_6 O}_{\substack{\text{Phenylic} \\ \text{acid.}}} + SH_2 O_4 + N_2$$

$$\underbrace{C_6 H_4 N_2, HBr}_{\substack{\text{Hydrobromate} \\ \text{of diazobenzol.}}} + H_2 O = \underbrace{C_6 H_6 O}_{\substack{\text{Phenylic} \\ \text{acid.}}} + HBr + N_2.$$
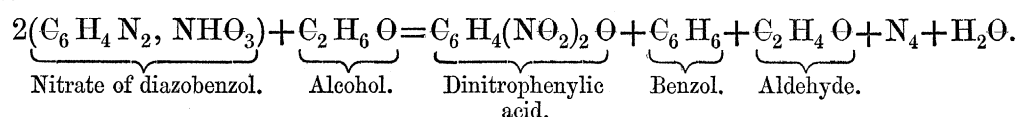
On the other hand, the compounds of diazobenzol with metallic hydrates exhibit a very different deportment with boiling water. By neutralizing the metal, however, with a mineral acid, the decomposition takes place in accordance with the above equations.

Action of Alcohol upon Nitrate of Diazobenzol.

By gradually and cautiously introducing the nitrate of diazobenzol into a moderate quantity of alcohol (previously warmed to about 50° C. in order to accelerate the solution), and submitting the whole to distillation in a water-bath, a yellow residue remains, which solidifies to a crystalline mass on cooling, and dissolves readily in alkaline solutions, whence it was inferred that it had the character of an acid. There was, in fact, no difficulty in ascertaining that this body was nothing else than dinitrophenylic acid, possessing all the well-pronounced properties of this compound; and to prove this most conclusively, it was converted into the characteristic amidonitrophenylic acid. Dinitrophenylic acid, however, is not the only product to which this reaction gives rise; for on mixing the distillate with water an oily body separates, which collects upon the fluid, especially when its specific gravity has been increased by the addition of a solution of chloride of sodium. This oil may be removed by means of a separating funnel and dried over chloride of calcium. It possesses, when rectified by distillation, all the properties of ordinary benzol. I have converted it into dinitrobenzol by the action of fuming nitric acid, and have found this latter identical with that prepared from coal-tar

benzol. The fusing-point of the dinitrobenzol was in both instances 89° C. The production of dinitrocarbolic acid and of benzol can be expressed by the following equation :—

$$2(C_6 H_4 N_2, NHO_3) + C_2 H_6 O = C_6 H_4 (NO_2)_2 O + C_6 H_6 + C_2 H_4 O + N_4 + H_2 O.$$

| Nitrate of diazobenzol. | Alcohol. | Dinitrophenylic acid. | Benzol. | Aldehyde. |

Sulphate of diazobenzol, when distilled with alcohol, is acted upon in a similar manner. The alcoholic distillate contains the benzol, whilst the residue in the flask consists of sulphuric acid and a small quantity of an organic acid.

Deportment of Nitric Acid and Nitrate of Diazobenzol.

Ordinary nitric acid, as well as the fuming acid, has no action upon this compound in the cold. The diazo-compound was dissolved in the strongest fuming nitric acid, allowed to stand for one hour, and cautiously diluted with water so as to prevent any rise of temperature; solution of terchloride of gold was then added, which gave an immediate precipitate. Analysis showed this precipitate to be identical with the gold-salt of hydrochlorate of diazobenzol.

0·8295 grm. gave, on precipitation with sulphuretted hydrogen and ignition of the tersulphide of gold, 0·3685 grm. of gold, corresponding to 44·42 per cent.

$$C_6 H_4 N_2, HCl, Au Cl_3.$$

	Calculated.	Found.
Gold	44·37	44·42

On boiling the solution of nitrate of diazobenzol in fuming nitric acid, trinitrophenylic acid is produced. By employing a somewhat weaker acid, an admixture of tri- and di-nitrophenylic acid is obtained.

Action of Sulphuric Acid upon Sulphate of Diazobenzol.

On dissolving the sulphate in a small quantity of concentrated sulphuric acid, and heating in a water-bath, a copious evolution of nitrogen gas ensues, and a brownish-coloured liquid remains, consisting of a mixture of the excess of acid employed and a new sulpho-acid. The separation of the two acids is readily accomplished by preparing their barium-salts. After diluting the brownish liquid with a sufficient quantity of water and adding carbonate of barium as long as the solution exhibits an acid reaction, the insoluble sulphate of baryta may be separated by filtration from the barium-salt of the new sulpho-acid. The filtrate is evaporated till a pellicle forms, when, on cooling, a large quantity of crystals of the barium-salt of the new sulpho-acid appears. After separating the crystals by filtration, and then evaporating the mother-liquor further and cooling, a new quantity of crystals is obtained. A single recrystallization from water renders them perfectly pure. This salt forms fine, white, well-developed prisms, attaining frequently to the length of half an inch, when the solution is allowed to cool very slowly. The crystals are readily soluble in hot, rather difficultly in cold water, and

almost insoluble in alcohol and ether. The solutions have a neutral reaction. The substance was dried at 160° C.; and on analysis

0·4587 grm. gave 0·3067 grm. of carbonic acid and 0·0649 grm. of water.

0·4505 grm., precipitated with sulphuric acid, gave 0·2495 grm. of sulphate of barium.

0·321 grm., analyzed by CARIUS's method, gave 0·379 grm. of sulphate of barium*.

These numbers lead to the formula

$$C_6 H_6 Ba_2 S_2 O_8.$$

	Theory.		Experiment.
C_6	72	17·70	18·23
H_6	6	1·47	1·55
Ba_2	137	33·66	33·59
S_2	64	15·72	16·21
O_8	128	31·45	——
	407	100·00	

The salt, dried over sulphuric acid, contained $3\frac{1}{2}$ atoms of water of crystallization, which escaped entirely at 130° C. No further loss of water was observed on heating to a higher temperature.
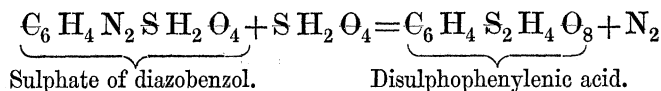
I. 0·5435 grm. of substance, dried over sulphuric acid, and lastly at 130° C., lost 0·0755 grm. of water.

II. 0·5398 grm. was dried at 190° C. and lost 0·073 grm. of water.

$$C_6 H_6 Ba_2 S_2 O_8 + 3\tfrac{1}{2} H_2 O.$$
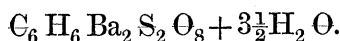
Calculated.	Found.	
	I.	II.
13·44	13·89	13·52

In accordance with the analysis of the barium-salt, the free acid must be expressed by the formula $C_6 H_8 S_2 O_8$, and I propose to call it disulphophenylenic acid, since it may be viewed as a compound of two molecules of sulphuric acid, with the hypothetical hydrocarbon $C_6 H_4$ (phenylene), viz. $C_6 H_4 S_2 H_4 O_8$. Its formation may be thus expressed :—

$$\underbrace{C_6 H_4 N_2 S H_2 O_4}_{\text{Sulphate of diazobenzol.}} + S H_2 O_4 = \underbrace{C_6 H_4 S_2 H_4 O_8}_{\text{Disulphophenylenic acid.}} + N_2$$

The free acid is easily prepared by dissolving the barium-salt in water, carefully precipitating the barium with sulphuric acid, and concentrating the filtrate on a water-bath till it acquires a syrupy consistency; when it is placed over sulphuric acid, it crystallizes out in the form of warty crystals, which are exceedingly soluble in water and alcohol, and deliquesce in a moist atmosphere.

* It is not even requisite to heat the substance with nitric acid in sealed glass tubes; for the sulphur in the substance is entirely converted into sulphuric acid by the action of concentrated nitric acid at the ordinary pressure. The acid is converted into a crystallized nitro-acid, resembling picric acid.

Besides the compound just described, there exists yet another barium-compound of disulphophenylenic acid of the composition $C_6 H_4 S_2 Ba_3 H O_8$, formed by the exchange of a third equivalent of the hydrogen for barium. It is obtained by digesting either the barium-compound with two atoms of barium, or the free disulphophenylenic acid with baryta-water for some time. The excess of baryta is neutralized by carbonic acid, and the filtrate evaporated till it begins to crystallize. The new salt forms very thin white plates, which, on being left for some time in contact with the mother-liquor, are likewise converted into well-formed prisms.

This salt differs, moreover, from the salt containing only two equivalents of barium, by its greater solubility in water[*], and the strong alkalinity of its solutions, which is not destroyed by the carbonic acid. When freshly prepared, the crystals of this compound are clear and transparent; they soon, however, lose a portion of their water of crystallization, and are reduced to a white powder. The substance employed for the following analyses was dried at 160° C., at which temperature the water of crystallization is rapidly given off.

I. 0·4518 grm. of substance gave 0·261 grm. of carbonic acid and 0·0396 grm. of water.

II. 0·3025 grm. gave 0·2225 grm. of sulphate of barium.

	Calculated.		Found.	
			I.	II.
C_6	72	15·18	15·75	——
H_5	5	1·05	0·97	——
S_2	64	13·48	——	——
Ba_3	205·5	43·31	——	43·24
O_8	128	26·98	——	——
	474·5	100·00		

It is possible that two more barium-salts of disulphophenylenic acid exist, of the respective formulæ $C_6 H_4 S_2 Ba H_3 O_8$ and $C_6 H_4 S_2 Ba_4 O_8$.

Disulphophenylenic acid is likewise capable of combining in two proportions with other metals; with lead it seems to combine even more freely, forming apparently no less than five distinct salts, viz. $C_6 H_4 S_2 H_3 Pb O_8$, $C_6 H_4 S_2 H_2 Pb_2 O_8$, $C_6 H_4 S_2 H Pb_3 O_8$, $C_6 H_4 S_2 Pb_4 O_8$, and $C_6 H_4 S_2 Pb_4 O_8 + Pb_2 O$.

The description of the preparation and properties of these bodies will be reserved for a future communication. The silver-salt of disulphophenylenic acid, however, may find a place here, since it exhibits the peculiar chemical deportment of the new acid in a striking manner.

Disulphophenylenate of Silver.—This salt is obtained by treating an aqueous solution of the free acid with carbonate of silver, evaporating the filtrate first on the water-bath, and lastly over sulphuric acid. It crystallizes either in warty masses or in small plates.

---

[*] On preparing the salt $C_6 H_4 S_2 H_2 Ba_2 O_8$, as described above, with excess of carbonate of barium, a certain amount of the second barium-compound is formed, which remains in the mother-liquor from which the first salt has crystallized.

It is easily soluble in water, difficultly so in alcohol, and almost insoluble in ether. It does not contain any water of crystallization. After drying over sulphuric acid it does not lose weight, even when heated to upwards of 160° C.

I. 0·5535 grm. of the salt, dried at 160°, gave 0·3112 grm. of carbonic acid and 0·0443 grm. of water.

II. 0·9153 grm. gave 0·5133 grm. of carbonic acid and 0·0726 grm. of water.

III. 0·502 grm. gave 0·3082 grm. of chloride of silver.

IV. 0·4975 grm. gave 0·302 grm. of chloride of silver.

These numbers lead to the formula $C_6 H_4 S_2 Ag_2 O_7$.

Theory.			Experiment.			
			I.	II.	III.	IV.
C_6	72	15·39	15·33	15·29	——	——
H_4	4	0·85	0·89	0·88	——	——
S_2	64	13·68	——	——	——	——
Ag_2	216	46·15	——	——	46·20	45·69
O_7	112	23·93	——	——	——	——
	468	100·00				

To judge from the composition of the silver-salt of disulphophenylenic acid, it appears to be bibasic ($C_6 H_4 S_2 H_2 O_7$), whilst the formula deduced from its barium and lead salts establishes its tetrabasic character ($C_6 H_4 S_2 H_4 O_8$). The new acid exhibits therefore the rare property of varying basicity, such as is possessed by phosphoric acid in the inorganic, and by terebinic acid in organic chemistry, as shown by EKMAN*.

Action of Sulphuretted Hydrogen upon the Gold-salt of Hydrochlorate of Diazobenzol.

By passing a current of sulphuretted hydrogen gas through cold water in which the gold-salt has been suspended, all the gold is converted into the trisulphide, whilst the diazobenzol is transformed into a volatile product. When the reaction is complete, the liquid is submitted to distillation, when a very nauseous, heavy, yellowish oil is found to pass over with the aqueous vapour. I have not pursued its examination further than to convince myself that it is not the phenylmercaptan ($C_6 H_6 S$) described by VOGT, which at first sight it appeared to be. Its mercaptanic odour and its derivation from the diazobenzol in the gold-compound (according to the equation

$$C_6 H_4 N_2 + SH_2 = C_6 H_6 S + N_2)$$
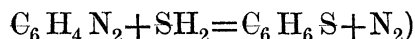
rendered this view very probable. Neither basic acetate of lead, however, nor nitrate of silver, even in the presence of ammonia, gave precipitates with the oil, which proved convincingly that it differed entirely from phenylmercaptan.

On examining the residue in the retort after the oil had been distilled off, it was found to consist of tersulphide of gold and an aqueous liquid; the latter is found to contain chloride of ammonium, together with a little free hydrochloric acid, and a small

* LIMPRICHT, Lehrbuch der Chemie, p. 1016.

quantity of the hydrochlorate of a base which is no other than aniline. The occurrence of these bodies shows that a small portion of the diazobenzol is decomposed as follows:—

$$C_6 H_4 N_2 + 3SH_2 = C_6 H_7 N + NH_3 + 3S.$$
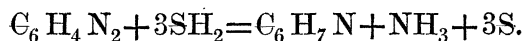
The same products of decomposition are met with when an alcoholic solution of the gold-salt is treated with sulphuretted hydrogen.

On passing the latter, however, over the dry gold-compound, it speedily causes an explosion. By employing only a very small quantity of the substance, and by spreading it in a thin layer in a glass tube, it is possible to avoid explosion and secure a quiet decomposition. The reaction is over when no more hydrochloric acid fumes escape with the current of sulphuretted hydrogen. The black residue which is left behind in the glass tube appears to contain, besides tersulphide of gold, free diazobenzol. I was not able to isolate this latter. The explosive nature of the residue and its deportment with ether, which speedily produces a rapid evolution of gas, leave, however, little doubt of its presence. Hydrochloric acid, tersulphide of gold, and diazobenzol are therefore the products of decomposition of the gold-salt by means of sulphuretted hydrogen.

Action of Nascent Hydrogen upon Diazobenzolimide.

If hydrogen is generated by means of zinc and sulphuric acid in an alcoholic solution of this body, a point is reached in a comparatively short time when, on the addition of water, no more turbidity occurs, indicating that the diazobenzolimide has completely disappeared.

By removing the excess of zinc and evaporating the alcohol on a water-bath, the residue, when treated with potassa, evolves much ammonia, and an oily base simultaneously separates; this is purified by distillation, and is found identical with ordinary aniline. The decomposition may be thus expressed:—

$$\underbrace{C_6 H_5 N_3}_{\text{Diazobenzolimide.}} + 8H = \underbrace{C_6 H_7 N}_{\text{Aniline.}} + 2NH_3.$$
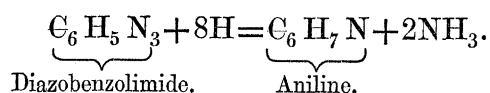
Action of Carbonate of Barium upon Nitrate of Diazobenzol.

By treating a cold aqueous solution of this salt with levigated carbonate of barium, a feeble evolution of gas is observed, which lasts for several days. A reddish-brown mass is produced insoluble in water, which remains with the excess of carbonate of barium when the reaction is over. The residue is a mixture of two distinct bodies. By filtering off the solution containing nitrate of barium and removing the excess of carbonate by means of dilute hydrochloric acid, these two products can be readily separated by treatment with cold alcohol, in which they are very unequally soluble. In order to obtain the more soluble one in a pure state, the alcohol is evaporated and the residue treated with ammonia. An intensely yellow-coloured solution is produced, which must be filtered to remove a small quantity of a resinous substance, and decomposed with hydrochloric acid, when the new compound is precipitated in crystals. These are obtained perfectly pure for analysis by repeated crystallization from weak alcohol.

0·250 grm. of substance gave 0·6679 of carbonic acid and 0·1135 grm. of water, corresponding to 72·52 per cent. of carbon and 5·04 of hydrogen.
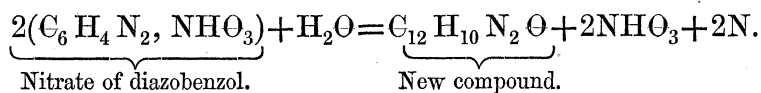
0·307 grm. gave 35·7 cub. centims. of nitrogen at 0° C. and 760 millims. bar. pressure, =0·04461 grm. of nitrogen, or 14·52 per cent.

The following formula is deduced from these numbers:—

$$C_{12} H_{10} N_2 O.$$
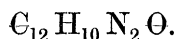
	Calculated.		Found.
C_{12}	144	72·73	72·52
H_{10}	10	5·05	5·04
N_2	28	14·14	14·52
O	16	8·08	——
	198	100·00	

The formation of this compound may be expressed by the following equation:—

$$2(C_6 H_4 N_2, NHO_3) + H_2O = C_{12} H_{10} N_2 O + 2NHO_3 + 2N.$$

$\underbrace{\qquad}_{\text{Nitrate of diazobenzol.}} \qquad \underbrace{\qquad}_{\text{New compound.}}$

It will be readily seen that this formula contains the elements of phenylic acid and diazobenzol *

$$C_6 H_4 N_2 + C_6 H_6 O = C_{12} H_{10} N_2 O,$$
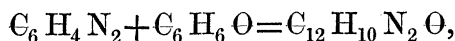
and I will therefore call it phenol-diazobenzol without prejudging its rational constitution. This body usually crystallizes from alcohol and ether (in which it is very easily soluble) in brittle brownish-yellow warts. It is almost insoluble in cold water, slightly so in boiling water, from which, on cooling, it crystallizes in small yet well-formed rhombic prisms of a fine yellow colour, with a tinge of violet. These crystals fuse at 148° C. to a brownish-yellow oil, which cannot be volatilized without decomposition, and is destroyed at a higher temperature with formation of yellow vapour. Although phenol-diazobenzol has the properties of an acid, forming with certain metals saline compounds, its acid character is so slightly pronounced, that it is not even capable of decomposing carbonates. On evaporating a solution of phenol-diazobenzol with aqueous carbonate of potassium to complete dryness, the former will be left behind unaltered. Evaporated with aqueous ammonia, the whole of the ammonia is driven off. Treated with nitrate of silver, a scarlet-red silver compound precipitates, which appears specially suited to serve for the determination of the atomic weight of this compound. It deserves mention that phenol-diazobenzol is isomeric with azoxybenzide. The properties just described show conclusively, however, that it has nothing in common with the latter compound beyond the formula.

The second product of the above-mentioned reaction may usually be obtained per-

* Nitrosoethyline, recently described by GEUTHER and KREUTZHAGE, will probably come under the same class of compounds, since its composition may be expressed by the addition of the hypothetical diazohydride of ethyl and alcohol, viz.,

$$C_2 H_4 N_2 + C_2 H_6 O = C_4 H_{10} N_2 O.$$
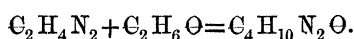
fectly pure by recrystallizing it once or twice from strong alcohol, afterwards dissolving it in ether, and allowing the solution to evaporate spontaneously. Sometimes, however, the crystals are slightly contaminated with traces of a body which has to be removed by means of caustic potassa*, in which the new compound is completely soluble, whilst the foreign substance remains behind as a brown resin. Hydrochloric acid precipitates it from the alkaline solution, and it can now be completely purified by crystallization from alcohol or ether.

I. 0·2155 grm. gave 0·564 grm. of carbonic acid and 0·096 grm. of water, corresponding to 71·31 per cent. of carbon and 4·95 of hydrogen.

II. 0·33 grm. gave 47·6 cub. centims. of nitrogen at 0° C. and 760 millims. bar. pressure, =0·059813 grm. of nitrogen, equal to 18·12 per cent.

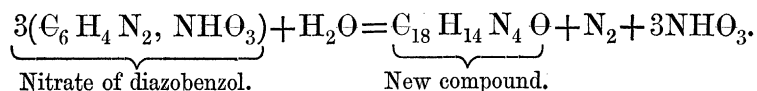III. 0·4605 grm. gave 66·5 cub. centims. of nitrogen at 0° C. and 760 millims. bar. pressure, =0·08356 grm. of nitrogen, equal to 18·14 per cent.
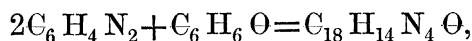
These numbers led to the formula

$$C_{18} H_{14} N_4 O.$$
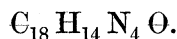
	Calculated.		Found.		
			I.	II.	III.
C_{18}	216	71·52	71·38	——	——
H_{14}	14	4·63	4·95	——	——
N_4	56	18·55	——	18·12	18·14
O	16	5·30	——	——	——
	302	100·00			

Its formation is explained by the equation

$$3(C_6 H_4 N_2, NHO_3) + H_2O = C_{18} H_{14} N_4 O + N_2 + 3NHO_3.$$

Nitrate of diazobenzol.   New compound.

It may likewise be viewed as composed of phenol and diazobenzol, viz.

$$2C_6 H_4 N_2 + C_6 H_6 O = C_{18} H_{14} N_4 O,$$

and I would therefore propose the name phenol-bidiazobenzol.

This new compound crystallizes in brownish-red needles or plates; it is readily soluble in ether, difficultly soluble in cold alcohol. Hot water dissolves it but very slightly. On heating, it deports itself like the compound previously described. It fuses at 113° C. Phenol-bidiazobenzol is an almost perfectly neutral body. Its deportment with potassa (in which it dissolves readily, forming a ruby-red solution) reminds one, however, of the properties of an acid. Ammonia-water dissolves it with difficulty, and aqueous carbonate of potassa not at all. Dilute acids exert likewise no solvent action; concentrated acids, however, dissolve it with a blood-red colour. Decomposition ensues when the latter solutions are heated.

* Instead of treating the mixture of the crude products of decomposition and carbonate of barium with hydrochloric acid in order to remove the latter, the new compounds may be extracted with potassa, then precipitated with hydrochloric acid, and lastly separated, as already described, by means of alcohol.

Action of Potassa upon Nitrate of Diazobenzol.

On mixing *diluted* aqueous solutions of these two bodies[*], a yellow liquid is obtained, which possesses a peculiar aromatic odour and soon begins to evolve nitrogen gas, a reddish-brown neutral substance being simultaneously formed. At the common temperature this reaction is very slow, and requires several weeks to be completed. If, however, heat is employed, the decomposition proceeds rapidly, and the reddish-brown substance is separated as a resinous, semifluid mass, quite insoluble in water, and only very slightly soluble even in boiling alcohol. Ether dissolves it readily. I have not been able to obtain this substance in crystals. By allowing its ethereal solution to evaporate spontaneously it is left behind in a resinous state. As a powder it is very electric. Boiling with nitric acid produces a new yellowish crystalline body.

In order to purify the amorphous product of decomposition, I have first washed it thoroughly with water, then boiled with alcohol, and finally dissolved it in ether; the substance remaining after the evaporation of the ether was submitted to analysis.
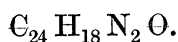
I. 0·2958 grm., dried *in vacuo*, gave 0·8888 grm. of carbonic acid and 0·1447 grm. of water.

II. 0·220 grm. gave 0·6667 grm. of carbonic acid and 0·1082 grm. of water.

III. 0·3926 grm. gave 29·8 cub. centims. of nitrogen at 0° C. and 760 millims. pressure.
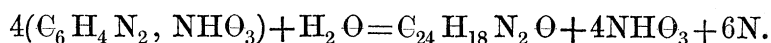
IV. 0·5054 grm. gave 32·0 cub. centims. of nitrogen at 0° C. and 760 millims. pressure.

These numbers agree best with the formula

$$C_{24} H_{18} N_2 O.$$

Calculated.			Found.			
			I.	II.	III.	IV.
C_{24}	288	82·29	81·95	82·68	——	——
H_{18}	18	5·14	5·44	5·45	——	——
N_2	28	8·00	——	——	9·53	7·66
O	16	4·57	——	——	——	——
	350	100·00				

The formation of this substance can be expressed by the following equation:—

$$4(C_6 H_4 N_2, NHO_3) + H_2 O = C_{24} H_{18} N_2 O + 4NHO_3 + 6N.$$

If instead of an aqueous, an alcoholic solution of potassa be added to the nitrate of diazobenzol, dissolved in water, the reaction which takes place is much more complicated. In this case, in addition to the reddish-brown body, two volatile substances are formed, viz. benzol and phenyl, $C_{12} H_{10}$, the hydrocarbon recently discovered by FITTIG[†]. When the reaction is conducted in a retort, on the application of heat the benzol passes over with the alcohol, and may be separated from it by the addition of water. The
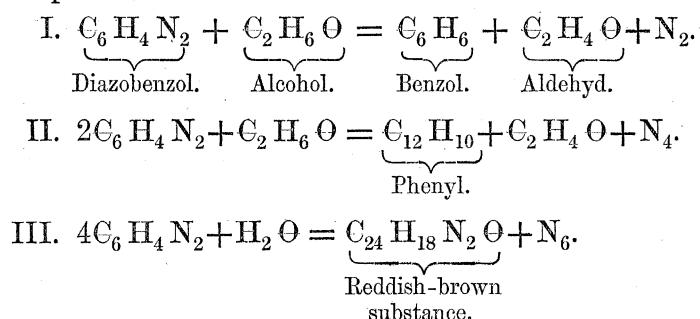
* The compound of hydrate of potassium and diazobenzol (page 675) does not seem to be formed in this case, as I was only able to separate this substance when very *concentrated* solutions of the nitrate of diazobenzol and potassa had been employed in its preparation.

† Ann. der Chem. und Pharm. Bd. cxxi. p. 363.

phenyl being less volatile, is obtained after the whole of the alcohol has distilled over; it condenses into a crystalline mass in the receiver. Repeated recrystallizations from alcohol render it quite pure, in white plates, resembling naphtaline, and fusible at 70° C. These properties leave no doubt as to its identity with the phenyl of Dr. FITTIG, to whom I am indebted for a small portion of his substance, which resembles in every respect the body obtained as mentioned above.

The third product of the decomposition in question, viz. the amorphous brown substance, is left behind in the retort as a resinous mass.

From the foregoing observations it will be seen that potassa, in the presence of alcohol, causes simultaneously three different decompositions of the diazobenzol-molecule, which may be expressed as follows:—

$$\text{I.} \quad \underbrace{C_6 H_4 N_2}_{\text{Diazobenzol.}} + \underbrace{C_2 H_6 O}_{\text{Alcohol.}} = \underbrace{C_6 H_6}_{\text{Benzol.}} + \underbrace{C_2 H_4 O}_{\text{Aldehyd.}} + N_2.$$

$$\text{II.} \quad 2C_6 H_4 N_2 + C_2 H_6 O = \underbrace{C_{12} H_{10}}_{\text{Phenyl.}} + C_2 H_4 O + N_4.$$

$$\text{III.} \quad 4C_6 H_4 N_2 + H_2 O = \underbrace{C_{24} H_{18} N_2 O}_{\substack{\text{Reddish-brown} \\ \text{substance.}}} + N_6.$$

### Action of Ammonia upon aqueous Nitrate of Diazobenzol.

On adding diluted ammonia to an aqueous solution of this diazo-compound, a similar reaction takes place as when the potassa is employed. On treating the brown mass, however, with alcohol, it becomes evident that it consists of two bodies. The difficultly soluble portion is absolutely identical with the nitrogenous body previously described, as was proved by the following analysis:—

0·245 grm. gave 0·744 grm. of carbonic acid and 0·1237 grm. of water. Carbon = 82·75, and hydrogen 5·60 per cent.

$$C_{24} H_{18} N_2 O.$$

	Calculated.	Found.
C	82·29	82·75
H	5·14	5·60

The body accompanying it, and which is readily soluble in alcohol, is obtained, by repeated crystallization, in the form of small, light-yellow plates which detonate on heating, and whose alcoholic solution gives precipitates with nitrate of silver and bichloride of platinum. This compound is, in fact, no other than the diazo-amidobenzol previously mentioned. The coincidence with this latter was so complete, that it appeared to me loss of time to analyze it. With regard to the first of the two products of decomposition, it is clear that its formation must be expressed by the same equation which illustrated the reaction with caustic potassa upon nitrate of diazobenzol, whilst the formation of the latter (the diazo-amidobenzol) is explained by assuming that a portion

of the original compound is decomposed, in the following manner:—

$$2(C_6 H_4 N_2, NHO_3)+3NH_3=C_{12} H_{11} N_3+N_2+2(NH_4, NO_3).$$

Nitrate of diazobenzol. Diazo-amidobenzol.
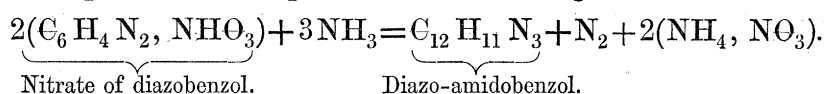
Two atoms of nitrogen in two equivalents of diazobenzol have, therefore, been simply replaced by one of ammonia.
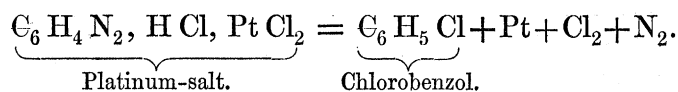
Decomposition of the Platinum-salt of Diazobenzol, and of the Perbromide of Diazobenzol, by the action of heat.

When speaking of the platinum-salt, I had occasion to mention that it detonates when heated. By mixing it, however, with a large excess of perfectly dry carbonate of sodium *, and heating the whole in a retort on a sand-bath, it is quietly decomposed. The decomposition begins at a moderate heat, and is marked at first by the evolution of gas, and subsequently by the distillation of an oily body. The residue in the retort consists of carbonate of sodium, metallic platinum, and chloride of sodium. The oily distillate contains chlorine. It is obtained perfectly pure by distilling once with chloride of calcium, and forms an almost colourless oil, which is heavier than water and has the odour of benzol. These properties, as well as the chlorine determination, which was made by igniting the substance with caustic lime, prove that it is chloro-benzol, $C_6 H_5 Cl$ †.

0·205 grm. gave 0·268 grm. of chloride of silver.

$$C_6 H_5 Cl.$$

	Calculated.	Found.
Chlorine . .	31·56	32·34

The formation of chlorobenzol may be expressed by the following equation:—

$$C_6 H_4 N_2, H Cl, Pt Cl_2 = C_6 H_5 Cl+Pt+Cl_2+N_2.$$

Platinum-salt. Chlorobenzol.

The platinum-salt of the bromide of diabenzol ‡ is decomposed in an exactly similar manner. The resulting bromobenzol differs in no way from the bromobenzol obtained by COUPER by the action of bromine upon benzol, as may easily be shown by converting it into nitrobromobenzol, which possesses all the properties of nitrobromobenzol prepared from coal-tar oil.

Bromobenzol can also be produced by the decomposition of perbromide of diazobenzol by heat, according to the equation

$$C_6 H_4 N_2, H Br, Br_2 = C_6 H_5 Br+N_2+Br_2.$$

Perbromide of diazobenzol. Bromobenzol.
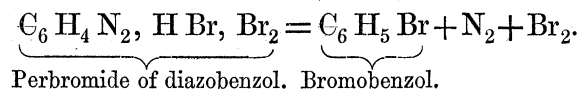
* It is self-evident that other carbonates, such as carbonate of barium, calcium, &c., may be used instead of carbonate of sodium.

† In all probability it is identical with chlorobenzol obtained from benzol or phenol.

‡ This compound is obtained as an insoluble reddish-yellow precipitate, on mixing bibromide of platinum with an aqueous solution of nitrate of diazobenzol.
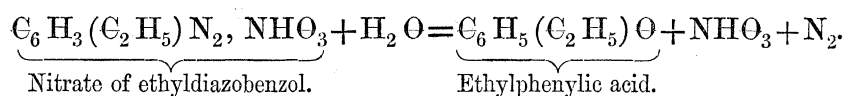
In order to decompose larger quantities of the perbromide of diazobenzol in this manner, it is likewise requisite to mix it first with a sufficient quantity of carbonate of sodium, to avoid a violent explosion.

By heating the mixture in a retort bromobenzol is obtained almost perfectly pure. The perbromide, when heated with alcohol, likewise gives rise to a decomposition in accordance with the previous equations. Bromobenzol separates as a heavy oil on the addition of water to the alcoholic solution.

It deserves to be mentioned that all these reactions are very well defined, and that the amount of the products of decomposition corresponds almost theoretically with the quantities employed.

APPENDIX.

It may be of some interest to mention an experiment I made to obtain ethylated diazobenzol compounds. For this purpose I submitted nitrate of ethylaniline to the same reaction which produced from nitrate of aniline the nitrate of diazobenzol. I obtained a body crystallizing, like the latter, in long needles. If this body had really been nitrate of ethyldiazobenzol, I expected to obtain, by boiling with water, a reaction according to the equation

$$\underbrace{C_6 H_3 (C_2 H_5) N_2, NHO_3}_{\text{Nitrate of ethyldiazobenzol.}} + H_2 O = \underbrace{C_6 H_5 (C_2 H_5) O}_{\text{Ethylphenylic acid.}} + NHO_3 + N_2.$$

It soon became evident, however, that the oily body produced was nothing else than ordinary phenylic acid; and since no other organic product of decomposition could be traced, I had to come to the conclusion that the above-mentioned crystals were nothing else than ordinary nitrate of diazobenzol. In order to decide this question the gold-salt was prepared, and, after being purified by recrystallization from alcohol, the well-known golden, brilliant crystals were obtained, which gave, on analysis—
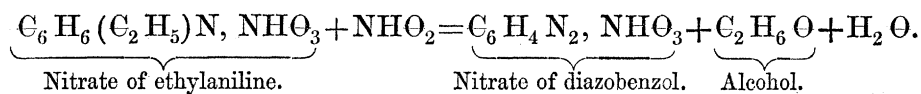
0·759 grm., decomposed by sulphuretted hydrogen and ignition of the tersulphide of gold, left 0·337 grm. of gold.
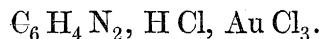
$$C_6 H_4 N_2, H Cl, Au Cl_3.$$

	Calculated.	Found.
Gold . . .	44·37	44·40

The compound $C_6 H_3 (C_2 H_5) N_2, H Cl, Au Cl_3$, requires 41·74 per cent. of gold.

The action of nitrous acid upon nitrate of ethylaniline may therefore be expressed by the equation

$$\underbrace{C_6 H_6 (C_2 H_5) N, NHO_3}_{\text{Nitrate of ethylaniline.}} + NHO_2 = \underbrace{C_6 H_4 N_2, NHO_3}_{\text{Nitrate of diazobenzol.}} + \underbrace{C_2 H_6 O}_{\text{Alcohol.}} + H_2 O.$$

PART II.

The peculiar and somewhat remarkable properties of the compounds derived from aniline in the manner previously described, have induced me to try whether bromaniline, nitraniline, &c., when similarly treated, would be converted into the corresponding substituted diazobenzols.

This I have succeeded in doing, and the new substances thus obtained exhibited all the properties which I found so characteristic of the normal diazobenzol-compounds. They are, if anything, more stable, owing, if I may so express myself, to the comparatively larger amount of more solid and stable materials which are more firmly combined with the extremely volatile and easily disturbed nitrogen. This property renders them more fit for many experiments in which the non-substituted diazobenzol-compounds are liable to give rise to dangerous accidents. They are likewise remarkable for great beauty, a property which certainly encourages a closer acquaintance.

Nitrate of Diazobromobenzol, $C_6H_3BrN_2, NHO_3$.

This compound may be prepared either by the action of nitrous acid gas upon nitrate of bromaniline or upon diazo-amidobromobenzol, and in an exactly similar manner to the nitrate of diazobenzol. If an aqueous solution of nitrate of bromaniline be employed, nitrous acid gas must be passed through very rapidly at first, or else diazo-amidobromobenzol (even in the presence of much free nitric acid) begins to separate. This it is very difficult to convert into the desired compound in an aqueous solution. Nitrate of diazobromobenzol remaining comparatively constant in aqueous solutions, it is possible to concentrate them, without any great loss, by spontaneous evaporation in the open air. In this manner solutions which are too dilute may be concentrated before precipitating by means of alcohol and ether. It can be obtained perfectly pure by repeatedly dissolving in alcohol and precipitating with ether, when it is obtained in the form of purely white scales which, when crystallizing out rapidly, present themselves in the form of regular rhombic plates. These crystals, like those of nitrate of diazobenzol, are exceedingly soluble in water, difficultly so in strong alcohol, and almost insoluble in ether. They explode when they are heated, struck, or compressed, though not so readily nor with the same violence as the nitrate of diazobenzol, and they can therefore be mixed without danger with oxide of copper and burnt in the usual mode of organic analysis.
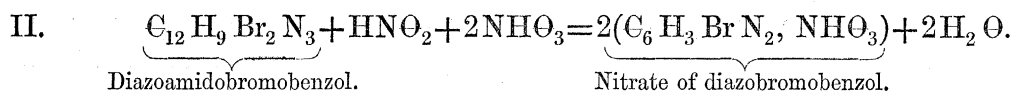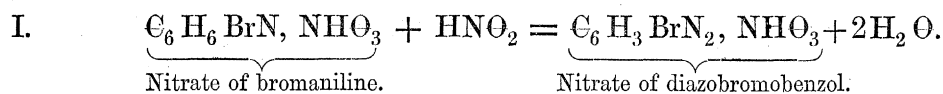
0·4692 grm. of the substance gave 0·503 grm. of carbonic acid and 0·0745 grm. of water.

These numbers correspond with the formula

$$C_6H_3BrN_2, NHO_3.$$
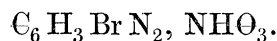
	Calculated.		Found.
C_6	72	29·27	29·24
H_4	4	1·63	1·76
Br	80	32·53	——
N_3	42	17·07	——
O_3	48	19·50	——
	246	100·00	

The formation of nitrate of diazobromobenzol may be represented by the following equations:—

I. $\underbrace{C_6\,H_6\,BrN,\,NHO_3}_{\text{Nitrate of bromaniline.}} + HNO_2 = \underbrace{C_6\,H_3\,BrN_2,\,NHO_3}_{\text{Nitrate of diazobromobenzol.}} + 2H_2\,O.$

II. $\underbrace{C_{12}\,H_9\,Br_2\,N_3}_{\text{Diazoamidobromobenzol.}} + HNO_2 + 2NHO_3 = \underbrace{2(C_6\,H_3\,Br\,N_2,\,NHO_3)}_{\text{Nitrate of diazobromobenzol.}} + 2H_2\,O.$

Sulphate of Diazobromobenzol, $C_6\,H_3\,Br\,N_2,\,SH_2\,O_4$.

The preparation of this compound from nitrate of diazobromobenzol and sulphuric acid corresponds so closely with that of the non-substituted (abromous) sulphate, that it may suffice simply to refer to the description already given of the preparation of the latter, and I will therefore restrict myself to a few remarks on its properties.
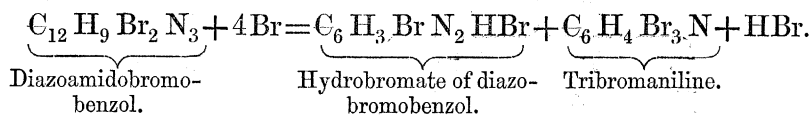
Sulphate of diazobromobenzol crystallizes in very fine colourless prisms, which are very soluble in water, very difficultly soluble in alcohol, and almost insoluble in ether. The new body is comparatively stable, and can be crystallized from water without suffering the least decomposition, by allowing its solution to evaporate over sulphuric acid. Boiling water decomposes the compound, and heat causes it to explode. Its formula has been established by a determination of the sulphuric acid only.

0·377 grm. gave 0·315 grm. of sulphate of barium.

	Calculated.		Found.
$C_6\,H_3\,Br\,N_2$	183	65·12	——
$SH_2\,O_4$	98	34·88	35·15
	281	100·00	

Hydrobromate of Diazobromobenzol, $C_6\,H_3\,Br\,N_2,\,HBr$.

This compound is prepared either by decomposing an aqueous solution of the previous salt by means of a sufficient quantity of bromide of barium and spontaneous evaporation of the filtrate, or by the action of an ethereal solution of bromine upon an ethereal solution of diazo-amidobromobenzol. If prepared by this latter method the new compound speedily separates in crystals, on account of its insolubility in ether, and is obtained pure by filtering off from the mother-liquor and washing the crystals with ether. Its formation may be expressed by the following equation:—

$\underbrace{C_{12}\,H_9\,Br_2\,N_3}_{\substack{\text{Diazoamidobromo-}\\\text{benzol.}}} + 4Br = \underbrace{C_6\,H_3\,Br\,N_2\,HBr}_{\substack{\text{Hydrobromate of diazo-}\\\text{bromobenzol.}}} + \underbrace{C_6\,H_4\,Br_3\,N}_{\text{Tribromaniline.}} + HBr.$

The hydrobromate of diazobromobenzol forms pearly white shining scales which dissolve very readily in water; like the hydrobromate of diazobenzol, they are more difficulty soluble in alcohol and quite insoluble in ether. In the dry state it can be preserved a long time without undergoing decomposition. On heating, it explodes

almost as violently as the corresponding nitrate. By treating an aqueous solution with freshly precipitated chloride of silver, the hydrobromate is converted into the hydro-chlorate of diazobenzol.

0·5315 grm. of substance, precipitated with nitrate of silver, gave 0·379 grm. of bromide of silver.

Calculated.		Found.
$C_6 H_3 Br N_2$	69·32	——
HBr	30·68	30·72
	100·00	

Perbromide of Diazobromobenzol, $C_6 H_3 Br N_2$, HBr, Br_2.

By treating an aqueous solution* of any one of the previously-described diazobromo-benzol-compounds with excess of bromine-water, a crystalline orange precipitate speedily falls, increasing rapidly till all the diazobromobenzol has been precipitated. If too much bromine has been added the precipitate becomes generally of an oily consistency, solidifying, however, to a yellow crystalline mass as soon as the mother-liquor has been removed and the excess of bromine allowed to evaporate spontaneously. In order to obtain the perbromide, thus prepared, in fine crystals, it is dissolved in the smallest possible quantity of warm, not boiling, alcohol, from which it separates on cooling in yellow monoclinic prisms. A small portion only remains in the alcoholic mother-liquor, from which evaporation rarely recovers it, since it usually undergoes decomposition. It will, however, be seldom necessary to run this risk of losing part of the substance by recrystallization, for the compound is almost perfectly pure from the very first, and at all events quite fit to be employed for the experiments to be described further on.

Under certain circumstances this perbromide is formed during the preparation of hydrobromate of diazobromobenzol from diazo-amidobromobenzol, in which case the two compounds are readily separated from one another by washing with cold water. Perbromide of diazobromobenzol crystallizes, as has been already remarked, in orange monoclinic prisms, insoluble in water, freely soluble in warm, difficultly so in cold alcohol, and very difficultly soluble in cold ether.

On boiling an alcoholic solution decomposition ensues, and on heating the crystals alone they explode feebly, with disengagement of bromine vapour and nitrogen gas.

Analysis gave the following results:—

0·558 grm. of substance gave 0·304 grm. of carbonic acid and 0·054 grm. of water.

0·4551 grm., ignited with caustic lime, gave with nitrate of silver 0·8135 grm. of bromide of silver.

These numbers lead to the formula

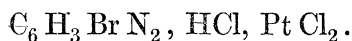$$C_6 H_3 Br N_2 HBr_3.$$

* The crude aqueous solution obtained by the action of nitrous acid upon the nitrate of bromaniline may conveniently be employed.

	Theory.		Experiment.
C_6	72	16·98	17·11
H_4	4	0·94	1·08
N_2	28	6·60	——
Br_4	320	75·48	76·06
	424	100·00	

Platinum-salt of the Hydrochlorate of Diazobromobenzol, $C_6 H_3 Br N_2$, HCl, $Pt Cl_2$.

Bichloride of platinum, even from a very dilute solution of the nitrate or sulphate of diazobromobenzol, separates a mass of small yellow crystals, which appear under the microscope as fractured plates, and which are almost insoluble in every neutral solvent. They are stable at 100° C.

0·568 grm. gave, on ignition with carbonate of sodium, 0·1447 grm. of platinum.

$$C_6 H_3 Br N_2, HCl, Pt Cl_2.$$
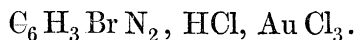
	Calculated.	Found.
Platinum . .	25·36 per cent.	25·47

Gold-salt of the Hydrochlorate of Diazobromobenzol, $C_6 H_3 Br N_2$, HCl, $Au Cl_3$.

This compound is precipitated from an aqueous solution of nitrate of diazobromobenzol on the addition of terchloride of gold, at first as a yellow oil, which, however, rapidly solidifies to a crystalline mass. The crystals are insoluble in water, but can be recrystallized from warm alcohol without much loss, and are thus obtained in the form of splendid small golden-yellow shining plates.

0·469 grm. of substance, dissolved in alcohol and decomposed with sulphuretted hydrogen, gave, after ignition of the tersulphide of gold, 0·1763 grm. of gold.

$$C_6 H_3 Br N_2, HCl, Au Cl_3.$$

	Calculated.	Found.
Gold . . .	37·67 per cent.	37·59

Compound of Hydrate of Potassium with Diazobromobenzol, $C_6 H_3 Br N_2$, KHO.

On the addition of caustic potash to a concentrated solution of nitrate of diazobromobenzol a lemon-yellowish precipitate of diazobromobenzol separates at first, but is soluble in excess of potash. On evaporation by means of a water-bath, the solution solidifies, when sufficiently concentrated, to a reddish-coloured crystalline paste of nitre and the new compound of hydrate of potassium and diazo-bromobenzol.

The latter is separated and purified exactly in a similar manner to the analogous compound of diazobenzol. It differs from this compound in being precipitated from its alcoholic solution by means of ether as a white gelatinous mass, and not in the form of crystals. White plates are obtained by allowing its aqueous solution to evaporate on a

watch-glass over sulphuric acid, which, however, turn red on keeping, owing to a partial decomposition.

Compound of Hydrate of Silver with Diazobromobenzol, $C_6 H_3 Br N_2$, Ag HO.

This body is obtained as an almost white insoluble precipitate, very similar to the hydrate of silver with diazobenzol. I abstain from describing any more of the compounds of diazobromobenzol with metallic hydrates, since they entirely resemble the corresponding diazobenzol-compounds in every respect.
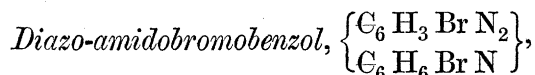
Diazobromobenzol, $C_6 H_3 Br N_2$.

This compound is obtained in slender, bright-yellow needles by adding weak acetic acid to the compound of hydrate of potassium with diazobromobenzol, or as a bright yellow amorphous precipitate on the addition of dilute potassa to the aqueous solution of the nitrate of diazobromobenzol. In either case it is necessary to remove it speedily from the mother-liquor, and to dry it rapidly over sulphuric acid.

Diazobromobenzol is an exceedingly dangerous compound; for the slightest pressure, or even touch with a rough object, causes it to go off in a fiery explosion almost exceeding in violence that of the nitrate of diazobenzol. Although much more stable than diazobenzol, it can, however, be kept only for a short time in a perfectly unchanged condition. After being kept for some time, a reddish-brown residue is left, which no longer explodes even on heating, and it seems that the nitrogen has been gradually eliminated. Ether dissolves diazobromobenzol and causes a violent evolution of gas, frequently of such intensity as to give rise to explosions. When freshly prepared, this body is soluble in caustic potassa as well as in mineral acids, with formation of the previously-described saline bodies.

COMPOUNDS OF DIAZOBROMOBENZOL WITH AMIDO-COMPOUNDS.

Diazobromobenzol, like diazobenzol, can enter into combination with amido-bases and amido-acids. Since, however, these new bodies possess absolutely no fresh chemical interest, but resemble in every respect the amido-compounds of diazobenzol, it may suffice to mention a few only, as briefly as possible.

Diazo-amidobromobenzol, $\begin{Bmatrix} C_6 H_3 Br N_2 \\ C_6 H_6 Br N \end{Bmatrix}$,

separates in yellow needles or small plates when a concentrated aqueous solution of nitrate of diazobromobenzol is treated with an alcoholic solution of bromaniline. This compound was obtained by me on a former occasion* by the action of nitrous acid upon alcoholic aniline.
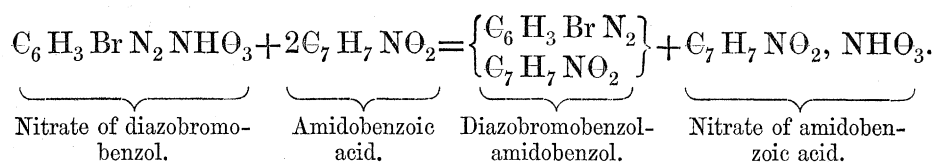
It needs no further proof that both methods furnish a product of identical properties.

* Annalen der Chem. und Pharm. Bd. cxxi. p. 273.

The action of aniline upon nitrate of diazobromobenzol gives rise to diazobromo-amido-benzol, which not only has the same empirical composition as the diazobenzol-amido-bromobenzol ($C_{12}H_{10}Br N_3$) (page 678), but resembles it in every other respect. It would, no doubt, be of interest to determine whether both compounds are identical or only isomeric. I must, however, defer answering this question till a future opportunity.

$$\textit{Diazobromobenzol-amidobenzoic acid,} \quad \begin{Bmatrix} C_6H_3Br N_2 \\ C_7H_7NO_2 \end{Bmatrix}.$$

This body is obtained as a yellow crystalline precipitate on mixing an aqueous solution of nitrate of diazobromobenzol and amidobenzoic acid, according to the equation

$$C_6H_3Br N_2 NHO_3 + 2C_7H_7NO_2 = \begin{Bmatrix} C_6H_3Br N_2 \\ C_7H_7NO_2 \end{Bmatrix} + C_7H_7NO_2, NHO_3.$$

| Nitrate of diazobromo-benzol. | Amidobenzoic acid. | Diazobromobenzol-amidobenzol. | Nitrate of amidoben-zoic acid. |

Recrystallized from ether it forms roundish lumps of small needles or plates. In every other respect it is identical with diazobenzol-amidobenzoic acid.

IMIDOGEN COMPOUNDS OF DIAZOBROMOBENZOL.

$$\textit{Diazobromobenzolimide,} \quad \begin{Bmatrix} (C_6H_3Br N_2)'' \\ H \end{Bmatrix} N.$$
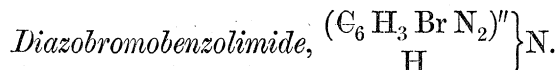
On mixing the yellow crystals of perbromide of diazobromobenzol with solution of ammonia, they are speedily converted into a yellowish oil, which, after a single distillation with water, is obtained in an almost colourless condition. This oil is diazobromo-benzolimide in a perfectly pure state.
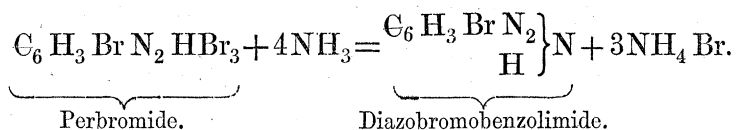
If the temperature of the atmosphere be not too high, the oil usually solidifies after a short time. If this does not take place, artificial cold must be resorted to. The new compound is obtained for analysis by removing the water and drying over sulphuric acid.

0·432 grm. of substance gave 0·5803 grm. of carbonic acid and 0·0958 grm. of water.

0·3213 grm. gave 53·8 cub. centims. of nitrogen at 0° C. and 760 millims. barom. pressure = 0·06704 grm. of this gas.

	Calculated.		Found.
C_6	72	36·36	36·63
H_4	4	2·02	2·45
Br	80	40·40	——
N_3	42	21·22	21·04
	198	100·00	

The formation of this compound is expressed by the following equation:—

$$C_6 H_3 Br N_2 HBr_3 + 4 NH_3 = \left. \begin{array}{c} C_6 H_3 Br N_2 \\ H \end{array} \right\} N + 3 NH_4 Br.$$

$$\underbrace{\hspace{4cm}}_{\text{Perbromide.}} \qquad \underbrace{\hspace{4cm}}_{\text{Diazobromobenzolimide.}}$$

The quantity of diazobromobenzolimide and bromide of ammonium which is obtained from a given quantity of perbromide corresponds accurately with the theoretical proportions.

0·8305 grm. of perbromide of diazobromobenzol, after decomposition with ammonia, gave with nitrate of silver 1·0945 grm. of bromide of silver, corresponding to 56·1 per cent. of bromine.

According to the above equation, one equivalent of the perbromide gives rise to the production of three equivalents of bromide of ammonium; the quantity of bromine capable of precipitation after the action of ammonia will therefore be 56·6 per cent.

Diazobromobenzolimide presents itself generally as a white or slightly yellowish mass of small crystalline plates, which melt at about 20° C. to a heavy oil. It is insoluble in water, rather difficultly soluble in alcohol, and easily soluble in ether and benzol. It distils readily in the presence of water; heated alone it explodes feebly. Left exposed to the open air it appears gradually to volatilize, giving off the same aromatic ammoniacal odour which characterizes diazobenzolimide. It resembles the latter, moreover, in its behaviour with various reagents; caustic potassa, hydrochloric acid, and bromine have no action upon it, strong sulphuric and nitric acids decompose it readily.

By the action of ethylamine, aniline, &c. upon perbromide of diazobromobenzol, corresponding substitution-compounds of diazobromobenzolimide are obtained.

Ethyldiazobromobenzolimide, $\left. \begin{array}{c} (C_6 H_3 Br N_2)'' \\ C_2 H_5 \end{array} \right\} N$, forms a yellowish oil which does not solidify even when cooled much below 0° C.

Phenyldiazobromobenzolimide, $\left. \begin{array}{c} (C_6 H_3 Br N_2)'' \\ C_6 H_5 \end{array} \right\} N$, is obtained in the form of orange crystals.

### REMARKS ON THE PRODUCTS OF DECOMPOSITION OF THE COMPOUNDS OF DIAZOBROMOBENZOL.

The great similarity existing between the properties of the diazobromobenzol-compounds and those of the corresponding abromous bodies, is likewise encountered in their products of decomposition obtained under similar circumstances; and I have therefore generally abstained from verifying the latter by analysis, having restricted myself to bringing forward analytical numbers in a few cases only.

On heating an aqueous solution of nitrate or hydrobromate of diazobromobenzol,

an evolution of nitrogen gas takes place, bromophenylic acid (which separates as a brownish oil of the odour of creosote) being simultaneously produced.

$$\underbrace{C_6 H_3 Br N_2, H Br} + H_2 O = \underbrace{C_6 H_5 Br O} + HBr + N_2.$$

Hydrobromate of diazo-   Bromophenylic
bromobenzol.   acid.
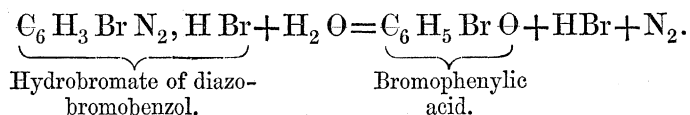
Ebullition of nitrate of diazobromobenzol with alcohol gives rise to the formation of bromobenzol, which distils over with the vapour of alcohol, a yellow acid (probably bromodinitrophenylic) being left behind. Ammonia forms a yellow body with the simultaneous production of diazo-amidobromobenzol, which, owing to its greater solubility in alcohol, can be readily separated from the former. The formation of diazo-amido-bromobenzol takes place according to the formula

$$\underbrace{2 C_6 H_3 Br N_2} + NH_3 = \underbrace{C_{12} H_9 Br_2 N_3} + N_2.$$

Diazobromobenzol.   Diazo-amidobromobenzol.
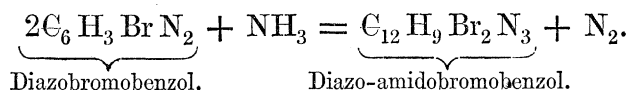
Sulphate of diazobromobenzol, when heated with sulphuric acid, is converted into a sulpho-acid, which is most probably disulphobromophenylenic acid, $C_6 H_3 Br, S_2 H_4 O_8$.

Nascent hydrogen, generated by the action of zinc upon sulphuric acid, in the presence of an alcoholic solution of bromobenzolimide converts the latter into bromaniline and ammonia.

$$\underbrace{C_6 H_4 Br N_3} + 8H = \underbrace{C_6 H_6 Br N} + 2H_3 N.$$
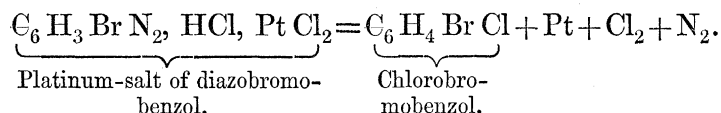
Diazobromoben-   Bromaniline.
zolimide.
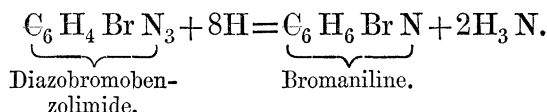
When the addition of water no longer gives rise to a precipitate, indicating that the whole of the imide has been decomposed, the bromaniline is most easily isolated by evaporating the alcoholic solution on a water-bath, and distilling with caustic potassa.

Bromaniline passes over in oily drops, which quickly solidify, and may be crystallized from alcohol in octahedra. These crystals, as well as the properties of the platinum-salt, prove it to be identical with the ordinary bromaniline.

0·2584 grm. of the latter left on ignition 0·0661 grm. of platinum, corresponding to 26·5 per cent.

$C_6 H_6 Br N, HCl, Pt Cl_2$ requires 26·1 per cent.

By heating the platinum-salt of diazobenzol with carbonate of sodium, chlorobenzol was obtained; so in like manner by the action of heat on the platinum-salt of hydro-chlorate of diazobromobenzol, chlorobromobenzol is produced, according to the following equation:—

$$\underbrace{C_6 H_3 Br N_2, HCl, Pt Cl_2} = \underbrace{C_6 H_4 Br Cl} + Pt + Cl_2 + N_2.$$

Platinum-salt of diazobromo-   Chlorobro-
benzol.   mobenzol.

By pressing the crystals which condense in the neck of the retort between filter paper, and after a second distillation and crystallization from alcohol, they are obtained sufficiently pure for analysis.
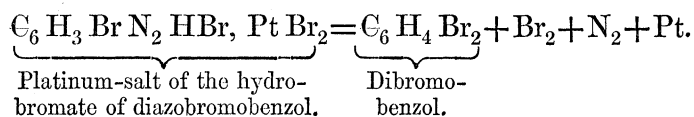
0·441 grm. of substance gave 0·6072 grm. of carbonic acid and 0·0832 grm. of water.

These numbers lead to the formula $C_6 H_4 Br Cl$.

	Calculated.		Found.
C_6	72	37·60	37·52
H_4	4	2·09	2·10
Br	80	41·77	——
Cl	35·5	18·54	——
	191·5	100·00	

Chlorobromobenzol is rather difficultly soluble in alcohol, readily so in ether, and crystallizes in white needles or plates from a hot saturated alcoholic solution on cooling, or by evaporation of the ethereal solution. The crystals possess a peculiar odour, resembling that of benzol.

The double salt of dibromide of platinum and hydrobromate of diazobromobenzol is obtained in the form of ruby-red crystals, by mixing a tolerably concentrated aqueous solution of the diazo-salt with dibromide of platinum. This compound shows, as might be expected, a similar deportment. Like the previous platinum-salt, it breaks up according to the equation

$$C_6 H_3 Br N_2 HBr, Pt Br_2 = C_6 H_4 Br_2 + Br_2 + N_2 + Pt.$$

Platinum-salt of the hydro-   Dibromo-
bromate of diazobromobenzol.   benzol.

Dibromobenzol is readily prepared also from the perbromide of diazobromobenzol by heating the latter alone*, or with carbonate of sodium, when it is decomposed according to the equation

$$C_6 H_3 Br N_2 HBr_3 = C_6 H_4 Br_2 + Br_2 + N_2.$$

Perbromide of diazo-   Dibromobenzol.
bromobenzol.
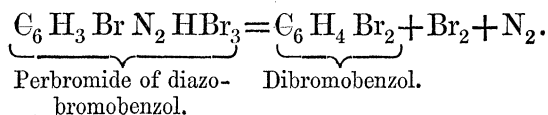
A still more convenient method of preparing dibromobenzol consists in the decomposition of the perbromide with alcohol, which is completed after a few minutes' boiling; and if too much alcohol has not been employed, a large portion of the dibromobenzol separates at once in the form of crystals. The remaining portion is precipitated on the addition of water, in the form of a thick oil, which soon solidifies to a crystalline mass. After washing with a little alcohol and pressing between bibulous paper, this mass, together with the crystals first precipitated, is subjected to distillation. Dibromobenzol distils over as an almost colourless oil, which speedily solidifies.

Dibromobenzol resembles very much chlorobromobenzol in its various physical properties. It crystallizes from ether in the form of rectangular prisms or small plates, which are frequently very regular and well formed, sometimes, however, agglomerated in various ways. It fuses at 89° C.

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* Only small quantities must be employed, in order to prevent violent explosions. By heating the perbromide in a long-necked flask the dibromobenzol condenses in the cold part of the vessel.

The properties of the dibromobenzol prepared in the manner just described can leave no doubt that it is identical with the dibromobenzol described by COUPER, obtained by the action of bromine upon benzol. Although large quantities of dibromobenzol can be prepared by COUPER'S method with perhaps greater facility, it is always difficult to obtain the dibromo- quite free from tribromo-benzol, which is simultaneously formed.

The above method might be preferred in all cases when absolutely pure dibromo-benzol is required, as, for instance, for certain physical purposes—the more so, since it invariably yields theoretical quantities. The same may be said of several other derivatives of benzol and its homologues, which are obtained from diazo-compounds to be described hereafter.

DIAZODIBROMOBENZOL COMPOUNDS.

Nitrate of Diazodibromobenzol, $C_6H_2Br_2N_2$, NHO_3.

This compound is readily obtained by the action of a rapid current of nitrous acid upon an aqueous solution of nitrate of bromaniline containing free nitric acid. The liquid is allowed to evaporate spontaneously, the residue taken up with weak alcohol, and the new compound precipitated by means of ether. It can be recrystallized without loss from water or alcohol by evaporating the respective solutions below their boiling-points. Its aqueous solution remains remarkably constant. Continued boiling even for hours frequently leaves some of the substance undecomposed.

Nitrate of diazodibromobenzol crystallizes in fine white prisms, or elongated hexagonal plates. It does not detonate with the same violence as the corresponding bodies previously described.

Perbromide of Diazodibromobenzol, $C_6H_2Br_2N_2$, HBr_3.

This compound is formed by the addition of bromine-water to an aqueous solution of the nitrate of diazodibromobenzol, when it is precipitated in the form of fine long needles. On boiling with alcohol, and the subsequent addition of water, an oily substance is thrown down which soon solidifies, and can be obtained perfectly pure by pressing the precipitate between bibulous paper, then distilling, and finally crystallizing from alcohol. Thus purified it presents itself in the form of fine long silky needles. This substance is evidently tribromobenzol, presenting all the properties of that compound obtained by the distillation of $C_6H_6Br_6$ with alkalies by LASSAIGNE *.

Platinum-salt of the Hydrochlorate of Diazodibromobenzol, $C_6H_2Br_2N_2$, HCl, $PtCl_2$.
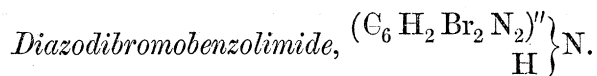
It separates in small orange oval plates, which are difficultly soluble in water, on adding dichloride of platinum to the hydrochlorate.

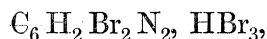0·722 grm. gave 0·154 grm. of platinum.

$$C_6H_2Br_2N_2, HCl, PtCl_2.$$
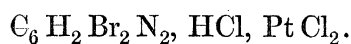
	Calculated.	Found.
Platinum . . .	21·08 per cent.	21·33

* Rev. Scient. vol. v. p. 360.

Diazodibromobenzolimide, $\begin{matrix} (C_6 H_2 Br_2 N_2)'' \\ H \end{matrix} \Big\} N.$

This compound is easily obtained in crystals by mixing the perbromide,

$$C_6 H_2 Br_2 N_2, HBr_3,$$

with ammonia. Repeated recrystallization from hot alcohol yields it in the form of white needles, which fuse at 62° C., and which detonate slightly at a higher temperature. It is very little soluble in water, more soluble in hot alcohol, and very readily so in ether.

DIAZOCHLOROBENZOL COMPOUNDS.

Perfect analogy exists between these bodies, as well as between the diazodichlorobenzol compounds, and the compounds I have just described, with regard not only to the modes of preparation from chlorine and dichloraniline, but also in respect to their various physical properties. I therefore abstain from entering into a minute description, and will simply enumerate some few experiments, which I hope will satisfactorily prove their great similarity.

Nitrate of Diazochlorobenzol, $C_6 H_3 Cl N_2, NHO_3.$

This substance crystallizes in small white plates, which yield on boiling with water chlorophenylic acid in the form of a brownish oil possessing the odour of creosote.

Perbromide of Diazochlorobenzol, $C_6 H_3 Cl N_2, HBr_3,$
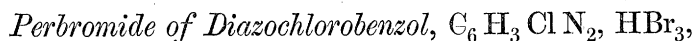
forms yellow columns which are decomposed in boiling alcohol with formation of bromochlorobenzol, the composition of which is thus expressed, $C_6 H_4 Cl Br$ *.
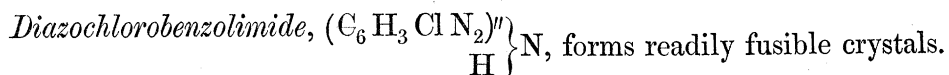
0·2005 grm. of the perbromide was decomposed with ammonia, and when precipitated with nitrate of silver gave 0·2952 grm. of bromide of silver.

$$C_6 H_3 Cl N_2, HBr_3.$$

	Calculated.	Found.
Bromine	63·24	62·64

Platinum-salt of the Hydrochlorate of Diazochlorobenzol, $C_6 H_3 Cl N_2, HCl, Pt Cl_2,$

forms fine yellow needles. On heating with carbonate of sodium it yields dichlorobenzol, which is obtained, according as it crystallizes slowly or rapidly, in long fine needles, or in elongated four-sided plates, possessing the same peculiar aromatic odour as the dibromobenzol.

Diazochlorobenzolimide, $\begin{matrix} (C_6 H_3 Cl N_2)'' \\ H \end{matrix} \Big\} N,$ forms readily fusible crystals.

---

* I leave it undecided whether the bromochlorobenzol thus obtained is identical with the body described on page 702 as derived from $C_6 H_3 Br N_2$, HCl, Pt Cl$_2$, and possessing the same elementary composition. Some observations, which shall be fully described when treating of the products of decomposition of diazonitrobenzol, do not favour the view of their identity.

Diazochlorobenzol, $C_6 H_3 Cl N_2$, is obtained as a highly explosive lemon-yellow precipitate.

DIAZODICHLOROBENZOL COMPOUNDS.

Nitrate of diazodichlorobenzol presents itself in the form of white plates. The perbromide, $C_6 H_2 Cl_2 N_2$, HBr_3, which is formed by the action of bromine-water, crystallizes in yellow prisms; the platinum-salt in small, beautiful, yellow, very brilliant plates.

0·3975 grm. of the latter compound gave 0·1015 grm. of platinum.

$$(C_6 H_2 Cl_2 N_2, HCl, PtCl_2).$$
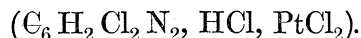
	Calculated.	Found.
Platinum	26·01 per cent.	25·54.

DIAZOIODOBENZOL COMPOUNDS.

It will suffice if I give likewise only a short outline of these bodies, owing to the great resemblance which usually exists between them and the compounds of diazobromobenzol, both in regard to their preparation and chemical deportment, and also with respect to their physical properties.

*Nitrate of Diazoiodobenzol*, $C_6 H_3 I N_2$, NHO_3,

is prepared from nitrate of iodaniline, precisely like the corresponding bromo-compound, and crystallizes in white needles or prisms, which are exceedingly soluble in water.

Sulphate of Diazoiodobenzol, $C_6 H_3 I N_2$, $SH_2 O_4$,
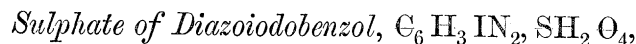
crystallizes in small plates, which are easily soluble in water, difficultly so in alcohol.

0·5665 grm. of substance gave 0·4025 grm. of sulphate of barium.

		Calculated.	Found.
$C_6 H_3 I N_2$	230	70·12	——
$SH_2 O_4$	98	29·88	29·92
	328	100·00	

Perbromide of Diazoiodobenzol, $C_6 H_3 I N_2$, HBr_3,
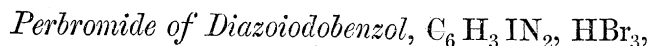
forms small lemon-yellow slender plates.

0·4395 grm. of substance, decomposed with solution of ammonia, gave 0·525 grm. of bromide of silver.

$$C_6 H_3 I N_2, HBr_3.$$

	Calculated.	Found.
Bromine	50·95 per cent.	50·83

On boiling this compound with alcohol it yields bromoiodobenzol, $C_6 H_4 Br I$, which crystallizes from ether or alcohol in large white plates, which are volatile without decomposition.

0·453 grm. of bromoiodobenzol gave 0·4082 grm. carbonic acid and 0·0612 grm. water.

		Calculated.	Found.
C_6	72	25·44	24·58
H_4	4	1·41	1·50
Br	80	28·27	——
I	127	14·88	——
	283	100·00	

Platinum-salt of the Hydrochlorate of Diazoiodobenzol, $C_6 H_3 IN_2$, HCl, Pt Cl$_2$, forms small bright yellow clusters of needles.

*Diazoiodobenzolimide,* $\left. \begin{array}{c} (C_6 H_3 IN_2)'' \\ H \end{array} \right\} N,$
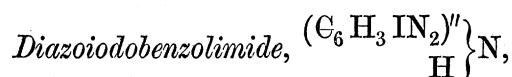
forms yellowish-white crystals, which are readily fusible, and pass over on distilling with water as a yellowish oil, soon solidifying. This likewise is of a peculiar aromatic ammoniacal odour.

Diazoiodobenzol, $C_6 H_3 IN_2$,

is obtained as a yellow explosive precipitate.

DIAZONITROBENZOL COMPOUNDS.

The remarkable isomerism observed between α and β nitraniline, and hitherto left unexplained by any chemical theory, likewise extends, as I have shown upon a former occasion, to the double compounds which I have described as α and β Diazo-amidonitro-benzol. This isomerism, however, is somewhat less striking, since these bodies retain one-half the nitraniline required for their formation in the original condition, as will be clearly seen on examining the rational formula

$$\left\{ \begin{array}{l} C_6 H_3 (NO_2) N_2 \\ C_6 H_4 (NO_2) H_2 N \end{array} \right\}$$
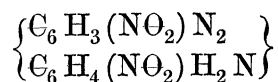
which I assign to these bodies. The simple diazo-compounds derived from these isomeric nitranilines cannot, however, be viewed similarly, and it was impossible therefore to decide *à priori* the question of their isomerism. The experiments presently to be described nevertheless leave no doubt that a similar isomerism exists between the several members of both series, and that, although of identical composition, differences in their physical properties become manifest, which are as striking as those observed between the original bases.

α Diazonitrobenzol compounds*.

Nitrate of Diazonitrobenzol, $C_6H_3(NO_2)N_2HNO_3$.

The preparation of this compound by the action of nitrous acid upon α nitraniline differs in no way from that of the analogous bodies already referred to. By gradually adding ether to its alcoholic solution till crystallization commences, it is obtained in fine long needles, which, however, do not exhibit any distinct form of crystallization.

This compound, like all the rest of the like bodies, is very readily soluble in water, more difficultly so in alcohol, and insoluble in ether, and explodes with the same violence on heating.

Perbromide of α Diazonitrobenzol, $C_6H_3(NO_2)N_2, HBr_3$.

On mixing an aqueous solution of the former compound with bromine-water, this new body is speedily thrown down in slender orange prisms, which are almost insoluble in water, and scarcely soluble in ether.   They dissolve, however, readily in warm alcohol, from which they are deposited, on cooling, in well-defined crystals.

Platinum-salt of the Hydrochlorate of α Diazonitrobenzol, $C_6H_3(NO_2)N_2, HCl, PtCl_2$.

On the addition of chloride of platinum to a hot aqueous solution of the hydrochlorate of diazonitrobenzol, this double salt, which crystallizes in long yellow needles, is precipitated.   On recrystallizing it from boiling water, in which it is soluble (although difficultly), the crystals are obtained as prisms, frequently very well formed.

α Diazonitrobenzolimide, $\left. \begin{array}{l} (C_6H_3(NO_2)N_2)'' \\ H \end{array} \right\} N.$

This compound is prepared by the action of ammonia upon perbromide of α diazonitrobenzol. By repeated recrystallization from alcohol it may be obtained in a perfectly pure state in the form of very brilliant yellow, rounded plates, which are so soluble in hot alcohol that a magma of crystals separates on cooling from a saturated solution.   The crystals dissolve as readily in ether.   In boiling water they fuse, producing a yellow oil but slightly soluble in water, the portion dissolved yields very fine, almost white crystals on cooling.   The fusing-point of the crystals obtained by recrystallization from alcohol was found to be 71° C.   The substance explodes when heated a little above the fusing-point.

0·3392 grm. of substance gave 0·548 grm. of carbonic acid and 0·805 grm. of water.

---

* The α nitraniline employed for these experiments was obtained according to ARPPE's method, by the action of alkaline liquids upon nitrated anilides.

The β nitraniline was prepared according to HOFMANN and MUSPRATT's method, from dinitrobenzol by the reduction with sulphuretted hydrogen.

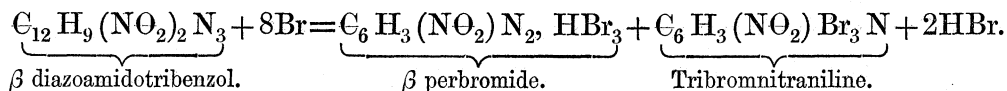|		Calculated.	Found.
C_6	72	43·90	44·06
H_4	4	2·44	2·64
N_4	56	34·15	——
O_2	32	19·51	——
	164	100·00	

β Diazonitrobenzol compounds.

Nitrate of β Diazonitrobenzol, $C_6 H_3 (NO_2) N_2, HNO_3$,

is obtained from the nitrate of β nitraniline. The β does not differ much from the corresponding α compound in solubility; they however exhibit perceptible differences in the forms of their crystals, which in the β compound are columns, frequently approaching the cubical form, whilst the crystals of the nitrate of α diazonitrobenzol are long needles of a somewhat unpronounced character.

Perbromide of β Diazonitrobenzol, $C_6 H_3 (NO_2) N_2, HBr_3$.

On treating an aqueous solution of the nitrate of β diazonitrobenzol with bromine-water the new compound is thrown down generally as an oil, which soon solidifies. It forms small plates or prisms of an orange colour, which seem to differ from the crystals of the α compound by their want of stability when treated with warm alcohol, and which I have scarcely ever been able to recrystallize. I have obtained the perbromide of β diazonitrobenzol also by the action of bromine upon β diazo-amidonitrobenzol by suspending the latter in water and adding bromine till the whole is converted into a heavy brownish-red oil. The supernatant aqueous mother-liquor is decanted and the excess of bromine allowed to evaporate spontaneously, when the oil solidifies to a crystalline mass.

Before, however, complete solidification occurs, thick yellowish-red prisms are frequently seen to shoot out, of about an inch in length, which consist of almost pure perbromide containing mere traces of tribromnitraniline, a body which forms in the reaction to nearly the same extent, as will be seen from the following equation:—

$$\underbrace{C_{12} H_9 (NO_2)_2 N_3}_{\text{β diazoamidotribenzol.}} + 8Br = \underbrace{C_6 H_3 (NO_2) N_2, HBr_3}_{\text{β perbromide.}} + \underbrace{C_6 H_3 (NO_2) Br_3 N}_{\text{Tribromnitraniline.}} + 2HBr.$$

The adhering tribromnitraniline* can be removed by washing the finely pulverized crystals with ether, in which the perbromide is almost insoluble.

* In order to obtain the tribromnitraniline in a pure state the ethereal solution is evaporated to dryness, and the residue dissolved by warm alcohol. Water is then added to the alcoholic solution till it becomes milky and deposits crystals. These are thrown upon a filter, and then pressed between sheets of filter paper, in order to remove any adhering bromonitrobenzol, and purified further by recrystallization from weak alcohol. Tribromnitraniline crystallizes in small, slightly yellowish plates, which cannot be sublimed without decomposition. The analysis of this compound will be found in another place.

If no crystals are formed after the bromine has evaporated in the manner described, but only a crystalline mass of perbromide and tribromaniline, the latter is pressed between bibulous paper, and then washed with ether in order to separate the two compounds. This, however, cannot be done without incurring a considerable loss of perbromide, since by the action of the ether it is partly converted into the nitrobromobenzol. Thus prepared it gave on analysis the following results:—

0·548 grm. gave 0·3895 grm. of carbonic acid and 0·0565 grm. of water.

0·363 grm. gave, on ignition with lime, 0·5275 grm. of bromide of silver.

|	Theory.		Experiment.
C_6	72	18·46	19·38
H_4	4	1·03	1·14
N_3	42	10·77	——
Br_3	240	61·54	61·85
O_2	32	8·20	——
	390	100·00	

Platinum-salt of the Hydrochlorate of β Diazonitrobenzol, $C_6 H_3 (NO_2) N_2,$ HCl, Pt Cl$_2$.

This compound crystallizes likewise in needles or prisms resembling much the crystals of the α compound.

0·847 grm. left, on ignition with carbonate of sodium, 0·236 grm. of platinum = 27·86 per cent.

$$C_6 H_3 (NO_2) N_2, HCl, Pt Cl_2.$$
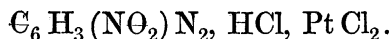
	Calculated.	Found.
Platinum	27·79 per cent.	27·86

β Diazonitrobenzolimide, $\left. \begin{array}{c} (C_6 H_3 (NO_2) N_2)'' \\ H \end{array} \right\} N,$
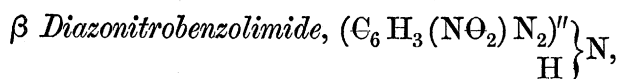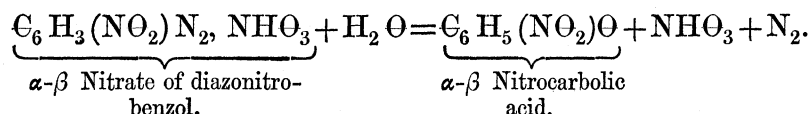
differs from the α compound by crystallizing invariably in orange-coloured needles which fuse at 52° C., and consequently much below the fusing-point of the α compound. It is likewise somewhat soluble in hot water, from which it crystallizes on cooling in whitish needles, which closely resemble those of the α diazonitrobenzolimide recrystallized also from hot water. It somewhat possesses the odour of nitrobenzol.

0·4317 grm. of substance gave 0·6927 grm. of carbonic acid and 0·1008 grm. of water.

	Calculated.		Found.
C_6	72	43·90	43·76
H_4	4	2·44	2·59
N_4	56	34·15	——
O_2	32	19·51	——
	164	100·00	

ON THE PRODUCTS OF DECOMPOSITION OF THE DIAZONITROBENZOL COMPOUNDS.

These substances, as far as my observations go, are decomposed under the influence of reagents like the other diazobenzol compounds; and their transformations may be expressed by corresponding equations. The nature of their products of decomposition may in fact be safely predicted beforehand, as the same isomerism which characterizes the compounds already described is observable. It appeared of sufficient interest to trace them somewhat more fully. I could not have given the comparative history of the products of decomposition, however, without deviating too far from the main direction of this investigation, and I must therefore reserve for a future opportunity a more intimate acquaintance with these interesting bodies. A few illustrations will show how promising a harvest of interesting results may be expected from such an investigation. One peculiar fact deserves mention here. I had taken it for granted that the same relations would be exhibited between the isomeric diazonitrobenzol compounds and the isomeric acids of the formula $C_6 H_5 (NO_2) O$ (the nitrocarbolic acid of HOFMANN and the isonitrocarbolic acid of FRITSCHE) as that observed between the compounds of diazobenzol and carbolic acid, and that their deportment would be represented by the formula

$$\underbrace{C_6 H_3 (NO_2) N_2, NHO_3}_{\text{α-β Nitrate of diazonitrobenzol.}} + H_2 O = \underbrace{C_6 H_5 (NO_2)O}_{\text{α-β Nitrocarbolic acid.}} + NHO_3 + N_2.$$

The assumption has not been verified. On boiling these diazonitrobenzol compounds with water, they are certainly decomposed, after some time, with evolution of nitrogen gas, but neither the α nor β compound furnishes under these circumstances either of the well-known phenylic substitutes. In both cases a brownish and easily fusible substance is obtained, which readily dissolves in alcohol and ether, but which can in no manner be made to crystallize. I have not ascertained whether this substance deports itself differently according to its origin (from the α or β compound), nor have I analyzed it, but I presume that, judging from the progress of its formation, and also from the weak acid properties it exhibits (dissolving in potassa and being reprecipitated by hydrochloric acid), its composition is probably represented by the formula

$$C_6 H_5 (NO_2) O.$$
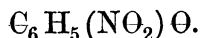
On heating an alcoholic solution of the perbromide of α diazonitrobenzol, it is readily decomposed according to the equation

$$\underbrace{C_6 H_3 (NO_2) N_2, HBr_3}_{\text{α perbromide.}} = \underbrace{C_6 H_4 (NO_2)Br}_{\text{Bromonitrobenzol.}} + N_2 + Br_2.$$
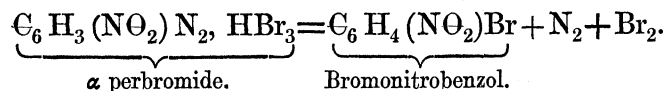
A portion of the bromonitrobenzol formed in this manner separates in crystals on cooling, provided the amount of alcohol employed has not been too large; the rest is precipitated on the addition of water. The crystals are purified by pressure between filter paper and distillation, when they pass over as a slightly yellowish oil, which soon solidifies to a crystalline mass. The bromonitrobenzol thus prepared is difficultly soluble

in cold, readily in hot alcohol and ether. It crystallizes from these solvents in long almost white needles, which fuse at 126° C., and which possess the odour of nitrobenzol. A bromine-determination gave the following results:—

0·3355 grm. was ignited with lime and gave 0·317 grm. of bromide of silver.

$$C_6 H_4 (NO_2) Br.$$
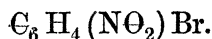
	Calculated.	Found.
Bromine	39·61 per cent.	40·19

If the perbromide of β diazonitrobenzol is decomposed in a similar manner with boiling alcohol, and the solid product of decomposition which forms purified as described before, a compound is obtained to which the formula $C_6 H_4 (NO_2) Br$ must likewise be assigned, which, however, differs greatly in its physical appearance and properties from the former bromonitrobenzol. It crystallizes from alcohol and ether, in which it seems to be more easily soluble, in the form of well-made, slightly yellowish, or almost white rhombic prisms, sometimes also in plates, and fuses at 56° C., or 70° below the fusing-point of the bromonitrobenzol derived from the α compound. The analysis of this body gave the following results:—

0·2745 grm. of substance gave 0·361 grm. of carbonic acid and 0·0535 grm. of water.

0·3365 grm. of substance gave, on ignition with caustic lime, 0·3145 grm. of bromide of silver.

	Calculated.		Found.
C_6	72	35·64	35·87
H_4	4	1·98	2·16
Br	80	39·61	39·77
N	14	6·93	——
O_2	32	15·84	——
	202	100·00	

The existence of these bromonitrobenzols suggests the question whether one of them be not identical with the bromonitrobenzol prepared by COUPER by the action of fuming nitric acid upon bromobenzol. COUPER's description of this body appeared to me scarcely conclusive of its nature; and in order to decide this question I have treated bromobenzol, prepared from coal-tar naphtha, with fuming nitric acid, and have compared the perfectly pure product, after repeated recrystallizations from alcohol, with the bromonitrobenzols prepared by my method. The striking coincidence between the crystalline form of COUPER's compound and of the bromonitrobenzol corresponding to the α nitraniline, which I will now call α bromonitrobenzol, became at once perceptible; and since both compounds crystallize in white needles that could by no means be distinguished from one another, I felt justified in coming to the conclusion that both are identical. In order, however, to make quite sure I have also determined the fusing-point of the respective compounds, and have found it uniformly at 120° C.*

* COUPER states (Ann. de Chim. et de Phys. [3] vol. lii. p. 309) that his compound fused below 90° C. This is evidently erroneous.

They are acted upon in a like manner by various reagents. When reduced in alcoholic solutions by sulphide of ammonium, they are both converted into bromaniline, which crystallizes in octahedra, and proves itself to be completely identical with that obtained from bromisatine or bromacetanilid by distillation with potash. Very different from this is the deportment of bromonitrobenzol (β bromonitrobenzol) prepared from perbromide of β diazonitrobenzol. On treating this compound with sulphide of ammonium, it is certainly also converted into bromaniline, but this base differs greatly from the above-described bromaniline. Ordinary bromaniline (which I would now designate as α bromaniline) crystallizes, as is well known, in octahedra which fuse at 57° C. The new base, however (the β bromaniline), forms an oil which does not solidify even in winter. The chemical deportment of both compounds is the same; they form, under like conditions, a series of derivatives which are of the same composition, and differ only in their physical properties.

In order to establish the composition of the β bromaniline experimentally, I have analyzed the hydrochlorate and its platinum-salt. *The hydrochlorate of β bromaniline* forms white, nacreous, brilliant plates, which are readily soluble in water and alcohol, and which are rapidly coloured red when exposed to the air.

0·2605 grm. of substance gave 0·176 grm. of chloride of silver.

$$C_6 H_6 Br N, HCl.$$

	Calculated.	Found.
Chlorine	17·02 per cent.	16·71

The Platinum-salt of the Hydrochlorate of β Bromaniline, $C_6 H_6 Br N, HCl, Pt Cl_2$,

crystallizes in yellow, often well-formed prisms, which are far more soluble in water than the slender highly lustrous plates of the platinum-salt of α bromaniline.

0·3735 grm. gave 0·097 grm. of platinum.

$$C_6 H_6 Br N, HCl, Pt Cl_2.$$
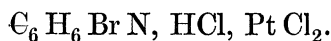
	Calculated.	Found.
Platinum	26·12 per cent.	25·97

I need scarcely state that *nitrochlorobenzol* compounds corresponding to α and β nitrobromobenzol can readily be obtained by submitting the platinum-salts of α and β diazonitrobenzol to distillation with carbonate of sodium. These two bodies differ likewise most characteristically; α nitrochlorobenzol crystallizes invariably in long, almost white needles which fuse at 83° C., whilst β nitrochlorobenzol crystallizes from its ethereal solution in thick columns which fuse at 46° C. The former is converted by sulphide of ammonium into the ordinary (α) chloraniline, the latter into a new base (β chloraniline), which is distinguished by its remaining an oil at the common temperature. The platinum-salt presents itself in the form of yellow crystals, which differ likewise considerably in form and solubility from the small slender plates of the platinum-salt of α bromaniline.

It may, I think, be safely deduced from these facts that two distinctly different series of compounds are obtained by the substitution of two atoms of hydrogen in benzol by two different elements, or groups of atoms, according as this substitution is accomplished, and that these two series differ most distinctly in their physical properties, although their chemical composition is the same. The great differences between the fusing-points form one of the most important means of distinction between the members of the two series. The fusing-points of series α lie considerably higher than those of the β series; sometimes a difference of 70° C. is observable, as will be seen by the accompanying Table.

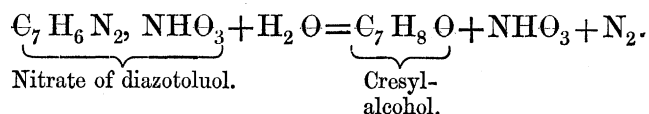|	α Series.	β Series.
Bromonitrobenzol . . .	126° C.	56° C.
Chloronitrobenzol . . .	83° C.	46° C.
Nitraniline	141° C.	108° C.
Bromaniline	57° C.	Liquid at the ordinary temperature.
Chloraniline		Liquid at the ordinary temperature.
Diazo-amidonitrobenzol .	245° C.	195° C.
Diazonitrobenzolimide . .	71° C.	53° C.

The compounds to which the experiments just described gave rise belonged exclusively to the aniline group. Now there could be little doubt that the homologues of aniline, and the similarly constituted bases, migh tbe also converted into diazo-compounds. This I have confirmed by experiment, the more readily since it was to be foreseen that the decomposition of some of these compounds would give rise to the formation of certain bodies which could not have been obtained by the ordinary methods, e. g. naphtylic alcohol, the existence of which, however, could not be doubted for a moment.

DIAZOTOLUOL COMPOUNDS.

These compounds exhibit considerable analogy with regard to preparation, solubility, and many other properties to the corresponding aniline derivatives. They seem, however, to be somewhat more constant, and to crystallize more readily.

Nitrate of Diazotoluol, $C_7 H_6 N_2, NHO_3$.

This substance is best prepared by the action of nitrous acid upon an aqueous solution of nitrate of toluidine, but it can also be obtained from diazo-amidotoluol. It forms long white needles, which are decomposed on boiling with water, according to the following equation:—

$$\underbrace{C_7 H_6 N_2, NHO_3}_{\text{Nitrate of diazotoluol.}} + H_2 O = \underbrace{C_7 H_8 O}_{\substack{\text{Cresyl-} \\ \text{alcohol.}}} + NHO_3 + N_2.$$

The other compounds are readily obtained from the nitrate in the ordinary manner.

Sulphate of Diazotoluol, $C_7 H_6 N_2$, $SH_2 O_4$,

is obtained in brilliant needles, plates, or prisms, according to the circumstances under which it crystallizes. On heating with sulphuric acid in the manner described when speaking of the sulphate of diazobenzol, it is converted into a sulpho-acid.

The barium-salt of this acid crystallizes in long white needles, and is disulpho-toluylenate of barium, which, according to the subjoined analysis, has the formula $C_7 H_6 S_2 Ba_2 O_7$.

0·530 grm. dried at 140° gave 0·276 grm. of sulphate of barium.

$$C_7 H_6 S_2 Ba_2 O_7.$$
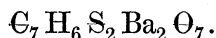
	Calculated.	Found.
Barium	33·99 per cent.	33·74

Perbromide of Diazotoluol, $C_7 H_6 N_2$, HBr, Br_2,

is thrown down as a yellow oil, which, after evaporation of the excess of bromine, solidifies to a crystalline mass.

Platinum-salt of the Hydrochlorate of Diazotoluol, $C_7 H_6 N_2$, $HCl\, Pt\, Cl_2$,

is precipitated from a dilute solution of the hydrochlorate of diazotoluol by means of bichloride of platinum, and forms fine yellow prisms. When ignited with soda it yields an aromatic oil, chlorotoluol ($C_7 H_7 Cl$). It remains to be seen whether this oil be identical, or only isomeric with the chlorobenzyl discovered by CANIZZARO.

0·360 grm. of substance gave 0·5765 grm. of carbonic acid and 0·1315 grm. of water. 0·6305 grm. gave, on ignition with carbonate of sodium, 0·1925 grm. of platinum.

	Calculated.		Found.
C_7	84	25·92	26·20
H_7	7	2·16	2·43
N_2	28.	8·63	——
Cl_3	106·5	32·85	——
Pt	98·7	30·44	30·53
	324·2	100·00	

Diazotoluol-amidobenzol, $\begin{cases} C_7 H_6 N_2 \\ C_6 H_5 (H_2 N). \end{cases}$

This body is obtained by the action of aniline upon nitrate of diazotoluol. It crystallizes in beautiful long yellow needles.

DIAZONITRANISOL COMPOUNDS.

These compounds are nearly related to the diazonitrobenzol-compounds, both with regard to physical properties and their deportment with reagents. They are prepared also in a similar manner, and it is only necessary therefore to refer respecting their preparation to these analogous bodies.

Nitrate of Diazonitranisol, $C_7 H_5 (NO_2) N_2 O, NHO_3$,

is obtained from nitrate of nitranisol. It separates from an alcoholic solution on the addition of ether, forming small white plates, which are difficultly decomposed on heating with water, giving rise to the formation of a brownish-red substance.

Perbromide of Diazonitranisol, $C_7 H_5 (NO_2) N_2 O, HBr_3$,

forms small yellow plates, which, on boiling with alcohol, furnish bromonitranisol $(C_7 H_6 (NO_2) Br)$, crystallizing in light-yellow opake needles, which may be sublimed, and possess the odour of nitrobenzol.

Diazonitranisolimide, $\left. \begin{array}{c} (C_7 H_5 (NO_2) N_2 O)'' \\ H \end{array} \right\} N$,

crystallizes in light-yellow needles, and possesses the odour of bitter almonds.

Platinum-salt of the Hydrochlorate of Diazonitranisol, $C_7 H_5 (NO_2) N_2 O, HCl, Pt Cl_2$.

When precipitated from a moderately concentrated solution, it forms a yellow powder, which under the microscope is found to consist of fine needles. Recrystallized from boiling water, it is obtained in orange-red, well-formed prisms. On heating with carbonate of sodium chloronitranisol $(C_7 H_6 (NO_2) Cl O)$ distils over, which crystallizes in fine, almost white needles.

0·8795 grm. of the platinum-salt gave 0·222 grm. of platinum.

$$C_7 H_5 (NO_2) N_2 O, HCl, Pt Cl_2.$$

	Calculated.	Found.
Platinum	25·62 per cent.	25·24

DIAZONAPHTOL COMPOUNDS.

Nitrate of Diazonaphtol, $C_{10} H_6 N_2, NHO_3$,

is prepared by the action of nitrous acid on moist nitrate of napthalidine (amidonaphtol); an amorphous reddish-brown substance* is formed at the same time, which must be separated by filtration when the reaction is over. As nitrate of diazonaphtol is not precipitated from its aqueous solution by alcohol and ether, it is not so easily obtained in a solid state as the corresponding bodies previously described; if, however, its aqueous solution be allowed to evaporate spontaneously in a shallow vessel, long white needles are formed, which are very soluble in water and alcohol, and likewise very explosive.

*Perbromide of Diazonaphtol*, $C_{10} H_6 N_2, HBr_3$,

is obtained in the form of orange crystals by the action of bromine-water upon the crude solution of the nitrate.

Platinum-salt of the Hydrochlorate of Diazonaphtol, $C_{10} H_6 N_2, HCl, Pt Cl_2$,

forms truncated, yellowish crystals, which are almost insoluble in water, alcohol, and ether.

* Probably impure nitrate of diazonaphtol-amidonaphtol.

1·0565 grm. of substance gave 0·2887 grm. of platinum.

$$C_{10}H_6N_2, HCl, PtCl_2.$$
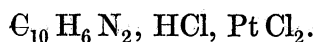
	Calculated.	Found.
Platinum . . .	27·40 per cent.	27·33

$$Diazonaphtolimide, \quad \left. \begin{array}{l} (C_{10}H_6N_2)'' \\ H \end{array} \right\} N,$$

passes over as a yellowish-coloured oil (which becomes brown when exposed to the air) by distilling with water the substance obtained by the action of ammonia upon the perbromide. It possesses somewhat the odour of naphtaline.

OBSERVATIONS ON THE PRODUCTS OF DECOMPOSITION OF THE DIAZONAPHTOL COMPOUNDS.

After being convinced that the products of decomposition of the diazonaphtol compounds so much resembled those of the other diazo-bodies, I could not entertain for a moment the intention of pursuing their study in all directions, especially since known bodies would frequently have formed the subject of such study. The decomposition of the perbromide, for instance, by means of alcohol gives rise to the formation of bromonaphtaline, that of the platinum-salt when ignited with carbonate of sodium to the formation of chlornaphtaline. I thought it, however, of sufficient importance to ascertain whether nitrate of diazonaphtol would split up according to the equation

$$C_{10}H_6N_2, NHO_3 + H_2O = C_{10}H_8O + N_2 + NHO_3,$$
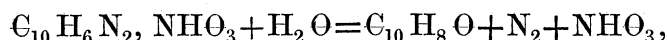
since the possibility of obtaining the long-sought-for naphtyl-alcohol presented itself. On boiling the solution of the nitrate of diazonaphtol, an immediate evolution of gas takes place, and a viscid violet-brown mass separates which remains on the filter when the solution is filtered hot.

The filtrate deposits generally small white plates, retaining, however, a portion of the substance dissolved, which can be recovered by shaking the aqueous solution with ether. On evaporating the ether it remains behind as a violet-coloured oil which quickly solidifies. This latter, as well as the plates first deposited, is in fact almost pure naphtyl-alcohol, whilst the violet-brown mass on the filter contains, besides naphtyl-alcohol, a considerable quantity of a reddish-brown body. In order to purify the naphtyl-alcohol, the united portions are treated with a cold solution of potassa, the residuary brown-red body* is filtered off, and the filtrate treated with acetic acid as long as precipitation ensues. Naphtyl-alcohol separates first as an oil, soon solidifying to a network of small plates, which are still somewhat violet-coloured. They are thrown on a filter, washed with cold water (which removes the mother-liquor), and then submitted to distillation.

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* This body is soluble in alcohol, to which it imparts a blood-red colour. On concentrating the alcoholic solution, reddish-brown indistinct crystals are deposited, which, on rubbing, acquire a green metallic lustre.

This process must be repeated until the mass of crystals, which is invariably found deposited in the condensing-tube, is quite white, and fuses, on heating, to a limpid oil. This body gave on analysis the following results:—

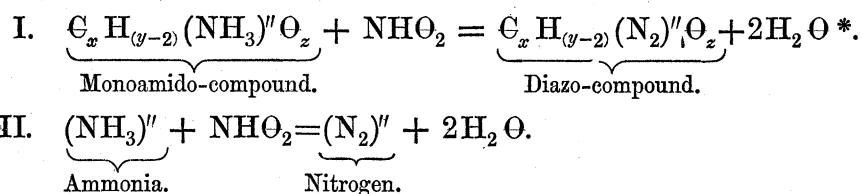0·2003 grm. of substance gave 0·6138 grm. of carbonic acid and 0·1047 grm. of water.

	Calculated.		Found.
C_{10}	120	83·33	83·57
H_8	8	5·56	5·81
O	16	11·11	——
	144	100·00	

Naphtyl-alcohol crystallizes in small white shining plates, fusing at 91° C. to a colourless, highly refractive oil which may be volatilized without decomposition. It is but slightly soluble in water, readily soluble in alcohol, ether, and benzol. When inflamed it burns with a thick smoky flame. Its formation and its physical properties prove its relationship with phenylic alcohol; it possesses a similar burning taste, and a creosotelike odour somewhat resembling that of naphtaline. The relation between it and phenylic alcohol is likewise indicated by its chemical deportment. It stands on the same narrow boundary line between acid and alcohol; and naphtyl-alcohol may, in like manner with phenol, be classified with alcohols or with acids. The strong bases form with the new alcohol (acid) a series of salts which are as unstable as those of phenylic acid, and are mostly decomposed even by the carbonic acid of the air. The potassium- or sodium-salt may also be obtained by the action of the respective metals upon the fused naphtylic acid with evolution of hydrogen. In both cases a crystalline saline mass is obtained which dissolves in water and alcohol. Basic acetate of lead produces in a solution of naphtyl-alcohol a white voluminous precipitate. An ammoniacal silver solution is decomposed, metallic silver being deposited. Nitric acid of sp. gr. 1·4 dissolves naphtyl-alcohol in the cold with evolution of red fumes. If the solution be boiled for some time and water added, a difficultly-soluble yellow acid precipitates, whilst a second readily-soluble acid is deposited in yellow crystals on evaporating the mother-liquor. The latter appears to be the picric acid of the naphtyl group. By treating the aqueous solution of naphtyl-alcohol with bromine-water, it deposits bromonaphtylic acid in the form of an oil which speedily crystallizes.
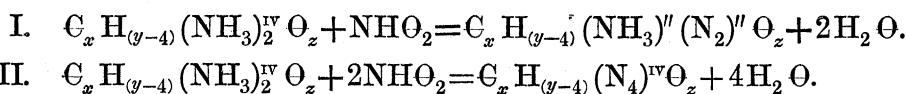

PART III.

All the diazo-compounds which have formed the subject of Parts I. and II. of this inquiry are derived from monoamido-compounds. If the composition of the latter be again expressed by the general formula $C_x H_{(y-2)} (NH_3)'' O_z$ (see page 667), it is at once perceived that the process of formation of the diazo-compounds is similar to the reaction which takes place by the action of nitrous acid on ammonia:

I. $\underbrace{C_x H_{(y-2)} (NH_3)'' O_z}_{\text{Monoamido-compound.}} + NHO_2 = \underbrace{C_x H_{(y-2)} (N_2)'' O_z}_{\text{Diazo-compound.}} + 2H_2O$ *.

II. $\underbrace{(NH_3)''}_{\text{Ammonia.}} + NHO_2 = \underbrace{(N_2)''}_{\text{Nitrogen.}} + 2H_2O$.

By viewing the diamido-compounds in like manner as represented by the general formula $C_x H_{(y-4)} (NH_3)_2'', O_z$, it is evident that the action of nitrous acid may give rise to two decompositions:

I. $C_x H_{(y-4)} (NH_3)_2^{IV} O_z + NHO_2 = C_x H_{(y-4)} (NH_3)'' (N_2)'' O_z + 2H_2O$.

II. $C_x H_{(y-4)} (NH_3)_2^{IV} O_z + 2NHO_2 = C_x H_{(y-4)} (N_4)^{IV} O_z + 4H_2O$.

The hydrogen contained in one atom of ammonia can thus be replaced by nitrogen, or both atoms of ammonia present in the original compound may be replaced by nitrogen, giving rise to a tetrazo-compound.

Although this theory has not been fully confirmed by the action (presently to be described) that nitrous acid exerts on benzidine, since an intermediate compound according to equation I. could not be obtained, it is nevertheless highly probable that nitrogenous compounds in accordance with equation I. exist, and that further experiments with other diamido-compounds will confirm this view.

Action of Nitrous Acid upon Benzidine.

Benzidine, which ZININ, its original discoverer, expressed by the formula

$$C_6 H_6 N,$$
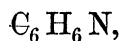
has been found, on further investigation by P. W. HOFMANN, to have double the atomic weight first assigned to it, and to be a base capable of combining with two molecules of acid. Very recently FITTIG has shown that it must be viewed as the diamido-compound of his newly discovered hydrocarbon-phenyl, and that it ought to be expressed by the rational formula $C_{12} H_8 (NH_2)_2$, or $C_{12} H_6 (NH_3)_2''$. I entirely abide by FITTIG's view, but find it necessary to select for both compounds a somewhat modified nomenclature, in order to avoid the use of the same names for some derivatives of these bodies (which I shall have occasion to describe) already employed for several long-known derivatives

* It must be borne in mind that nitrous acid acts upon the nitrates of the amido-compounds; if otherwise, the reactions would frequently give rise to the formation of diazoamido-compounds formerly described by me.

of phenylic acid. I propose, therefore, to designate Fittig's hydrocarbon, $C_{12}H_{10}$, as diphenyl, and to call benzidine diamidodiphenyl.

Nitrate of Tetrazodiphenyl, $C_{24}H_6N_4$, $2NHO_3$.

This compound is most readily and copiously obtained by passing nitrous acid through a cold concentrated aqueous solution of nitrate of diamidobenzidol, when only traces of a brown amorphous body are formed, whilst from an alcoholic solution the latter is deposited in considerable quantities. When a sufficient current of gas has been passed through the solution, the brown body is separated by filtration, the filtrate mixed with twice its volume of strong alcohol, and ether added as long as any white crystals are deposited. By once more dissolving the crystals in a very small quantity of water, and reprecipitating with alcohol and ether, they are obtained perfectly pure: it will be readily perceived that this mode of preparation closely resembles that for the preparation of nitrate of diazobenzol, which body presents a striking analogy to the nitrate of tetrazodiphenyl. The latter crystallizes in white or slightly yellowish-tinged needles, which are readily soluble in water, more difficultly so in alcohol, and insoluble in ether. On heating they explode with the same violence as the analogous diazo-compound.

Sulphate of Tetrazodiphenyl, $C_{12}H_6N_4$, $3SH_2O_4$.

After mixing a concentrated aqueous solution of the nitrate of tetrazodiphenyl with a sufficient quantity of cold sulphuric acid, diluted previously with its own bulk of water, this new body separates, on the addition of strong alcohol, either in the form of a white crystalline powder, or in white needles. If alcohol does not completely precipitate it, ether must be added to complete its separation. It is very soluble in water. On heating in a dry state an explosion ensues.

I. 0·820 grm. of substance gave, on direct precipitation with chloride of barium, 0·811 grm. of sulphate of barium.

II. 0·441 grm. gave 0·4355 grm. of sulphate of barium.

	Calculated.		Found. I.	Found. II.
$2C_{12}H_6N_4$	412	58·36		
$3SH_2O_4$	294	41·64	41·60	41·54
	706	100·00		

This compound partakes of the nature of an acid salt.

Platinum-salt of the Hydrochlorate of Tetrazodiphenyl, $C_{12}H_6N_4$, $2HCl$, $2PtCl_2$.

This salt is precipitated from a moderately dilute solution of the nitrate or sulphate by means of bichloride of platinum. It forms light-yellow very small narrow plates. By employing a very dilute solution, it falls slowly, in small, elongated, well-formed

hexagonal plates. These crystals are almost insoluble in water, alcohol, and ether. Exposure to light during drying causes them to assume a slightly brown colour.

0·6125 grm. gave 0·5252 grm. of carbonic acid and 0·0915 grm. of water.

0·6065 grm. gave 44·1 cub. centims. of nitrogen at 0° C. and 760 millims. bar. pressure, =0·055415 grm.

0·739 grm. gave on ignition with carbonate of soda 0·232 grm. of platinum.
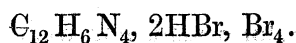
	Calculated.		Found.
C_{12}	144	23·29	23·38
H_8	8	1·30	1·66
N_4	56	9·05	9·44
Pt_2	197·4	31·92	31·40
Cl_4	213	34·44	——
	618·4	100·00	

Perbromide of Tetrazodiphenyl, $C_{12}H_6N_4$, $2HBr$, Br_4.
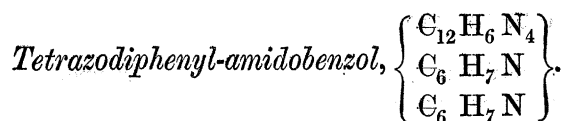
This compound is formed on the addition of bromine-water to an aqueous solution of the nitrate of the tetrazodiphenyl, being precipitated in the form of round reddish crystals, which are collected on a filter, thoroughly washed with water, and dried without delay over sulphuric acid and caustic lime. They are thus obtained sufficiently pure for analysis. Further purification indeed is impossible, since this body is decomposed by dissolving in alcohol, with evolution of gas. Even at the ordinary temperature it undergoes a gradual decomposition and evolves bromine, which is recognizable by its odour. For this reason the bromine-determinations, which were made with portions of this body that had been left for several days under the desiccator, were found a little too low.

I. 0·583 grm., decomposed with alcoholic potash, gave 0·931 grm. of bromide of silver =67·96 per cent.

II. 0·742 grm. gave, on ignition with caustic lime, 1·192 grm. of bromide of silver =68·36 per cent.

$$C_{12}H_6N_4, 2HBr, Br_4.$$

	Calculated.	Found.	
		I.	II.
Bromine	69·77	67·96	68·36

Tetrazodiphenyl-amidobenzol, $\begin{cases} C_{12}H_6N_4 \\ C_6H_7N \\ C_6H_7N \end{cases}$.

By adding aniline to an aqueous solution of nitrate of tetrazodiphenyl, this complex substance, corresponding to the diazo-amidobenzol in the diazobenzol series, is at once separated as a yellow crystalline mass; by repeatedly washing with alcohol it is easily obtained in a pure state for analysis.

0·2693 grm. gave 0·7233 grm. of carbonic acid and 0·1315 grm. of water. These numbers correspond to the above formula, $C_{24} H_{20} N_6$.

	Calculated.		Found.
C_{24}	288	73·47	73·24
H_{20}	20	5·10	5·42
N_6	84	21·43	——
	392	100·00	

The formation of this new substance can be expressed as follows:

$$C_{12} H_6 N_4, 2NHO_3 + 4C_6 H_7 N = C_{24} H_{20} N_6 + 2(C_6 H_7 N, NHO_3).$$

Nitrate of tetrazo-   Aniline.   Tetrazodiphenyl-   Nitrate of aniline.
diphenyl.   amidobenzol.

Tetrazodiphenyl-amidobenzol is insoluble in water, and, although very little soluble even in boiling alcohol and ether, can be recrystallized from them. By this means lance-shaped crystals are obtained, which are generally grouped together in a star-like form. When heated they explode; boiled with mineral acids they are decomposed with evolution of nitrogen gas.

$$\textit{Diphenylimide,} \quad \left.\begin{matrix}(C_{12} H_6 N_4)^{\text{IV}} \\ H_2\end{matrix}\right\} N_2.$$

This body is obtained in crystals when the perbromide is acted upon by solution of ammonia. The crystals are purified by repeated recrystallization from strong alcohol, when they are obtained in small very brilliant white, or slightly yellowish plates, insoluble in water, very difficultly soluble in cold alcohol, and only moderately soluble in ether. Boiling alcohol, however, dissolves them very readily, and yields on cooling a mass of crystals. The compound fuses at 127° C. to a yellow oil, which is decomposed at a higher temperature, giving rise to slight explosions. It does not combine with acids or alkalies, and is perfectly neutral to test-paper. No change is produced even by boiling with concentrated hydrochloric acid, nor with aqueous or alcoholic potash. It is decomposed, however, by nitric or strong sulphuric acid.

I. 0·2503 grm. of substance gave 0·5577 grm. of carbonic acid and 0·0816 grm. of water.

II. 0·3118 grm. gave 0·6918 grm. of carbonic acid and 0·0983 grm of water.

	Calculated.		Found.	
			I.	II.
C_{12}	144	61·02	60·76	60·51
H_8	8	3·39	3·62	3·50
N_6	84	35·59	——	——
	236	100·00		

The formation of this compound may be expressed by the following equation:—

$$\underbrace{C_{12}H_6N_4, 2HBr, Br_4}_{\text{Perbromide.}} {}^* + 8NH_3 = \underbrace{C_{12}H_8N_6}_{\text{Tetrazodiphenylimide.}} + 6NH_4Br.$$

It has been my endeavour to study somewhat more closely the compounds which tetrazodiphenyl forms with metallic hydrates, but all my attempts to obtain them more definitely have failed, and their preparation seems indeed to be beset with insurmountable difficulties. I omit a lengthened description of the unsuccessful attempts, and will merely show by one instance how tetrazodiphenyl can play the part of an acid. An aqueous solution of nitrate of tetrazodiphenyl, when mixed with caustic potash, yields a yellow liquid exhibiting such properties as might be looked for in a solution of the compound of hydrate of potassa with tetrazodiphenyl. On treating it with chloride of platinum, it gives rise to the formation of the platinum-compound above described, a proof that the tetrazodiphenyl remains unchanged in the alkaline solution. It is invariably decomposed on the application of heat, with evolution of gas and separation of a reddish-brown amorphous substance.

PRODUCTS OF DECOMPOSITION OF THE COMPOUNDS OF TETRAZODIPHENYL.

By applying the laws of classification just now accepted by chemists to the tetrazotized derivatives of benzidine, specially taking into account their manner of formation and combination, these bodies must be classified with the diatomic compounds, whilst the respective diazo-compounds belong to the monatomic bodies. It has been of late a favourite subject of chemical research to trace the analogies which monatomic bodies exhibit under the influence of certain agents with polyatomic bodies. In illustration of this I may refer to the results obtained in the comparative study of the products of decomposition of the ethyl- and ethylene-alcohols in order to show how simple are the laws which regulate these chemical transformations. The experimental results which I am able to adduce prove likewise that the decomposition of the tetrazo-compound gives rise to derivatives which differ in nothing from those obtained under similar circumstances from diazo-compounds, beyond the distinctive features imparted to them by the polyatomic nature of the compound from which they are derived.

Action of Water upon Nitrate of Tetrazodiphenyl.

An aqueous solution of this body, when left in a cold place, gradually undergoes a spontaneous decomposition. When heated it gives rise to a copious evolution of nitrogen gas with separation of two substances—one an amorphous brown, and the other a white crystalline body. An additional quantity of the latter is obtained when the liquid has

---

* Leaving aside the hydrobromic acid, this compound may be looked upon as the bromide of a tetratomic radical $(C_{12}H_6N_4)^{IV}Br_4$.

become quite cold. It is easy to separate these two bodies by filtering off the acid mother-liquor, pressing the residue between bibulous paper, and repeatedly extracting with dilute alcohol, which takes up the crystalline substance and leaves the brown body undissolved: this latter being very probably identical with the brown compound obtained as a by-product in the formation of nitrate of tetrazobenzidol, and being moreover of a very unpromising nature, I have not pursued its study any further. The crystalline product of decomposition dissolved by the alcohol is obtained on evaporation as a yellowish crystalline mass, from which the least traces of the brown body are removed by repeatedly dissolving in ether, and lastly recrystallizing from dilute alcohol.

0·3037 grm. of substance gave 0·8603 grm. of carbonic acid and 0·154 grm. of water.

Qualitative tests showed the absence of nitrogen; these numbers correspond therefore with the formula $C_{12}H_{10}O_2$, as will be seen from the following calculations:—

	Theory.		Experiment.
C_{12}	144	77·42	77·26
H_{10}	10	5·38	5·63
O_2	32	17·20	——
	186	100·00	

The formation of this compound, for which I propose the name of diphenyl-alcohol or diphenylic acid, takes place according to the equation

$$C_{12}H_6N_4, 2NHO_3 + 2H_2O = C_{12}H_{10}O_2 + 2NHO_3 + 4N.$$

Nitrate of tetrazodiphenyl. Diphenyl-alcohol.
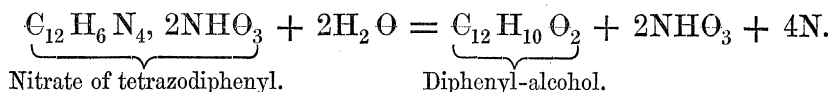
Diphenyl-alcohol (diphenylic acid) crystallizes in small white, or slightly tinged plates or needles, which possess slight solubility in water, but are soluble to any extent in alcohol and ether. It fuses on heating, and can be sublimed in small quantities by heating it cautiously in a test-tube. It is thus obtained in the form of soft, white, very lustrous plates. The chemical deportment of diphenyl-alcohol shows it to be most closely allied to the class of compounds the best-known representative of which is phenylic alcohol. It may in fact be considered as the first biatomic representative of this peculiar group of chemical compounds. The new alcohol is readily soluble in potash, and can be reprecipitated by the addition of an acid. Concentrated ammonia also dissolves it. On heating an ammoniacal solution with basic acetate of lead, a white voluminous precipitate ensues. Heated with ordinary strong nitric acid it is changed into a nitro-acid, which crystallizes out in yellow roundish crystals; the ammonium-salt of this acid crystallizes in beautiful long needles.

Action of Alcohol upon Sulphate of Tetrazodiphenyl.

On heating an admixture of alcohol and sulphate of tetrazodiphenyl, violent decomposition takes place. The products formed are nitrogen, sulphuric acid, and a solid sub-
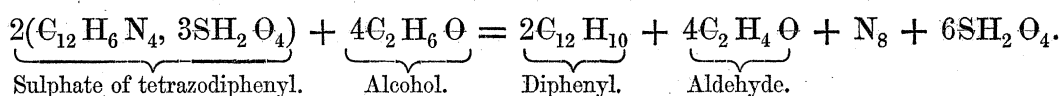
tance, which separates in small indistinct plates on mixing the alcoholic fluid (after the reaction is entirely over) with a large quantity of water. In order to free the precipitate from a trace of a brown substance, which likewise forms in the reaction, it is filtered off from the mother-liquor, dried, and then sublimed through paper, according to the method proposed by GORUP-BESANEZ. The substance is thus obtained in the form of perfectly white plates, which dissolve easily in ether and hot alcohol, and which crystallize from the latter very much like naphtaline. The new compound fuses at 70° C. to an oil, which distils at a higher temperature without decomposition. It possesses a peculiar aromatic odour like that of cinnamol and benzol combined.

0·1787 grm. of substance gave 0·607 grm. of carbonic acid and 0·107 grm. of water. These numbers lead to the formula $C_{12}H_{10}$.

	Calculated.		Found.
C_{12}	144	93·50	92·70
H_{10}	10	6·50	6·65
	154	100·00	

Its chemical composition, combined with the before-mentioned physical properties, prove that the hydrocarbon is identical with the diphenyl described by FITTIG[*]. Its formation may be described by the following equation:—

$$2(C_{12}H_6N_4, 3SH_2O_4) + 4C_2H_6O = 2C_{12}H_{10} + 4C_2H_4O + N_8 + 6SH_2O_4.$$

Sulphate of tetrazodiphenyl.   Alcohol.   Diphenyl.   Aldehyde.

Nitrate of tetrazodiphenyl is decomposed in a similar manner by boiling alcohol, but simultaneously the formation of a yellow nitro-acid takes place, which stands probably to the diphenylic alcohol in the same relation as the nitrophenol to phenylic alcohol (compare also the corresponding decomposition of nitrate of diazobenzol, p. 683).

Action of Sulphuric Acid upon Sulphate of Tetrazodiphenyl.

On heating sulphate of tetrazodiphenyl dissolved in a small quantity of oil of vitriol, a violent evolution of nitrogen gas is observed. The brown liquid which remains after the reaction has ceased contains, besides the excess of sulphuric acid employed, two new sulpho-acids, which can be separated by means of their barium-salts. For this purpose the brown liquid is diluted with at least thirty times its volume of water, boiled, and saturated with carbonate of barium. The precipitated sulphate of barium is then filtered off, the saline solution evaporated to dryness on the water-bath, and the residue several times extracted with hot water. The portion remaining undissolved is the

[*] If the diphenyl, prepared according to my method, has not been previously sublimed through paper as described, it crystallizes only in the form of small indistinct silvery white plates, which are so different from the large naphtaline-like plates described by FITTIG, that they appear at first sight to be crystals of quite a different compound.

barium-salt of a new acid which I will call tetrasulphodiphenylenic acid; the soluble portion contains another new acid, for which the name trisulphodiphenylenic acid may be adopted.

I will first endeavour to give a brief description of the former. The barium-salt of this acid, obtained as before mentioned, being only very slightly soluble in water, could not well be purified by recrystallization; I preferred therefore to convert it into the ammonium-salt, which served me as a starting-point for the preparation of all the saline compounds presently to be described. The ammonium-salt is readily obtained by decomposing the barium-salt with a solution of carbonate of ammonium. The mixture is heated for a short time, the insoluble carbonate of barium filtered off, and the filtrate concentrated on a water-bath till the ammonium-salt crystallizes out on cooling. One recrystallization from alcohol renders it in the form of perfectly pure white prisms.

Barium-salt of Tetrasulphodiphenylenic Acid, $C_{12}H_6, S_4H_2Ba_4O_{15}$.

To a rather concentrated boiling solution of the ammonium-salt chloride of barium is added, when this salt is precipitated as white needles or prisms; the crystals are allowed to subside, and, after the mother-liquor has been separated by filtration, repeatedly washed with cold water; in this manner they are obtained quite pure. The substance employed for the following analyses was dried between 150° and 160°.

I. 0·612 grm. gave 0·4055 grm. of carbonic acid and 0·070 grm. of water.

II. 0·365 grm., decomposed by nitric acid, gave 0·4327 grm. of sulphate of barium, corresponding to 16·28 per cent. of sulphur.

III. 0·2845 grm., treated with sulphuric acid, gave 0·177 grm. of sulphate of barium $= 34·14$ per cent. of barium.

IV. 0·6185 grm., treated as before, gave 0·4327 grm. of sulphate of barium $= 34·77$ per cent. of barium.

These numbers lead to the formula

$$C_{12}H_8S_4Ba_4O_{15}.$$
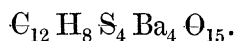
		Calculated.	I.	II.	III.	IV.
C_{12}	144	18·14	18·07	—	—	—
H_8	8	1·00	1·27	—	—	—
S_4	128	16·21	—	16·28	—	—
Ba_4	274	34·51	—	—	34·14	34·77
O_{15}	240	31·35	—	—	—	—
	794	100·00				

Dried over sulphuric acid, the salt retains four molecules of water of crystallization. 0·452 grm., dried as above, lost between 150° and 160° 0·037 grm. of water.

$$C_{12}H_8Ba_4S_4O_{15}+4H_2O.$$
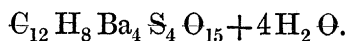
	Calculated.	Found.
$4H_2O$	8·03	8·00

If the ammonium-salt of tetrasulphophenylenic acid be, instead of chloride of barium, treated with baryta-water, another barium-salt is formed, which, according to the subjoined barium-determination, has the composition $C_{12}H_6, S_4 Ba_6 O_{15}$. It is precipitated as a white amorphous powder, which, on washing with water, is converted into small prisms.

0·6085 grm., dried at 150°, gave 0·4585 grm. of sulphate of barium.

$$C_{12}H_6, S_4 Ba_6 O_{15}.$$

	Calculated.	Found.
Ba	44·24	44·29

### Silver-salt, $C_{12}H_6, S_4 H_3 Ag_3 O_{15}$.
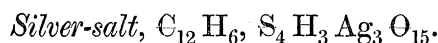
On mixing a concentrated solution of the ammonium-salt with an equally concentrated solution of nitrate of silver, separation of warty crystals of this salt takes place after some time. They may be purified by recrystallization from water, in which they are easily soluble. The concentration of their solution must be conducted *in vacuo*.

0·3955 grm., dried at 150°, gave 0·2025 grm. of chloride of silver.

$$C_{12}H_9 S_4 Ag_3 O_{15}.$$
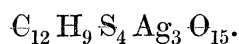
	Calculated.	Found.
Ag	38·34	38·50

0·4205 grm. of silver-salt, dried over sulphuric acid, lost at 150° 0·025 grm. of water.

$$C_{12}H_9 S_4 Ag_3 O_{15} + 3H_2 O.$$
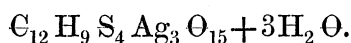
	Calculated.	Found.
$3H_2O$	6·00	5·95

When describing disulphophenylenic acid (page 687), it was shown that it is capable of forming two series of salts exhibiting an analogous relationship to each other, as metaphosphates to ordinary phosphates. Tetrasulphodiphenylenic acid behaves in a similar manner. Thus the salts previously described point most naturally to the conclusion that it is hexabasic, while the salts which will be presently mentioned indicate its capability of assuming also an octabasic character.

### Lead-salt, $C_{12}H_6, S_4 Pb_8 O_{16}$.
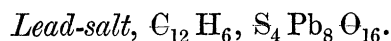
When a boiling solution of tetrazodiphenylenate of ammonium is mixed with a solution of neutral acetate of lead, this salt is precipitated in the form of white needles. Repeated washings with water render it quite pure.

1·0195 grm., dried at 150°, gave 0·3797 grm. of carbonic acid and 0·054 grm. of water.

0·3135 grm.* gave 0·2755 grm. of sulphate of lead, corresponding to 60·04 per cent. of lead and 9·28 per cent. of sulphur.

$$C_{12} H_6 S_4 Pb_8 O_{16}.$$

	Calculated.		Found.
C_{12}	144	10·57	10·16
H_6	6	0·45	0·59
Pb_8	828	60·79	60·04
S_4	128	9·39	9·28
O_{16}	256	18·80	——
	1362	100·00	

Basic Lead-salt, $C_{12} H_6, S_4 Pb_8 O_{16} + P_4 O_2$
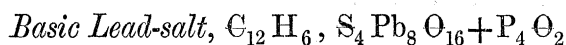
This salt is obtained by treating the hot solution of the amm acetate of lead. It is a white amorphous precipitate.

0·5935 grm., dried at 150°, gave 0·592 grm. of sulphate of lea

$$C_{12} H_6 S_4 Pb_{12} O_{18}.$$

	Calculated.	Found.
Pb	68·69	68·14

Tetrasulphodiphenylenic acid is easily to be obtained in a free state, either by decomposing the lead- or silver-salt with sulphuretted hydrogen, or by treating the barium-salts with an equvalent quantity of sulphuric acid. The filtered aqueous solution is evaporated on a water-bath to a syrupy consistence, and placed over sulphuric acid; after some time white needles or plates are obtained, which are very soluble in water and alcohol, but not deliquescent in the air. I have not yet analyzed this acid; but according to the above-mentioned salts it seems very probable that it can exist in two different states, as expressed by the formulæ $C_{12} H_6, S_8 H_6 O_{15}$ and $C_{12} H_6, S_8 H_8 O_{16}$.

The second compound (trisulphodiphenylenic acid) to which the reaction of sulphuric acid or sulphate of tetrazobenzidol gives rise deserves likewise a few passing remarks. The separation of its barium-salt from the barium-salt of tetrasulphodiphenylic acid by means of hot water has already been described. The aqueous extracts thus obtained, sufficiently evaporated and allowed to cool, will generally solidify to a gelatinous mass from which distinct crystals cannot be obtained, even by repeated solution and evaporation. Crystallization may, however, be effected thus: The gelatinous salt is converted into the ammonia-compound, by boiling with an aqueous solution of carbonate of ammonium.

* This substance was boiled with concentrated nitric acid till red fumes ceased to be evolved, and evaporated to dryness. The sulphate of lead was then collected on a filter and well washed with alcohol; the alcoholic filtrate contains neither a trace of lead nor sulphuric acid.

The excess of ammonia is removed by evaporation, and the crystalline residue dissolved in a little hot water and treated with a solution of chloride of barium. On cooling, warty crystals, or globular groups of small plates, of the barium-salt are obtained, which can be freed from the difficultly-soluble tetrasulphodiphenylenate of barium with which it may still be contaminated, and also from the mother-liquor, by repeated crystallization from water.

The analysis of this salt (dried at 130° C., at which temperature it turns to a dirty green colour owing to the loss of water of crystallization) gave the following numbers:

0·526 grm. of substance gave 0·4403 grm. of carbonic acid and 0·0766 grm. of water.

0·453 grm. gave 0·2535 grm. of sulphate of barium.

0·3605 grm. gave 0·388 grm. of sulphate of barium.

These amounts lead to the formula

$$C_{12} H_6 S_3 H Ba_3 O_{11}.$$

	Calculated.		Found.
C_{12}	144	22·91	22·80
H_7	7	1·11	1·60
Ba_3	205·5	32·70	32·80
S_3	96	15·28	14·78
O_{11}	176	28·00	——
	628·5	100·00	

Lead-salt, $C_{12} H_6, S_3 Pb_6 O_{12}.$

White amorphous precipitate obtained by treating a hot solution of the barium-salt with a solution of neutral acetate of lead.

0·711 grm., dried at 130°, gave 0·604 grm. of sulphate of lead.

$$C_{12} H_6, S_3 Pb_6 O_{12}.$$

	Calculated.	Found.
Pb	58·63	58·05

0·7375 grm., dried over sulphuric acid, lost at 130° 0·0265 grm. of water.

$$C_{12} H_6 S_3 Pb_6 O_{12} + 2H_2 O.$$

	Calculated.	Found.
$4H_2O$	3·29	3·52

Basic Lead-salt, $C_{12} H_6, S_3 Pb_6 O_{12}, Pb_4 O_2,$

is precipitated from a solution of the ammonium- or barium-salt with basic acetate of lead. It scarcely differs in its properties from the previous salt.

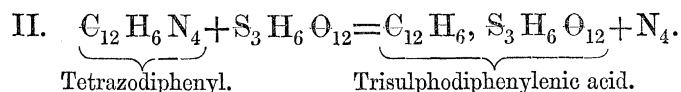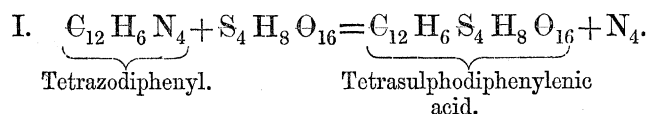0·750 grm., dried at 130°, gave 0·2483 grm. of carbonic acid and 0·0557 grm. of water.

0·5395 grm., dried at the same temperature, gave 0·532 grm. of sulphate of lead.

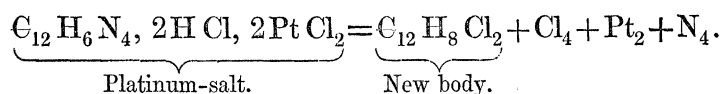|	Calculated.		Found.
C_{12}	144	9·57	9·03
H_6	6	0·40	0·82
S_3	96	6·38	——
Pb_{10}	1035	68·77	68·59
O_{14}	224	14·88	——
	1505	100·00	

Trisulphodiphenylenic Acid

is obtained in a free state in exactly the same manner as tetrasulphodiphenylenic acid, which it resembles in every other respect. It is evident at a glance that its composition may also be expressed in two different ways, viz. $C_{12}H_6$, $S_3H_4O_{11}$, or $C_{12}H_6$, $S_3H_6O_{12}$.

In accordance with the experiment just described, the decomposition which the tetrazodiphenyl undergoes by the action of sulphuric acid may be expressed by the following equations:—

$$\text{I.} \quad \underbrace{C_{12}H_6N_4}_{\text{Tetrazodiphenyl.}} + S_4H_8O_{16} = \underbrace{C_{12}H_6S_4H_8O_{16}}_{\substack{\text{Tetrasulphodiphenylenic}\\\text{acid.}}} + N_4.$$

$$\text{II.} \quad \underbrace{C_{12}H_6N_4}_{\text{Tetrazodiphenyl.}} + S_3H_6O_{12} = \underbrace{C_{12}H_6, S_3H_6O_{12}}_{\text{Trisulphodiphenylenic acid.}} + N_4.$$

Decomposition of the Platinum-salt of Tetrazodiphenyl and of the Perbromide.

On mixing the platinum-salt of tetrazodiphenyl with from four to six times its weight of carbonate of sodium, and heating the mixture in a retort, a copious evolution of gas speedily ensues; and on increasing the heat an oily body distils, which solidifies in the neck of the retort to a white mass. By pressing this body between bibulous paper, and by repeated recrystallization from boiling alcohol, it is obtained perfectly pure. Analogy leads to the supposition that the formation of this body takes place according to the equation

$$\underbrace{C_{12}H_6N_4, 2HCl, 2PtCl_2}_{\text{Platinum-salt.}} = \underbrace{C_{12}H_8Cl_2}_{\text{New body.}} + Cl_4 + Pt_2 + N_4.$$

The following chlorine-determination corroborates this transformation:—

0·235 grm. gave 0·2938 grm. of chloride of silver = 30·93 per cent. of chlorine.

Calculated.	Found.
Chlorine = 31·84 per cent.	30·93.

This new body, which I will call dichlorodiphenyl, crystallizes in white, usually well-formed prisms; it is difficult of solution even in boiling alcohol, but readily soluble in

ether, and quite insoluble in water. It fuses at 148° C. to a yellowish oil, which can be distilled without decomposition.

On heating in like manner the perbromide of tetrazodiphenyl with carbonate of sodium, a mixture of bromine and nitrogen gas is evolved, and on heating more strongly an oily substance distils over, which quickly solidifies. It is obtained pure for analysis by repeated recrystallization from ether.

0·322 grm. gave 0·5513 grm. of carbonic acid and 0·082 grm. of water.

These numbers correspond, as might be expected, with the formula

$$C_{12} H_8 Br_2.$$

	Theory.		Experiment.
C_{12}	144	46·15	46·69
H_8	8	2·57	2·84
Br_2	160	51·28	——
	312	100·00	

This compound, which may be called dibromodiphenyl, resembles the previously described chlorine-compound; it crystallizes likewise in well-formed prisms, which appear to be even more insoluble in alcohol and ether than the above, and which fuse at 164° C. This substance is obtained, moreover, by boiling the perbromide with alcohol, as in the following equation:—

$$\underbrace{C_{12} H_6 N_4 H_2 Br_2 Br_4}_{\text{Perbromide.}} = \underbrace{C_{12} H_8 Br_2}_{\text{Dibromodiphenyl.}} + N_4 + Br_4.$$
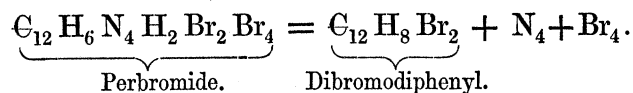
The substance separates from the alcoholic solution on cooling in crystals; it is best purified by distillation.

Dr. FITTIG informs me that he obtained a compound of like composition by acting with bromine upon diphenyl. The description of this new compound given by him applies so entirely to the dibromodiphenyl prepared by me, that no doubt remains of the identity of the bodies obtained by different methods.