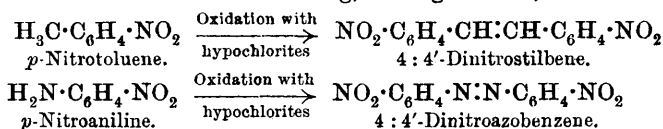


CCXXII.—*The Alkaline Condensations of Nitro-hydrazo-compounds. Part I.*

By ARTHUR GEORGE GREEN and ERNEST ARTHUR BEARDER.

IN a series of researches on the constitution of the stilbene dyestuffs conducted by Green and former collaborators (Trans., 1904, **85**, 1424, 1432; 1906, **89**, 1602; 1907, **91**, 2076; 1908, **98**, 1721), it has been shown that the production of azostilbene compounds, whether by alkaline condensation of derivatives of *p*-nitrotoluene or by alkaline reduction of derivatives of 4:4'-dinitrostilbene, is preceded by the formation of unstable intermediate products, to which the constitution of nitrosostilbenes was assigned.

In view of the parallelism between the  $\cdot\text{N}:\text{N}\cdot$  and  $\cdot\text{CH}:\text{CH}\cdot$  series which is exhibited in the following, amongst other, reactions:



it seemed not improbable that condensations might occur in the azo-series similar to those which give rise to the stilbene dyestuffs. It has long been known that by partial reduction of 4:4'-dinitroazobenzene a product is obtained which dissolves in alkali hydroxides with an intense blue colour, and it appeared possible that an analogy might exist between this product and the above-mentioned intermediate compounds of the stilbene class, which dissolve in alkalis with a crimson to blue colour. This anticipation was strengthened when we found that the former substance exhibited

in its general behaviour a remarkable similarity to the latter class of compounds. Thus, in alkaline solution both are readily decolorised by air, the former yielding dinitroazobenzene, the latter dinitrostilbene. On heating their alkaline solutions, both are finally converted into stable yellow condensation products, which dissolve in concentrated sulphuric acid with a similar cherry-red colour. Further, in both cases these stable condensation products are converted by alkaline reducing agents into other products dissolving in concentrated sulphuric acid with a blue colour.

Assuming that the intermediate products of the stilbene condensation are correctly regarded as nitroso-compounds, the existence of a series of parallel condensations in the azo-class would necessitate the conclusion, either that the above reduction product of dinitroazobenzene, which is usually regarded as dinitrohydrazobenzene, is actually a nitroso-compound, or that such a nitroso-compound is formed in an early stage of its alkaline condensation. The present research has been undertaken with the object of investigating these questions, and, incidentally, of obtaining further light on the course of the stilbene reactions.

The product of the partial reduction of 4:4'-dinitroazobenzene, which dissolves with a bright blue colour in aqueous alkalis, has already been the subject of frequent investigations, which have led to very divergent views as to its constitution. It was discovered by Lermontoff in 1872 (*Ber.*, 1872, 5, 232), who regarded it as a dinitrohydrazobenzene,  $N_2H_2(C_6H_4 \cdot NO_2)_2$ , a conclusion which was strongly supported later by the work of Werner and Stiasny (*Ber.*, 1899, 32, 3272). On the other hand, Janovsky (*Monatsh.*, 1885, 6, 160), whose analytical results differ widely from those of other authors, ascribes to the compound the constitution of a nitrolic acid,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N(OH) \cdot N(OH) \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NO_2$ . Willgerodt (*J. pr. Chem.*, 1890, [ii], 42, 51) regards it as an "az-hydroxyazo" compound,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH(OH) \cdot O$ ; whilst Freundler and Beranger (*Compt. rend.*, 1902, 134, 1219) support the quinonoid formula:  $HO_2N \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot NO_2H$ . Another possible structure hitherto unconsidered is that of a hydrated dinitrosoazobenzene,  $(HO)_2N \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N(OH)_2$ .

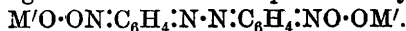
The preparation of this product at first offered some difficulties, owing to the absence of details in the published accounts, but it was finally obtained in a pure state and in good yield by reduction with colourless ammonium sulphide. When crystallised from acetone it had the characteristic crystalline form described by Janovsky, and after drying at  $140^\circ$  it melted (if heated quickly) at  $228^\circ$ , as given by Werner and Stiasny. The great variation in melting point observed by different investigators (L.,  $220^\circ$ ; J.,  $218^\circ$ ;

W., 248—250°; W. and S., 228°), which at first sight seems to suggest that they had varying products in hand, is more probably to be referred to the different rate of heating. The nitrogen value obtained for the compound agreed exactly with a dinitrohydrazobenzene, although it also approximated to the figure required for the hydrated dinitrosoazobenzene. On oxidising the blue alkaline solution by shaking with air or by addition of iodine, dinitroazobenzene was regenerated. Titration of the alkaline solution with a standard solution of iodine until complete disappearance of the blue colour, gave results which indicated the removal of two atoms of hydrogen. Titration of the acetic acid solution with titanium trichloride also gave figures in agreement with the dinitrohydrazobenzene formula, and this was further supported by the behaviour of the compound with acetic anhydride. When heated with this reagent for a short time only it remained unaltered, whereas if it were a hydrated form of dinitrosoazobenzene, or had the "az-hydroxyazo" formula suggested by Willgerodt, it should lose the elements of water. When boiled with a large excess of acetic anhydride for two hours it was converted into a diacetyl derivative, melting at 188—189°, which is doubtless identical with the dinitro-diacetylhydrazobenzene (m. p. 186—187°) obtained by Freundler and Beranger by nitration of diacetylhydrazobenzene. There is thus no reason to doubt the correctness of the conclusion arrived at by Werner and Stiasny, that the reduction product is actually dinitrohydrazobenzene.

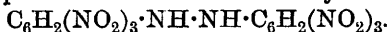
The question next arises whether the blue colour of the alkaline solution is due to the formation of a salt of dinitrohydrazobenzene or whether a molecular change occurs under the influence of the alkali.

To ascertain this, a series of experiments was conducted, in which weighed quantities of the dinitrohydrazobenzene were dissolved in cold aqueous sodium hydroxide (10 to 20 per cent. NaOH), and then filtered into aqueous acid, both solution and filtration being effected in an apparatus from which air was completely excluded by means of hydrogen. If intermolecular oxidation and reduction occurred, it was to be expected that a precipitate of dinitroazobenzene would be produced. The dinitrohydrazobenzene dissolved completely, and the deep blue liquid, when not allowed to remain for more than fifteen minutes, left no appreciable precipitate on the filter. We further found that the freshly prepared blue solution gave when immediately acidified a light yellow precipitate of unaltered dinitrohydrazobenzene. It must therefore be concluded that the blue compound actually represents an alkali salt of dinitrohydrazobenzene, and if its entirely different colour and

much greater oxidisability in comparison with the free compound be considered, the assumption seems justified that the latter is a pseudo-acid, giving rise to salts of the quinonoid type,

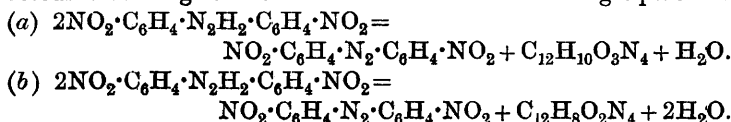


This conclusion is also in agreement with the work of Grandmougin and Leeman (*Ber.*, 1906, **39**, 4384; 1908, **41**, 1295), who have isolated a blue dipotassium salt of hexanitrohydrazobenzene,

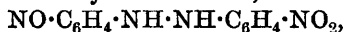


In the course of the above experiments it was observed that if the blue solution in aqueous sodium hydroxide (10 per cent. NaOH) is kept with exclusion of air for several hours, the colour becomes slightly more violet, whilst a small precipitation of dinitroazobenzene occurs. If the blue solution is now acidified, the precipitate has a much more orange colour than previously, is more voluminous, and is completely soluble in cold glacial acetic acid, in which dinitrohydrazobenzene scarcely dissolves at all. It also exhibits a much greater solubility in alcohol and in ether. In aqueous sodium hydroxide it dissolves readily with the same blue colour as dinitrohydrazobenzene, but, on the other hand, dissolves in sulphuric acid with a reddish-orange colour, in contrast to the pure yellow of the latter. When dry it forms a brick-red, amorphous powder, which could not be obtained crystalline. Analysis of this product gave numbers for carbon, hydrogen, and nitrogen conforming to dinitrohydrazobenzene, with which the results of titration with titanium trichloride were also in correspondence. If boiled, however, with acetic anhydride under conditions in which dinitrohydrazobenzene is quantitatively converted into the diacetyl derivative, the product in question gave rise to dinitroazobenzene (yield of about 70 per cent.). These results appeared at first sight to indicate that we had in hand a compound isomeric with the original dinitrohydrazobenzene. Such a supposition was, however, very difficult to express by any probable formula, and doubts arose as to its validity when it was found possible by repeated crystallisation from acetone to separate from the product a small quantity of pure dinitrohydrazobenzene. Subsequent experiments proved that the substance was in fact a mixture consisting of about four-fifths of unaltered dinitrohydrazobenzene with about one-fifth of a new compound. The latter was obtained pure by effecting the conversion with weaker alkali (3 per cent. NaOH), and allowing the solution to remain at the summer temperature (about 25°) for from six to sixteen hours. A violet-blue solution was thus produced, in which was suspended a considerable amount of dinitroazobenzene. After filtration from the latter the blue solution was acidified with acetic acid, which produced a very voluminous, colloidal, orange-red

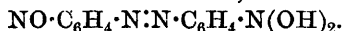
precipitate. By rapid crystallisation from acetone the new compound was obtained in small, red cubes with a violet reflex. In concentrated sulphuric acid it dissolved with a pure crimson colour, which on addition of a drop of dilute nitric acid was changed to yellow (formation of dinitroazobenzene). It dissolved in alkali hydroxides to a violet-blue solution, which, like that of dinitrohydrazobenzene, is decolorised by air or iodine. A determination of the relative quantities of the new compound and of dinitroazobenzene produced from a given weight of dinitrohydrazobenzene gave results in agreement with the supposition that the reaction proceeds according to one or other of the two following equations:



The estimation of carbon, hydrogen, and nitrogen, and the results obtained by titration with titanium trichloride, establish for the compound the constitution  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_4$ ; it is therefore formed in accordance with the first equation. The substance is therefore either a 4-nitro-4'-nitrosohydrazobenzene,

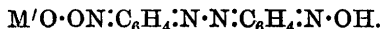


or a hydrated 4:4'-dinitrosoazobenzene,



As, however, the titration of the alkaline solution with standard iodine indicates the loss of two atoms of hydrogen in a similar manner to dinitrohydrazobenzene, the first of these formulæ appears the more probable.

Accepting the conclusion that the free compound is nitronitrosohydrazobenzene, it is probable that its violet-blue alkaline solutions contain quinonoid salts of the constitution

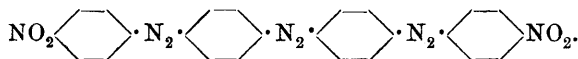


These salts should be identical with the oxime corresponding with the red alkaline salts of *p*-nitrobenzeneazophenol, to which Hewitt assigns the formula  $\text{M}'\text{O} \cdot \text{ON} : \text{C}_6\text{H}_4 : \text{N} \cdot \text{N} : \text{C}_6\text{H}_4 : \text{O}$ . Attempts to prepare the former by the action of hydroxylamine on the latter have not, however, been successful.

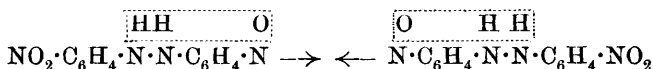
In respect to the incomplete action of cold alkali hydroxides on dinitrohydrazobenzene, it was found by direct experiment that a mixture composed of one part of nitronitrosohydrazobenzene and four parts of dinitrohydrazobenzene, when precipitated together, exhibited exactly the same properties as the product at first supposed to be an isomeric dinitrohydrazobenzene. The orange colour in sulphuric acid, its colloidal properties, and much greater solubility in solvents are therefore all due to the admixture of

nitronitrosohydrazobenzene. The different behaviour of the product with acetic anhydride appears also to be referable to the same cause, for the nitroso-compound on account of its greater reducibility may effect oxidation of dinitrohydrazobenzene to dinitroazobenzene before acetylation can occur.

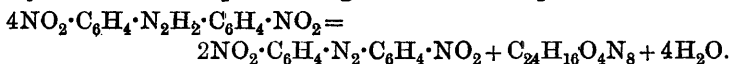
As mentioned above, the final product of the action of alkali hydroxides on dinitrohydrazobenzene is very analogous to the final product of the stilbene condensation. It was obtained by heating the solution of nitronitrosohydrazobenzene in 3 per cent. sodium hydroxide to 100° until complete disappearance of the blue colour (air being rigidly excluded). The orange-coloured precipitate, after crystallisation from xylene, was obtained in sparingly soluble, orange needles, melting at 285—286°. Analysis supported the constitution:



The compound is therefore a *bisnitrobenzeneazo-azobenzene*, and owes its formation to the condensation of two molecules of nitronitrosohydrazobenzene, in accordance with the scheme:



In preparing the compound it is not necessary to employ the isolated nitronitrosohydrazobenzene, but the blue alkaline solution of dinitrohydrazobenzene may be heated at once to 100° until the blue colour disappears. The orange precipitate then obtained is a mixture of bisnitrobenzeneazo-azobenzene with dinitroazobenzene, and can be readily separated by solvents, in which the former compound is much less soluble. A quantitative determination of the yield of the two products agreed with the equation:

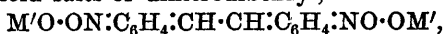


It was further found that the condensation of nitronitrosohydrazobenzene to bisnitrobenzeneazo-azobenzene can also be effected by merely boiling the former with neutral solvents.

The above experiments fully justify our original expectation of the existence of a parallelism between the derivatives of dinitroazobenzene and those of dinitrostilbene. If this analogy is complete it would seem to suggest that the intermediate products of the stilbene reaction are not, as hitherto believed, dinitrostilbenes,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}$ , but rather nitronitrosodibenzyls,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ,

from which the final condensation products (stilbene dyestuffs) are formed in the manner indicated above for bisnitrobenzeneazo-azo-

benzene. The mobility of the two methylene hydrogen atoms may very probably be connected with the tendency to form quinonoid salts. The chief difficulty in this view lies in the fact that coloured (blue?) quinonoid salts of dinitrodibenzyl,



corresponding with the blue quinonoid salts of dinitrohydrazobenzene, have hitherto not been observed. The dinitrodibenzyl salts and those of its derivatives which have been investigated all give no colour with alkali hydroxides, except on heating. It is, however, possible that owing to the firmer attachment of hydrogen to carbon compared with that of hydrogen to nitrogen, the formation of quinonoid salts may take place with greater difficulty, or only at temperatures at which conversion into the nitronitroso-compound follows immediately. This is supported to some extent by the observation made by Green and Wahl, that dinitrodibenzyl-disulphonic acid when heated with sodium hydroxide is converted, in the first instance, into a mixture of dinitrostilbenedisulphonic acid with the crimson intermediate product. If the latter is nitronitrosodibenzyl-disulphonic acid, the reaction is exactly analogous to the above-described formation of dinitroazobenzene and nitronitrosohydrazobenzene from two molecular proportions of dinitrohydrazobenzene, and just as in this case may be preceded and conditioned by the prior formation of a quinonoid salt.

#### EXPERIMENTAL.

##### 4:4'-Dinitroazobenzene.

This compound was prepared both by nitration of azobenzene and by oxidation of *p*-nitroaniline with calcium hypochlorite, identical products being obtained in both cases. The latter method, by which the pure product can readily be obtained in quantity, was that finally adopted. In conformity with Meigen and Normann (*Ber.*, 1900, **33**, 2711), we found that the product of this reaction is the azo- and not the azoxy-compound. The operation is best conducted in the following manner: One hundred grams of *p*-nitroaniline are dissolved in a mixture of hydrochloric acid and hot water, filtered through glass wool, and poured into about 2½ litres of cold water, the base being thus obtained in a fine state of division. The mixture is then rendered alkaline with sodium hydroxide, and a clear solution of calcium hypochlorite added, containing about 50 per cent. more chlorine than that theoretically required. After stirring for about six hours and leaving overnight, the orange precipitate is collected, washed well with cold water, and then without drying extracted on the filter with cold acetone,



in order to remove unaltered *p*-nitroaniline and dark-coloured by-products. The residue is recrystallised from boiling xylene, from which it separates in long, orange-red leaflets, melting at 222—223°. To facilitate the subsequent reduction, it was found very advantageous to convert the product into a fine state of division by dissolving it in cold concentrated sulphuric acid, and pouring into water. In this case it is not necessary to crystallise from xylene, and the purification with acetone may be conveniently replaced by an extraction with cold dilute hydrochloric acid to remove *p*-nitroaniline, calcium carbonate, and other impurities. (Found, N=20·87. Calc., N=20·59 per cent.)

4:4'-Dinitrohydrazobenzene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ .

After a number of experiments with various alkaline reducing agents, such as zinc dust and sodium hydroxide, dextrose and alkali, sodium sulphide, yellow ammonium sulphide, etc., none of which gave good results, the following method of preparation with colourless ammonium sulphide was adopted. The reagent was prepared just before use by saturating a mixture of equal parts of concentrated aqueous ammonia and water with hydrogen sulphide. Eleven grams of finely divided dinitroazobenzene are mixed in a mortar to a uniform paste with 150 c.c. of 95 per cent. alcohol, to which a few c.c. of acetone are added. The paste is transferred to a flask, heated to boiling, and 100 c.c. of the above aqueous ammonium sulphide are brought in. An immediate reaction occurs, and after about two minutes' boiling an equal volume of cold water is added. After cooling, the yellow precipitate is collected, washed with hot water, and then with alcohol, after which it is extracted with chloroform to remove any sulphur that may be present. The product is then dissolved in about 300 c.c. of boiling acetone (to which a little alcohol is added), and on cooling dinitrohydrazobenzene separates in pale yellow, transparent, rhombic prisms. The product on drying at 140° loses acetone, becoming opaque and of a deeper yellow colour. The yield was 6 or 7 grams. The product dried at 140° was found to melt at 228° if heated quickly, but on slower heating it melted at various other temperatures up to 250°. (Found, N=20·4. Calc., N=20·4 per cent.)

Reduction in acetic acid solution with standard titanium trichloride, titrating back the excess with ferric alum, gave the following result:

Hydrogen used=5·08, 5·27, 5·17.

Hydrogen theoretically necessary for reduction of dinitrohydrazobenzene to *p*-phenylenediamine=5·11 per cent.

In order to estimate the quantity of oxygen required to effect



decolorisation of the alkaline solution, titration with standard iodine in an atmosphere of hydrogen was employed. The end-point, indicated by the disappearance of the blue colour, is sharply defined. To secure rapid solution of the dinitrohydrazobenzene in the dilute sodium hydroxide employed and thus avoid any condensation, it was found advisable previously to dissolve the compound in acetone, reprecipitate with water, and wash thoroughly until every trace of acetone was removed. The fine precipitate was then transferred to a closed flask with 50 c.c. of water, the air displaced by hydrogen, and 50 c.c. of 6 per cent. sodium hydroxide were introduced from a tap funnel. Titration is then effected with  $N/20$ -iodine immediately solution has occurred:

Oxygen consumed = 6.3 and 5.96.

Oxygen required to oxidise dinitrohydrazobenzene to dinitroazobenzene = 5.79 per cent.

*Dinitrodiacetylhydrazobenzene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{Ac}) \cdot \text{N}(\text{Ac}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ .

One gram of dinitrohydrazobenzene was boiled for two hours with 20 c.c. of acetic anhydride, air being excluded. After evaporating off the excess of acetic anhydride, the mass was extracted with cold chloroform, and the residue crystallised from boiling glacial acetic acid. The product separated in colourless plates, which melted at 188–189°. It was insoluble in cold alkali hydroxides, but on boiling gave the deep blue colour of dinitrohydrazobenzene. (Found,  $N = 15.81$ . Calc.,  $N = 15.64$  per cent.)

*4:4'-Nitronitrosohydrazobenzene*,  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ .

This compound constitutes the first stage of the action of alkali hydroxides on dinitrohydrazobenzene. The best conditions for obtaining it in a pure state free from unconverted dinitrohydrazobenzene and from the bisnitrobenzeneazo-azobenzene produced by further condensation were only ascertained after a long series of experiments. Although the condensation commences almost immediately, the rate of the reaction is dependent on the temperature of the solution and its concentration in alkali hydroxide; thus with sodium hydroxide solutions of from 10 to 20 per cent. the reaction is much slower than with solutions of only 3 per cent. With solutions of the former strength and at a temperature of about 15° we obtained colloidal mixtures, in which dinitrohydrazobenzene largely preponderated, but which, nevertheless, exhibited very different properties from the latter in the pure state (see introduction). It was finally ascertained that a complete conversion into

the nitronitroso-compound, without any further condensation, is effected by allowing dinitrohydrazobenzene dissolved in eighty parts of 3 per cent. sodium hydroxide to remain at 25° (laboratory summer temperature) for from six to sixteen hours. The operation is best carried out in a bottle provided with a well-fitting, greased stopper, and nearly filled in order to exclude air. The progress of the reaction can be followed by precipitating at intervals small samples of the filtered solution with acetic acid, and dissolving the precipitate in concentrated sulphuric acid. After only a minute or two the solution in sulphuric acid is pure yellow (unaltered dinitrohydrazobenzene), after ten minutes it is reddish-orange, after half an hour red, and after five hours pure crimson, whilst after sixteen hours no further change is visible. When this point is reached the violet-blue solution is filtered quickly from precipitated dinitroazobenzene, and the filtrate allowed to run directly into an excess of dilute acetic acid. The product was a highly voluminous, gelatinous, reddish-orange precipitate, readily soluble in cold glacial acetic acid, acetone, ether, etc. It was washed thoroughly with water, pressed, dried at the ordinary temperature, and dissolved in acetone. On quickly evaporating the acetone the compound crystallised in small, orange-red cubes with a violet reflex. It is necessary to work quickly in order to avoid condensation of the nitronitroso-compound to bisnitrobenzeneazo-azobenzene. *Nitronitrosohydrazobenzene* is readily soluble in solvents such as acetone, alcohol, ether, acetic acid, but sparingly so in hydrocarbons. The solution in acetone has a deep yellow colour, which was found to be about forty times as intense as a similar solution of dinitrohydrazobenzene. The substance has pronounced tinctorial properties, dyeing silk from an aqueous alcoholic solution in red shades, which are changed to blue by immersion in dilute sodium hydroxide. It has no definite melting point, but begins to decompose at about 203°. Its alkali hydroxide solution has a more violet tint of blue than that of dinitrohydrazobenzene. Like the latter it is decolorised by air or iodine. In addition to its acid properties the compound appears also to be a weak base, giving pink solutions with aqueous acids. It dissolves in concentrated sulphuric acid with a pure crimson colour, which is changed to pure yellow (dinitroazobenzene) on adding a drop of dilute nitric acid.

On account of its instability the compound was analysed in the air-dried condition, the percentage of moisture it contained being determined simultaneously by drying at 140°, and the correction introduced:

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0.0967 \* gave 0.1990 CO<sub>2</sub> and 0.0348 H<sub>2</sub>O. C=56.05; H=3.95.  
 0.0964 \* „ 0.1992 CO<sub>2</sub> „ 0.0367 H<sub>2</sub>O. C=56.34; H=4.22.  
 0.0950 \* „ 0.1917 CO<sub>2</sub> „ 0.0355 H<sub>2</sub>O. C=55.1; H=4.1.  
 0.0991 \* „ 19.6 c.c. N<sub>2</sub> at 25° and 757.5 mm. N=22.64.  
 0.1006 \* „ 19.9 c.c. N<sub>2</sub> „ 26.5° „ 760.3 mm. N=22.73.  
 0.0943 \* „ 18.3 c.c. N<sub>2</sub> „ 23° „ 754 mm. N=22.73.

Mean: C=55.83; H=4.09; N=22.7.

C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>N<sub>4</sub> requires C=55.67; H=3.91; N=21.7 per cent.

Reduction in a boiling acetic acid solution with a standard solution of titanium trichloride gave the following results:

Hydrogen consumed=5.36 and 5.06.

Hydrogen required for reduction to *p*-phenylenediamine=4.70 per cent.

Titration of the alkaline solution with standard iodine in an atmosphere of hydrogen (in the manner described above, but without previously dissolving in acetone) gave the following results:

Oxygen consumed=5.55 and 5.53.

Oxygen required to oxidise nitronitrosohydrazobenzene to nitro-nitrosoazobenzene=6.15 per cent.

Attempts to isolate nitronitrosoazobenzene from the orange-yellow precipitate formed in this reaction proved unsuccessful, the nitroso-compound apparently undergoing further condensation in the alkaline medium or during subsequent purification.

The conclusion based on the above analyses, that under the influence of alkali hydroxides two molecular proportions of dinitrohydrazobenzene give rise to one of nitronitrosohydrazobenzene and one of dinitroazobenzene, was further supported by the following quantitative experiments:

A. 3.75 Dinitrohydrazobenzene gave 1.632 nitronitrosohydrazobenzene and 1.879 dinitroazobenzene. The quantities theoretically required are 1.765 of the former and 1.861 of the latter.

B. A solution of 0.0522 dinitrohydrazobenzene in 3 per cent. sodium hydroxide was allowed to remain for five hours at 25°, air being carefully excluded by means of hydrogen. At the end of this time the solution was titrated with standard iodine (in absence of air) until the disappearance of the blue colour.

The iodine required was equivalent to 0.00132 gram of oxygen.

Percentage of oxygen consumed=2.5, that is, approximately half the quantity (5.79) which would have been required had the solution been titrated immediately.

\* Dry.

*Bisnitrobenzeneazo-azobenzene,*  
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ .

This substance is readily formed by further condensation of nitronitrosohydrazobenzene, either by heating the alkaline solution or by boiling the substance itself with neutral solvents. In place of employing nitronitrosohydrazobenzene itself, the alkaline solution of dinitrohydrazobenzene may be directly heated, in which case dinitroazobenzene is formed simultaneously.

I. Finely powdered nitronitrosohydrazobenzene was placed in a well-stoppered bottle filled with about fifty parts of aqueous 3 per cent. sodium hydroxide, and heated in boiling water until the blue colour had entirely disappeared, leaving a red liquid, in which was suspended a bright orange precipitate. The time of heating required was about four hours. The orange precipitate was collected, well washed with water, and dried. The crude product was almost pure, and melted at about  $285^\circ$ . It contained no dinitroazobenzene.

II. About  $1\frac{1}{2}$  grams of dinitrohydrazobenzene were heated as above with 70 c.c. of aqueous 3 per cent. sodium hydroxide. When the conversion was complete, the precipitate was collected, washed, and dried. It was then boiled with glacial acetic acid, which dissolved about half the whole, and on cooling deposited dinitroazobenzene in the characteristic orange plates, melting at  $222\cdot5$ — $223^\circ$ . The insoluble residue was dissolved in a large volume of boiling solvent-naphtha, from which after filtration and cooling bisnitrobenzeneazo-azobenzene crystallised in very small, brownish-orange needles, melting at  $285$ — $286^\circ$ .

III. 0·1748 Gram of nitronitrosohydrazobenzene was boiled with 50 c.c. of solvent naphtha until it dissolved completely (about six hours' boiling were necessary). The solution was concentrated to about half its volume, and allowed to cool, when the condensation product crystallised out in microscopic, orange-brown needles, which melted at  $284$ — $285^\circ$ . The yield was 0·1042 gram, the conversion being complete.

For analysis the substance was dried at  $140^\circ$ :

0·0923 gave 0·2022  $\text{CO}_2$  and 0·0297  $\text{H}_2\text{O}$ .  $\text{C}=59\cdot74$ ;  $\text{H}=3\cdot57$ .

0·0863 „ 16·6 c.c.  $\text{N}_2$  at  $30\cdot5^\circ$  and 773 mm.  $\text{N}=22\cdot2$ .

0·0718 „ 14 c.c.  $\text{N}_2$  at  $28^\circ$  and 767 mm.  $\text{N}=22\cdot5$ .

$\text{C}_{24}\text{H}_{16}\text{O}_4\text{N}_8$  requires  $\text{C}=60\cdot0$ ;  $\text{H}=3\cdot33$ ;  $\text{N}=23\cdot3$  per cent.

This constitution is further supported by a determination of the relative quantity of condensation product and dinitroazobenzene produced from a given weight of dinitrohydrazobenzene:

0·9024 dinitrohydrazobenzene gave 0·4531 bisnitrobenzeneazo-azobenzene and 0·4372 dinitroazobenzene. This approximates very closely to that theoretically required.

*Bisnitrobenzeneazo-azobenzene* crystallises in very small, orange needles or leaflets, and is very sparingly soluble in all solvents. Its concentrated sulphuric acid solution is cherry-red, which becomes more crimson on addition of a small quantity of water, and is not decolorised by a drop of dilute nitric acid (distinction from the nitronitroso-compound). Alkaline reducing agents convert it into a compound which dissolves in concentrated sulphuric acid with a blue colour, and the investigation of which is at present proceeding.

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