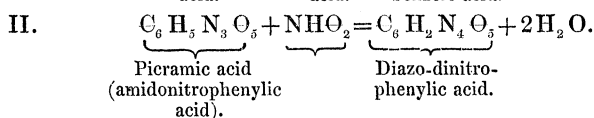
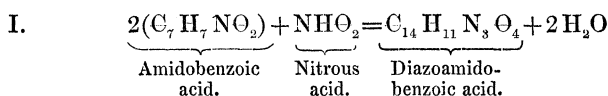


pretend in such delicate experiments to have arrived at nearer approximations than that of a degree or two of the electrometer, or within quantities less than that of .25 of a circular inch. If the manipulation, however, be skilfully conducted, and the electrical insulations perfect, it is astonishing how rigidly exact the numerical results generally come out.

XX. "On a New Class of Compounds in which Nitrogen is substituted for Hydrogen." By PETER GRIESS, Esq. Communicated by Dr. HOFMANN. Received June 2, 1864.

(Abstract.)

All the bodies in which nitrogen is substituted for hydrogen which I have discovered during the last few years* may be divided into two distinctly different classes. The first class comprises those bodies which are obtained when three atoms of hydrogen in two atoms of an amido-compound are replaced by one of nitrogen from nitrous acid. The members of the second group are formed by the action of nitrous acid upon one equivalent of an amido-compound only. The following equations will best show these various reactions:—



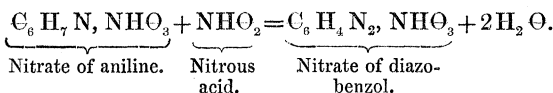
I have hitherto chiefly examined into the constitution of the bodies that form according to the first equation (diazoamidobenzol, diazoamidobenzoic acid), and have only incidentally explored the field of bodies which equation II. opens up. I have had occasion since to study more closely several representatives of the latter class of compounds, which are derived from aniline (amidobenzol) and analogous organic bases; and since the results which I obtained cannot but excite some interest, I may be permitted to submit them briefly to the Royal Society.

Nitrate of Diazobenzol, C₆H₄N₂, NHO₃.

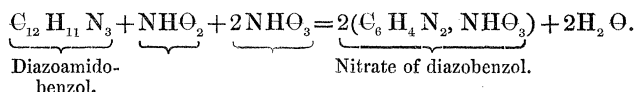
This compound is most readily obtained by passing a rapid current of nitrous acid gas through a solution of nitrate of aniline, saturated in the cold, until aniline ceases to be separated by the addition of solution of caustic potash to the liquid. On diluting the solution then with three times its volume of alcohol, and adding a sufficient quantity of ether, nitrate of diazobenzol separates in long white needles. In order to remove a trace of a colouring substance, the crystals are redissolved in a small quantity of

* Ann. der Chem. und Pharm. vol. cxiii. p. 201; vol. cxvii. p. 1; vol. cxxi. p. 257. Proceedings of the Royal Society, vol. x. p. 591; vol. xi. p. 263; vol. xii. p. 418.

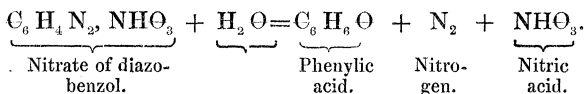
cold dilute alcohol and precipitated by ether. The following equation expresses the reaction :—



Nitrate of diazobenzol may also be prepared from diazoamidobenzol, a substance described by me on a former occasion*, by treating an ethereal solution of the latter with nitrous acid,



The new compound dissolves very readily in water, more difficultly in alcohol, and is almost insoluble in ether. On heating, the solutions are decomposed with evolution of gas. The dry substance explodes with the greatest violence when gently heated, and it is necessary to observe great precautions whilst working with it. The chemical analysis could not, for the same reason, be performed by the usual methods. Its composition was, however, readily established by studying the products of decomposition to which boiling with water gives rise, according to the equation

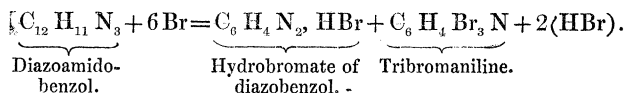


Sulphate of Diazobenzol, C₆H₄N₂SH₂O₄.

This salt forms when a highly concentrated aqueous solution of the former compound is treated with a sufficient quantity of cold sulphuric acid diluted with its own bulk of water. The solution is treated, as before, with three times its volume of alcohol, and ether added, which causes the sulphate of diazobenzol to separate in a layer of a very concentrated aqueous solution at the bottom of the vessel. On placing this latter solution over sulphuric acid, crystallization ensues after a short time. The crystals are freed from the mother-liquor by washing with absolute alcohol. In this manner large white prisms, which rapidly deliquesce in moist air, are obtained, and which are decomposed with slight deflagration when heated by themselves.

Hydrobromate of Diazobenzol, C₆H₄N₂, HBr.

This compound is obtained in small white soft plates when an ethereal solution of diazoamidobenzol is mixed with an ethereal solution of bromine,



* Ann. der Chem. und Pharm. vol. cxxi. p. 258.

Hydromate of diazobenzol is very unstable. The beautifully white crystals change so rapidly that in a few moments they acquire a reddish colour, and in a few days the decomposition is almost complete. They explode on heating almost with the same violence as was experienced with nitrate of diazobenzol.

Dibromide of Hydromate of Diazobenzol, $C_6H_4N_2$, HBr, Br₂.

On adding excess of bromine-water to an aqueous solution of any one of the compounds previously described, an orange-coloured oil is obtained which rapidly solidifies, after the mother-liquor has been removed, to small orange-coloured plates. The crystals of dibromide are obtained in a perfectly pure state by washing with a little alcohol. This compound is rather difficultly soluble in cold alcohol and ether; and the solutions are rapidly decomposed, particularly on the application of heat.

Platinum-salt of the Hydrochlorate of Diazobenzol, $C_6H_4N_2$, HCl, PtCl₂.

This salt forms beautiful yellow prisms which are almost insoluble in water. The gold-salt, $C_6H_4N_2$, HCl, AuCl₃, can be recrystallized from alcohol, and is obtained in very fine golden-yellow brilliant plates.

It has thus been sufficiently shown that diazobenzol deports itself like an organic base, being capable, like aniline, of forming salts with various acids. It possesses, however, also the property of combining with the hydrates of the metals, thus playing the part of a weak acid.

Compound of Hydrate of Potassium with Diazobenzol, $C_6H_4N_2$, KHO.

This body is obtained when a concentrated aqueous solution of nitrate of diazobenzol is treated with excess of concentrated aqueous potassa. By evaporating on the water-bath, the liquid solidifies, when sufficiently concentrated, to a magma of yellow crystals consisting of nitre and the compound of hydrate of potassa with diazobenzol. The crystalline mass is pressed between porous stones, and thus partly freed from moisture. By dissolving in absolute alcohol and treating with ether, the new compound of hydrate of potassium with diazobenzol is obtained in a pure state, crystallizing in small soft white plates, which rapidly become reddish, especially in the moist condition. It is very readily soluble in water and alcohol; the solutions, however, decompose slowly, and deposit a reddish amorphous body. Heat does not seem to accelerate this decomposition materially.

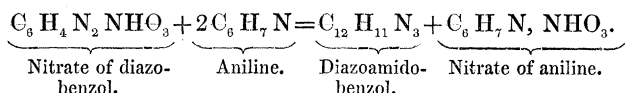
Compound of Hydrate of Silver with Diazobenzol, $C_6H_4N_2$, AgHO.

This substance is obtained in the form of an almost white precipitate when a solution of silver is added to an aqueous solution of the former compound. It is very stable. Similar compounds are obtained with lead- and zinc-salts.

Diazobenzol, $C_6H_4N_2$.

This substance is obtained when an aqueous solution of the compound of hydrate of potassium with diazobenzol is neutralized with acetic acid. It separates as a thick yellow oil of very little stability. After a few moments an evolution of gas ensues, and the diazobenzol is rapidly converted into a reddish-brown viscid mass. Diazobenzol is soluble in acids, as well as bases, with formation of the saline compounds previously described.

By acting in the cold with aniline upon nitrate of diazobenzol*, the following change takes place:—



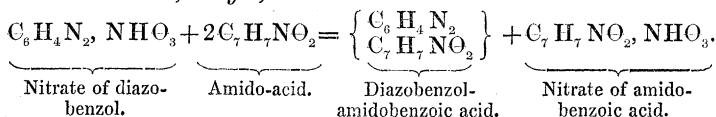
I was formerly of opinion that diazoamidobenzol must be viewed as a double compound of diazobenzol and aniline. The above equation seems to confirm this view.

New compounds analogous to diazobenzol-amidobenzol are obtained by the action of other organic bases upon nitrate of diazobenzol, viz. diazo-

benzol-amidobromobenzol, $\left\{ \begin{array}{c} C_6H_4N_2 \\ C_6(H_6Br)N \end{array} \right\}$, by the action of bromaniline.

Naphthalidine and nitrate of diazobenzol combine directly and form nitrate of diazobenzol-amidonaphtol, crystallizing in magnificent large green prisms.

The action of amido-acids upon nitrate of diazobenzol is analogous to that of the aniline; *ex. gr.*,



Diazobenzol-amidobenzoic acid separated quickly as a yellow crystalline mass on mixing the aqueous solutions of both substances. It is purified by recrystallization from ether in the form of small yellow plates. It combines with bases and forms saline bodies. Bichloride of platinum precipitates from an alcoholic solution a yellowish-white crystalline platinum-salt of the composition $C_{13}H_{11}N_3O_2 \cdot 2HCl, 2PtCl_2$.

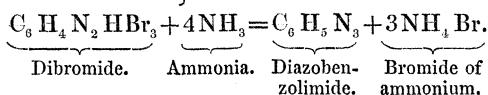
Similar double acids to the one just described are obtained by the action of amidodracylic acid, amidoanic acid, &c., upon nitrate of diazobenzol.

Imidogen Compounds of Diazobenzol.

These peculiar compounds are formed when aqueous ammonia, as well as certain organic bases, are made to act upon the dibromide of diazobenzol.

* It is self-evident that for this and similar experiments sulphate and hydrobromate of diazobenzol may also be employed.

Diazobenzolimide, $\text{C}_6\text{H}_4\frac{\text{N}_2}{\text{H}}\}$ N, is obtained according to the equation



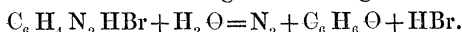
It forms a yellowish oil, which must be distilled *in vacuo* with the aid of a current of steam. Exposed by itself to a higher temperature, it decomposes with detonation. It is remarkable for its stupefying ammoniacal-aromatic odour.

Ethyldiazobenzolide, $\text{C}_6\text{H}_4\text{N}_2\text{C}_2\text{H}_5\text{O}$, is analogous in its properties, and is formed in a similar manner.

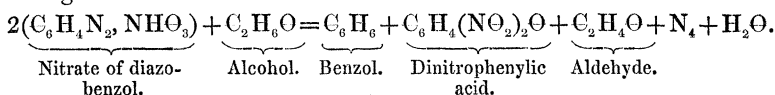
Products of Decomposition of Diazobenzol Compounds.

The transformations which the molecule of diazobenzol undergoes under the influence of various reagents are numerous. The products often represent some peculiar classes of entirely new compounds; more frequently, however, they belong to the phenyl- and benzol-group. I will describe a few of them somewhat more fully.

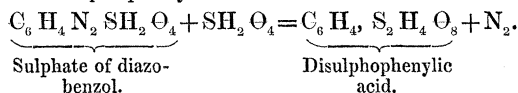
It has already been mentioned that, on boiling with water, nitrate of diazobenzol is broken up into nitrogen, phenylic acid, and nitric acid. Hydrobromate of diazobenzol undergoes an analogous decomposition, viz.,



Treated with alcohol, nitrate of diazobenzol is decomposed in the following manner :—

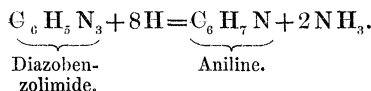


On dissolving sulphate of diazobenzol in a small quantity of concentrated sulphuric acid, it gives rise to the formation of a new sulpho-acid which I propose to call disulphophenylenic acid,

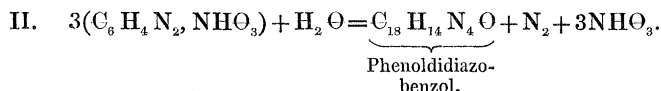
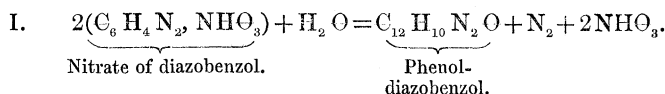


The excess of sulphuric acid may be removed from the new acid by means of carbonate of barium. The new barium-salt crystallizes in beautiful prisms. Its composition must be expressed by the formula $C_6H_4S_2H_2Ba_2O_8$. The free acid obtained by the addition of sulphuric acid to the barium-salt is deposited in warty masses of radiating crystals which deliquesce in the air. Disulphophenylenic acid is four-basic, and is capable of forming four series of salts. The silver-salt forms, however, an exception, its composition being expressed by the formula $C_6H_4S_2Ag_2O_7$. Disulphophenylenic acid, like phosphoric acid, appears to be capable of existing in different modifications, possessing different powers of basicity.

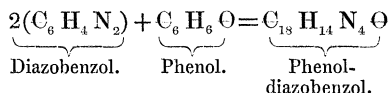
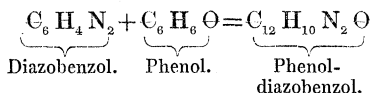
Diazobenzolide in alcoholic solutions is decomposed by nascent hydrogen, generated with zinc and sulphuric acid in the following manner:—



On adding to an aqueous solution of nitrate of diazobenzol levigated carbonate of barium, a feeble evolution of gas ensues, which lasts for several days, until the original compound has been completely decomposed. Two new substances are formed, which are very differently soluble in alcohol, and can thus readily be separated. The easily soluble compound, which I will call phenyldiazobenzol, crystallizes from alcohol in yellowish warty masses; from water (in which it dissolves very difficultly) in small rhombic prisms. The difficultly soluble one, which I propose to call phenyldiazobenzol, crystallizes in reddish-yellow needles. The following equation expresses the formation of these two bodies:—

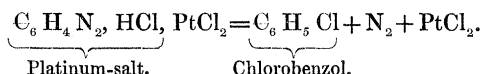


On looking at these formulæ, it becomes evident at a glance that both compounds contain phenylic acid and diazobenzol; viz.



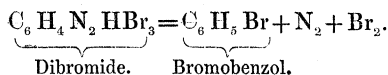
Both compounds are weak acids; the first being capable of forming a well-characterized silver-salt, which is obtained in the form of a blood-red precipitate when an ammoniacal solution of phenoldiazobenzol is treated with nitrate of silver.

On heating the platinum-salt of diazobenzol mixed with carbonate of sodium in a retort, chlorobenzol is obtained, the formation of which may be expressed as follows:—



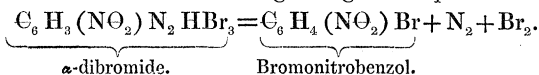
A similar decomposition ensues when the dibromide is heated with carbo-

nate of sodium,



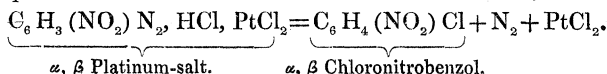
The same change may also be effected by simply boiling an alcoholic solution of the dibromide.

The peculiar and often remarkable properties of the diazobenzole-compounds have induced me to try whether analogous bodies could not be prepared also from bromaniline, nitraniline, dibromaniline, &c. Experiment has fully borne out theory. These analogous diazo-substitutions exhibit, however, so much resemblance to the normal diazobenzol compounds, that I should frequently have to repeat almost literally what has already been said of the latter, were I to describe these compounds in detail. I may be permitted, however, to mention a remarkable and interesting fact which their investigation prominently brought out. There are, as is well known, two isomeric nitranilines—the alphanitraniline of Arppe, and the betanitraniline of Hofmann and Muspratt. This isomerism, I found, extends itself to their respective nitrogen-substitution compounds, and even to their products of decomposition. On heating, *ex. gr.*, the dibromide of alphadiazonitrobenzol with alcohol, the following change takes place:—



The bromonitrobenzol thus obtained is identical with that prepared by Cooper from benzol derived from coal-tar. It crystallizes in the same form, and fuses, like the latter, at 126° C.; sulphide of ammonium converts it into bromaniline, which crystallizes in octahedra, and is identical with the bromaniline of Hofmann obtained from bromisatine. Bromonitrobenzol, prepared in a perfectly similar manner by the decomposition of the dibromide of betadiazonitrobenzol, possesses, however, widely different properties. The α -bromonitrobenzol just described crystallizes in long needles, whilst the new benzol-derivative, which I will designate by the name of β -bromonitrobenzol, forms well-developed prisms, the fusing-point of which lies at 56° C. Sulphide of ammonium converts it likewise into bromaniline; but this base differs in its physical properties entirely from the bromaniline obtained by Hofmann. It forms a colourless oil, which combines with acids, and gives rise to a series of beautiful salts, which in their turn differ greatly from the ordinary bromaniline salts in their physical properties. I will distinguish this bromaniline by calling it β -bromaniline from that obtained by Hofmann, which I will call α -bromaniline.

It deserves to be mentioned briefly that there exist likewise two isomeric chloronitrobenzols (alpha and beta) obtained by heating the platinum-salts of the respective diazonitrobenzole with carbonate of sodium,

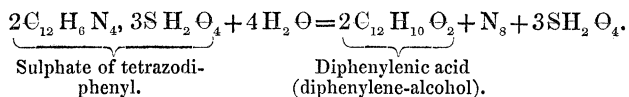


Alpha-nitrochlorobenzol furnishes, when reduced by means of sulphide of ammonium, the ordinary (alpha-) chloraniline; beta-chloronitrobenzol yielding a new base of like composition (beta-chloraniline), distinguished from the former by its oily nature.

Corresponding diazo-compounds can readily be prepared from the homologues of aniline and other analogous bases by submitting them to a treatment exactly similar to that which in case of aniline yielded diazobenzol. Thus I have obtained the diazo-compounds from toluidine, naphthalidine, and nitranisidine, $C_7H_7(NO_2)O$. I have abstained from entering more fully into a description of their physical and chemical habitus, as well as the respective products of decomposition to which they give rise, since they offer nothing characteristically new*.

All compounds already described have been derivations from monoatomic amido-bases.‡ I have on a former occasion† had an opportunity of pointing out that the action of nitrous acid upon diatomic bases, such as nitrate of benzidine, is perfectly analogous to that which gives rise to the formation of nitrate of diazobenzol from nitrate of aniline. Whilst, however, in the last-mentioned reaction only one atom of nitrous acid exchanges its nitrogen for three atoms of hydrogen of the original compound, six atoms of hydrogen are exchanged for two atoms of nitrogen when nitrous acid reacts upon nitrate of benzidine. Respecting these compounds I shall only briefly describe a few general properties and a few products of decomposition.

Sulphate of Tetrazodiphenyl, $2C_{12}H_6N_4, 3SH_2O_4$, crystallizes in white or slightly yellowish-coloured needles, which are very soluble in water, and almost insoluble in strong alcohol and ether. On boiling the alcoholic solution, the following decomposition takes place:—



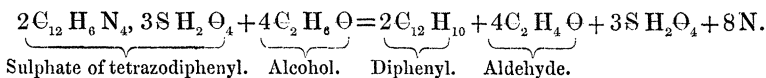
I have already had occasion to describe diphenylenic acid (diphenylene-alcohol) obtained by decomposition, analogous to that of nitrate of tetrazodiphenyl with water, and I have therefore only to refer to what has been stated on that occasion.

The decomposition which tetrazodiphenyl undergoes on boiling with

* In a former notice (Proceedings, Jan. 22, 1863) I briefly described the formation of nitrate of naphthol, which by its decomposition with water gave rise to the long-sought-for naphthyl-alcohol, $C_{10}H_8O$.

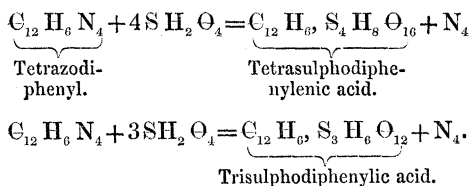
† Proceedings, Jan. 22, 1863.

alcohol differs from the previous one, and takes place according to the equation



The diphenyl which results from this reaction is identical with the compounds obtained by Fittig from bromobenzol. A comparative examination of the two demonstrates this most unmistakeably.

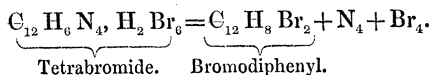
The transformation which sulphate of tetrazodiphenyl undergoes when it is heated with a small quantity of strong sulphuric acid is likewise of great interest. Two new sulpho-acids are formed, which I shall call tetra- and tri-sulphodiphenylenic acid. The following equation explains their formation in the most natural manner:—



The separation of these two acids is based upon the unequal solubility of their barium-salts. The process is, however, somewhat complicated, and I therefore abstain from describing it. Both acids are capable of combining with bases in various proportions. Tetrasulphodiphenylenic acid is octobasic. The lead-salt crystallizes in beautiful needles, and has the composition $\text{C}_{12}\text{H}_6, \text{S}_4\text{Pb}_8\text{O}_{16}$. Trisulphodiphenylenic acid appears to be hexabasic. I have as yet only prepared the former acid in a free state. It crystallizes in white needles, which are readily soluble in water and alcohol.

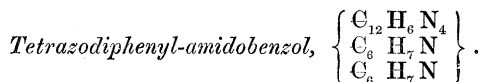
Tetrabromide of the Tetrazodiphenyl, $\text{C}_{12}\text{H}_6\text{N}_4, 2\text{HBr}, \text{Br}_4$.

This compound forms crystals of an orange colour with curved faces. On heating with alcohol, it splits up according to the equation

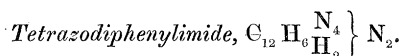
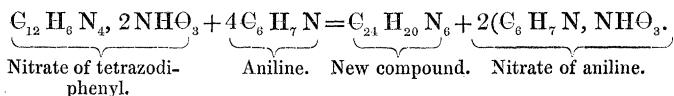


Bromodiphenyl crystallizes from alcohol and ether (in which it is rather difficultly soluble) in beautiful prisms which fuse at 164°C . This substance can be distilled without undergoing decomposition. Bromodiphenyl has also been obtained by Fittig (according to a private communication) by the action of bromine upon diphenyl.

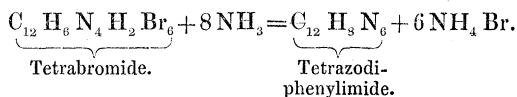
The platinum-salt of tetrazodiphenyl, $\text{C}_{12}\text{H}_6\text{N}_4, \text{H}_2\text{Cl}_2(\text{PtCl}_2)_2$, forms small yellow plates, which furnish, when heated with carbonate of sodium, chlorodiphenyl closely resembling the analogous bromine-compound.



This complex body is formed when an aqueous solution of nitrate of tetrazodiphenyl is mixed with aniline. It is deposited in a yellow crystalline mass, which can be recrystallized from alcohol or ether (in which it is but slightly soluble), and is obtained in lancet-like plates. When heated in a dry state, it is decomposed with slight explosion. Its formation is expressed by the equation



This body is obtained in the form of slightly yellowish-tinged lustrous plates, which are very difficultly soluble in cold, readily, however, in hot alcohol and in ether. It combines neither with acids nor with bases. Heated by itself it explodes. The following equation explains its formation:—



I have not succeeded in preparing tetrazodiphenyl in a free state, nor have I been able to obtain compounds of tetrazodiphenyl with bases in anything like a well-characterized condition. I pass over the abortive experiments made by me in this direction.

Many of the experiments just described have been carried on in the laboratory of the Royal College of Chemistry, London, others in that of the University of Marburg; and I take this opportunity of returning my thanks to Prof. Hofmann of London, and Prof. Kolbe of Marburg, for allowing me the use of these institutions.

XXI. "New Observations upon the Minute Anatomy of the Papillæ of the Frog's Tongue." By LIONEL S. BEALE, M.B., F.R.S., F.R.C.P., Professor of Physiology and of General and Morbid Anatomy in King's College, London; Physician to the Hospital, &c. Received June 16, 1864.

(Abstract.)

After alluding to the observations of Axel Key, whose results accord with his own more closely than those of any other observer, the author refers particularly to the drawings of Hartmann, the latest writer upon the structure of the papillæ. According to the author, Dr. Hartmann, owing