CCXX.—*Studies in the Diphenyl Series. Part V. Derivatives and Substitution Products of the Two Isomeric o-Dinitrobenzidines and Synthesis of Derivatives of Benzerythrene.*

By JOHN CANNELL CAIN, ALBERT COULTHARD, and
FRANCES MARY GORE MICKLETHWAIT.

IN Part II of this series (T., 1912, **101**, 2298) proof was adduced of the existence of two different *o*-dinitrobenzidines, and it was also shown that these yield two different acetyl derivatives, and, by elimination of the amino-groups, two different dinitrodiphenyls.

In order further to study the difference between these bases, several derivatives have been prepared from each (*di*formyl, *dibenzoyl*, and *disuccinyl*), each pair proving to be different.

In addition, a study of the action of phthalic anhydride and of its di- and tetra-chloro-derivatives on the two dinitrobenzidines led to results which may help to throw light on the constitution of these bases. It has been shown by Koller (*Ber.*, 1904, **37**, 2880) that when benzidine and phthalic anhydride are boiled together in aqueous suspension, the cyclic compound, phthalylbenzidine, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot C_6H_4 \\ \text{CO} \cdot \text{NH} \cdot C_6H_4 \end{smallmatrix}$, is formed, and the unimolecular character of such compounds has been proved by Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250). When, however, the above materials are heated together, 4:4'-diphthaliminodiphenyl,

is formed (Bandrowski, *Ber.*, 1884, **17**, 1181). On applying these two reactions to the two dinitrobenzidines, the 3:3'-isomeride furnished, in both cases, the cyclic compound, 3:3'-*dinitrophthalylbenzidine*, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot C_6H_3 \cdot \text{NO}_2 \\ \text{CO} \cdot \text{NH} \cdot C_6H_3 \cdot \text{NO}_2 \end{smallmatrix}$, whilst the 3:5'-isomeride did not react at all in aqueous suspension, and, when heated with phthalic anhydride, gave 4:4'-*diphthalimino*-3:5'-*dinitrodiphenyl*,

It would thus appear that under these conditions 3:3'-dinitrobenzidine exhibits much more tendency to form a cyclic compound with phthalic anhydride than does the 3:5'-isomeride, and it may be that, when further results have been accumulated, Kaufler's stereochemical formula for benzidine (*Annalen*, *loc. cit.*) will be

of help in deciding the influence of the nitro-groups in these reactions.

With 3:6-dichlorophthalic anhydride both bases gave the corresponding dichlorophthalimino-derivative, whilst with 3:4:5:6-tetrachlorophthalic anhydride the cyclic phthalyl compounds were produced.

Besides the above compounds, certain bisazo-derivatives of each base have been prepared by the aid of phenol, β -naphthol, 1-naphthylamine-4-sulphonic acid (naphthionic acid) and 8-amino-1-naphthol-3:6-disulphonic acid (H-acid), the corresponding pairs of bisazo-compounds being found to be markedly different in each case.

Further, each base has been submitted to the diazo-reaction with the object of replacing the amino-groups by chlorine, bromine, iodine, hydroxyl, cyanogen, and the thiocyno-group.

Through this reaction the two *o*-dinitrobenzidines have been found to exhibit a still greater difference in their chemical behaviour than was disclosed by the reactions studied in the former paper (*loc. cit.*). In carrying out the replacement of the amino-groups by chlorine, bromine, and cyanogen, by means of copper bronze (Ullmann's method), and by the thiocyno-group (without the use of copper), 3:3'-dinitrobenzidine gave the expected substitution products (except in the case of bromine, see p. 2081), but 3:5'-dinitrobenzidine showed an entirely different behaviour. Instead of the expected substitution products, it was found that two diphenyl nuclei coalesced, with the production of derivatives of benzerythrene:

So far as we know, the compounds described in this paper are the first substitution products of this hydrocarbon that have been obtained, and their formation, represented thus:

is paralleled in an interesting manner in the case of *o*-nitroaniline, which, under similar conditions (using either copper powder or cuprous chloride), yields a mixture of *o*-chloronitrobenzene and

2: 2'-dinitrodiphenyl (Niementowski, *Ber.*, 1901, **36**, 3325; Ullmann and Forgan, *ibid.*, 3803), thus:

In the replacement of the amino-group by iodine (where no copper was used), the reaction followed the normal course, the two di-iododinitro-derivatives differing from each other.

Some ten years ago, during an investigation of the action of water on dianisidine and 3: 3'-dichlorobenzidine, bases containing acidic groups in the ortho-position with respect to the amino-groups (Cain, T., 1903, **83**, 688), it was found that the chief product in each case was a dark-coloured insoluble substance, to which a quinonoid constitution was assigned, and that only in the case of 3: 3'-dichlorobenzidine was it possible to isolate a trace of 3: 3'-dichloro-*p*-diphenol. It was to be anticipated, therefore, that on applying this reaction to the case of the *o*-dinitrobenzidines containing strongly acidic groups in the ortho-position to the amino-groups, difficulties might be experienced in substituting the amino-groups by hydroxyl. By carrying out the reaction in the ordinary manner, namely, by heating the bisdiazonium salts of the two dinitrobenzidines with water or dilute sulphuric acid, only traces of phenolic substances were formed, but by a variation of this method three different substances, all of the composition of the corresponding dinitrodiphenol, were obtained from 3: 3'-dinitrobenzidine, and one dinitrodiphenol, apparently different from any of the above, was produced from 3: 5'-dinitrobenzidine. All these dinitrodiphenols appear to be of high molecular weight, as they are brown and amorphous, and do not resemble in any way the dinitrodiphenol obtained by nitrating 4: 4'-diphenol (see below). Since the work on dianisidine and 3: 3'-dichlorobenzidine was carried out, it was shown by Orton, Coates, and Burdett (T., 1907, **91**, 35) that in many cases (in the benzene series) where this reaction was difficult or impossible to bring about, the substitution could be effected easily by means of sunlight. Accordingly, solutions of the diazotised bases were exposed to sunlight until no more diazonium salt was present. Incidentally this experiment showed the great stability of the diazonium salts; that from 3: 3'-dinitrobenzidine, exposed to light in June, 1913, at the ordinary temperature (about 20°) required two weeks, and that from 3: 5'-dinitrobenzidine, about three weeks, before the decomposition was at an end. The experiments were successful in so far as hydroxy-compounds were produced; in fact, two different hydroxy-compounds were isolated from each base, but from neither base

was there obtained a dinitrodiphenol identical with that described by Kunze (*Ber.*, 1888, **21**, 3331; compare also Schütz, *ibid.*, p. 3530), namely:

prepared by nitrating 4:4'-diphenol, or that discovered by Goldstein (*J. Russ. Phys. Chem. Soc.*, 1874, **6**, 193; 1878, **10**, 318) by oxidising *o*-nitrophenol, the constitution of which is not known.* From each base was obtained a compound having the composition of a dinitro-4:4'-diphenol and one having the composition of a tetranitrodihydroxybenzerythrene, the latter evidently having been produced by the coalescence of two diphenyl nuclei as in the case of the experiments mentioned above; they were easily separated by means of alcohol, but only one of the four compounds melted below 300°.

EXPERIMENTAL.

I.—*Derivatives of 3:3'- and 3:5'-Dinitrobenzidine.*

3:3'-Dinitrodiformylbenzidine, prepared by heating the base with anhydrous formic acid, is very soluble in nitrobenzene, and separates from acetic acid in brownish-yellow crystals, melting at 188°:

0.2596 gave 38 c.c. N₂ at 21° and 761 mm. N=17.09.

C₁₄H₁₀O₆N₄ requires N=16.97 per cent.

3:5'-Dinitrodiformylbenzidine separates from nitrobenzene in golden-yellow crystals, melting and decomposing at 282°:

0.1054 gave 15.2 c.c. N₂ at 19° and 759 mm. N=16.97.

C₁₄H₁₀O₆N₄ requires N=16.97 per cent.

A mixture of the above two compounds melted at 260°.

Dibenzoyl-3:3'-dinitrobenzidine, prepared by heating the base with benzoyl chloride, separates from nitrobenzene in yellow crystals, melting at 290°:

0.2719 gave 26.6 c.c. N₂ at 17° and 761 mm. N=11.63.

C₂₆H₁₈O₆N₄ requires N=11.62 per cent.

Dibenzoyl-3:5'-dinitrobenzidine crystallises from nitrobenzene in golden-yellow needles, melting at 298°:

0.1691 gave 17 c.c. N₂ at 21° and 760 mm. N=11.77.

C₂₆H₁₈O₆N₄ requires N=11.62 per cent.

A mixture of the above two compounds melted at 270°.

* Experiments are in progress with the object of elucidating the constitution of this compound.

3: 3'-Dinitro-4: 4'-disucciniminodiphenyl,

was prepared by heating 3: 3'-dinitrobenzidine with succinic anhydride at 150—160° for six hours. The alcoholic extract of the product furnished bright yellow crystals, melting at 203°:

0.0824 gave 9.1 c.c. N₂ at 18° and 763 mm. N=13.00.

C₂₀H₁₄O₈N₄ requires N=12.78 per cent.

3: 5'-Dinitro-4: 4'-disucciniminodiphenyl, prepared similarly at 140°, is insoluble in alcohol or benzene, but separates from nitrobenzene in yellow crystals, melting at 238°:

0.1016 gave 11.1 c.c. N₂ at 15° and 760 mm. N=12.93.

C₂₀H₁₄O₈N₄ requires N=12.78 per cent.

3: 3'-Dinitrophthalylbenzidine, C₆H₄ < $\begin{array}{c} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2 \\ \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{NO}_2 \end{array}$ — This

compound is formed when molecular proportions of phthalic anhydride and 3: 3'-dinitrobenzidine are boiled in aqueous suspension for seven to eight hours. The orange-yellow product was crystallised first from dilute alcohol, and then from nitrobenzene, when it melted at 297—298°:

0.1124 gave 13.4 c.c. N₂ at 21° and 767 mm. N=13.96.

C₂₀H₁₂O₆N₄ requires N=13.86 per cent.

The substance is also formed when 3: 3'-dinitrobenzidine and phthalic anhydride (2 mols.) are heated together at 140—150° for four hours (Found, N=14.00. Calc., N=13.86 per cent.).

4: 4'-Diphtalimino-3: 5'-dinitrodiphenyl,*

—When 3: 5'-dinitrobenzidine was boiled in aqueous suspension with phthalic anhydride, no action took place even after two days, but on heating the materials at 140—150° for four hours, interaction occurred. The product was crystallised from nitrobenzene, and was found to consist of a mixture of a greyish-yellow substance (m. p. 265°), of which the amount formed was not sufficient for analysis, and canary-yellow crystals; the latter, which did not melt at 305°, were specifically lighter than the former, and mechanical separation was effected by means of benzene:

0.1582 gave 14.7 c.c. N₂ at 22° and 761 mm. N=10.78.

C₂₈H₁₄O₈N₄ requires N=10.48 per cent.

* The corresponding compound from 3: 3'-dinitrobenzidine, which was analysed by Bandrowski (*Monatsh.*, 1887, **8**, 472), separates from nitrobenzene in pale yellow crystals melting at 284°; Bandrowski did not give the melting point.

4: 4'-Di(3:6-dichloro)phthalimino-3: 3'-dinitrodiphenyl,

was prepared by heating a mixture of 3:6-dichlorophthalic anhydride and 3:3'-dinitrobenzidine at 100—135° for four to five hours. The product was extracted with alcohol, and the greyish-yellow residue, which was soluble in benzene, melted at 191—192°:

0.1103 gave 8.1 c.c. N_2 at 19° and 760 mm. $\text{N}=8.58$.

$\text{C}_{28}\text{H}_{12}\text{O}_8\text{N}_4\text{Cl}_4$ requires $\text{N}=8.30$ per cent.

4: 4'-Di(3:6-dichloro)phthalimino-3: 5'-dinitrodiphenyl was prepared by heating a mixture of 3:6-dichlorophthalic anhydride and 3:5'-dinitrobenzidine at 150—160° for four hours. The product was extracted with alcohol, and the residue dissolved in benzene; on adding alcohol to the solution, a gelatinous, pale grey substance separated, which melted at 205° after turning yellow and shrinking at about 184°:

0.1377 gave 10.0 c.c. N_2 at 17.5° and 763 mm. $\text{N}=8.56$.

$\text{C}_{28}\text{H}_{12}\text{O}_8\text{N}_4\text{Cl}_4$ requires $\text{N}=8.30$ per cent.

(3:4:5:6-Tetrachloro)phthalyl-3:3'-dinitrobenzidine,

was obtained by heating 3:3'-dinitrobenzidine with tetrachlorophthalic anhydride (2 mols.) at 100—130° for four hours. The product, after extraction with alcohol and then with benzene, separated from nitrobenzene in yellow crystals, melting at 312°:

0.1798 gave 16.5 c.c. N_2 at 20° and 760 mm. $\text{N}=10.69$.

$\text{C}_{20}\text{H}_8\text{O}_6\text{N}_4\text{Cl}_4$ requires $\text{N}=10.33$ per cent.

(3:4:5:6-Tetrachloro)phthalyl-3:5'-dinitrobenzidine, similarly prepared from 3:5'-dinitrobenzidine, crystallises in pale yellow needles, which do not melt at 310°:

0.2211 gave 19.8 c.c. N_2 at 24° and 767 mm. $\text{N}=10.40$.

$\text{C}_{20}\text{H}_8\text{O}_6\text{N}_4\text{Cl}_4$ requires $\text{N}=10.33$ per cent.

A mixture of this and the preceding compound melted at 270°.

Azo-derivatives.

3:3'-Dinitrodiphenyl-4:4'-bisazophenol,*

prepared by adding a diazotised solution of the base to an alkaline solution of phenol, separates from xylene as a reddish-brown powder melting at 240—245°.

* Estimations of nitrogen in this and the three following compounds gave results from 0.6 to 1.8 below the calculated percentage, evidently due to the extreme difficulty in burning them.

3:5'-Dinitrodiphenyl-4:4'-bisazophenol, $C_{24}H_{16}O_6N_6$, separates from acetic acid as a black, amorphous powder, melting and decomposing at 250—255°.

3:3'-Dinitrodiphenyl-4:4'-bisazo- β -naphthol, $C_{32}H_{20}O_6N_6$, is a bright red powder insoluble in the usual organic solvents. It melts and decomposes at about 297° with previous sintering.

3:5'-Dinitrodiphenyl-4:4'-bisazo- β -naphthol is a black powder, very sparingly soluble in xylene, which does not melt at 335°. The diazotised bases were also combined with 1-naphthylamine-4-sulphonic acid (naphthionic acid) and with 8-amino-1-naphthol-3:6-disulphonic acid (H-acid) in order to obtain soluble bisazo-colouring matters, the shades of which on cotton could be compared.

The colouring matter from 3:3'-dinitrobenzidine and naphthionic acid dyes cotton in reddish-violet shades resembling those produced by "Congo Corinth B," whilst the corresponding colouring matter from 3:5'-dinitrobenzidine produces a bluer shade on cotton, similar to that furnished by "Azo-violet." Both these dyeings are changed to red by mineral acids. With "H-acid," 3:3'-dinitrobenzidine gave a reddish-grey (similar to "Direct Grey B"), whilst 3:5'-dinitrobenzidine gave a greenish-grey.

II.—The Diazo-reaction Applied to the Dinitrobenzidines: *Synthesis of Derivatives of Benzerythrene.*

In these experiments the bases were dissolved in concentrated sulphuric acid, the solutions cooled in ice, diluted slightly with water until the base began to separate, and diazotised by adding sodium nitrite. The solution was then filtered, and treated in the usual way.

Chlorine.—The diazo-solution was poured on copper bronze and hydrochloric acid.

From 3:3'-dinitrobenzidine there was obtained 4:4'-dichloro-3:3'-dinitrodiphenyl, which crystallises from glacial acetic acid in pale yellow needles melting at 111—112°:

0.1011 gave 7.7 c.c. N_2 at 18.5° and 764.3 mm. $N=8.9$.

$C_{12}H_6O_4N_2Cl_2$ requires $N=8.9$ per cent.

3:5'-Dinitrobenzidine, when similarly treated, gave 4'':4'''-dichlorotetranitrobenzerythrene*:

* The ring system of benzerythrene has not yet been numbered. In Richter's "Lexikon" the name "4:4'-diphenylbiphenyl" is assigned to it. Neither this name nor "*p*-bisdiphenyl" appears to be suitable when substitution

which is soluble in benzene or glacial acetic acid, but insoluble in light petroleum or alcohol, and forms yellow crystals melting at 203° :

0.1082 gave 9.4 c.c. N_2 at 20° and 765 mm. $N=10.2$.

$C_{24}H_{12}O_8N_4Cl_2$ requires $N=10.1$ per cent.

In various preparations of this substance it was obvious that an azo-compound was simultaneously formed, as the values obtained in the estimation of nitrogen were often considerably higher than required by the above formula.

Bromine.—The products obtained in various experiments by treating the diazotised solution of 3:3'-dinitrobenzidine with hydrobromic acid and copper bronze or cuprous bromide all contained more nitrogen than was required by the expected dibromodinitrodiphenyl, or even by the corresponding derivative of benzerythrene, and evidently this was due to the presence of some azo-compound. 4:4'-Dibromo-3:3'-dinitrodiphenyl was, however, easily prepared by treating the diazotised solution with hydrobromic acid and bromine, and decomposing the perbromide formed in this way with glacial acetic acid (Saunders, *Amer. Chem. J.*, 1891, **13**, 486). It separates from glacial acetic acid in orange crystals melting at 137 – 138° :

0.1418 gave 8.6 c.c. N_2 at 23° and 765 mm. $N=7.0$.

$C_{12}H_6O_4N_2Br_2$ requires $N=7.0$ per cent.

The diazotised solution from 3:5'-dinitrobenzidine, when partly neutralised with sodium hydroxide and then treated with hydro-products are concerned. We therefore prefer to use "benzerythrene" and number the carbon atoms thus:

Further, in the absence of any direct chemical evidence (except as to the ortho-position of the nitro-groups) we have been compelled to refer to the two bases as 3:3'- and 3:5'-dinitrobenzidine (T., 1912, **101**, 2301; compare also this vol., p. 591). This being so we do not feel justified in assuming these positions in the benzerythrene compounds, as an additional complication is introduced as indicated in the two formulæ given.

bromic acid and copper powder, yielded 4'':4'''-dibromotetranitrobenzerythrene, which is soluble in benzene or alcohol, and separates from the latter solvent in greyish-yellow crystals melting and decomposing at 184°:

0.1218 gave 9.4 c.c. N₂ at 30° and 762 mm. N=8.7.

C₂₄H₁₂O₈N₄Br₂ requires N=8.7 per cent.

This formula was confirmed by an estimation of bromine. By treating the diazotised solution of 3:5'-dinitrobenzidine with hydrobromic acid and bromine, and decomposing the perbromide formed with glacial acetic acid, 4:4'-dibromo-3:5'-dinitrodiphenyl was obtained. This separates from glacial acetic acid in orange-yellow crystals melting at 247°:

0.1603 gave 9.7 c.c. N₂ at 20° and 759 mm. N=7.0.

C₁₂H₆O₄N₂Br₂ requires N=7.0 per cent.

Cyanogen.—The diazotised solution prepared from 3:3'-dinitrobenzidine was partly neutralised with sodium hydroxide, and treated in the usual manner with cuprous cyanide. 3:3'-Dinitro-4:4'-dicyanodiphenyl, which was extracted from the product by means of benzene, separates from this solvent as a brown powder melting and decomposing at 190—192°:

0.1322 gave 22.2 c.c. N₂ at 29° and 762 mm. N=19.0.

C₁₄H₆O₄N₄ requires N=19.0 per cent.

This nitrile, when hydrolysed, furnishes an acid, which, however, could not be obtained in a pure state.

3:5'-Dinitrobenzidine, when similarly treated, gave 4'':4'''-dicyanotetranitrobenzerythrene, which is insoluble in ether, benzene, or alcohol, but dissolves in glacial acetic acid, and separates, on diluting the solution with water, as an amorphous, yellow powder, melting and decomposing at 195—198°:

0.0944 gave 12.5 c.c. N₂ at 22° and 767.2 mm. N=15.5.

C₂₆H₁₂O₈N₆ requires N=15.7 per cent.

Hydrolysis of this nitrile furnished an acid, which could not be obtained in a pure state.

Iodine.—3:3'-Dinitrobenzidine gave, on diazotisation and treatment of the solution with potassium iodide, 4:4'-di-iodo-3:3'-dinitrodiphenyl, which crystallises from dilute alcohol in yellow needles melting at 151—152°:

0.2342 gave 11.45 c.c. N₂ at 11° and 754.6 mm. N=5.8.

C₁₂H₆O₄N₂I₂ requires N=5.6 per cent.

3:5'-Dinitrobenzidine gave 4:4'-di-iodo-3:5'-dinitrodiphenyl, which is soluble in glacial acetic acid, alcohol, or xylene, but insoluble in acetone or benzene, and forms yellow crystals melting at 252—253°:

0.2010 gave 10.7 c.c. N_2 at 24° and 762 mm. $N=6.1$.

$C_{12}H_6O_4N_2I_2$ requires $N=5.6$ per cent.

Thiocyano-group.—The diazotised solution prepared from 3:3'-dinitrobenzidine was treated with sodium acetate until little mineral acid was present, and then poured into aqueous potassium thiocyanate. The 3:3'-dinitro-4:4'-dithiocyanodiphenyl separated from alcohol in very pale, brick-red crystals, melting at 158° :

0.1028 gave 13.5 c.c. N_2 at 15° and 768 mm. $N=15.74$.

$C_{14}H_6O_4N_4S_2$ requires $N=15.64$ per cent.

3:5'-Dinitrobenzidine, when treated in the same way, gave tetranitro-4'' : 4'''-dithiocyanobenzerythrene, which separates from nitrobenzene as a yellow powder decomposing at 301° :

0.1668 gave 19.7 c.c. N_2 at 18° and 770 mm. $N=14.04$.

$C_{26}H_{12}O_8N_6S_2$ requires $N=14.00$ per cent.

Hydroxyl.—When the two dinitrobenzidines are diazotised and the solutions boiled, minute amounts of phenolic substances are formed, the main products being brown, amorphous, insoluble substances. By adding the diazotised solution from 3:3'-dinitrobenzidine to a boiling mixture of a solution of sodium sulphate and sulphuric acid (Eng. Pat. 7233 of 1897), a yellowish-brown, amorphous substance was obtained, which was soluble in sodium hydroxide. A portion of this dissolved in alcohol, but did not melt below 300° . Analysis indicated that the substance had the composition of a 3:3'-dinitro-4:4'-diphenol, but its amorphous and infusible condition indicates that it possesses a higher molecular weight than that calculated from the simple formula:

0.1523 gave 13.7 c.c. N_2 at 22° and 757 mm. $N=10.38$.

$(C_{12}H_8O_6N_2)_x$ requires $N=10.14$ per cent.

The alcoholic filtrate from the above, on evaporation, yielded a brown, amorphous substance melting at 105° , which had the composition of a 3:3'-dinitro-4:4'-diphenol combined with water:

0.3055 gave 24.0 c.c. N_2 at 17° and 761 mm. $N=9.26$.

0.2574 lost 0.0170 at $110-120^\circ$. $H_2O=6.19$.

$C_{12}H_8O_6N_2 \cdot H_2O$ requires $N=9.52$; $H_2O=6.12$ per cent.

The anhydrous substance decomposed at $200-205^\circ$.

The part of the above-mentioned yellowish-brown substance which did not dissolve in alcohol (or glacial acetic acid) did not melt at 310° :

0.1646 gave 14.35 c.c. N_2 at 23° and 761 mm. $N=10.08$.

$(C_{12}H_8O_6N_2)_x$ requires $N=10.14$ per cent.

This substance has thus the composition of a 3:3'-dinitro-4:4'-diphenol of high molecular weight.

On decomposing the diazo-solution with a boiling solution of copper sulphate (D.R.-P. 167211), the product was only partly soluble in sodium hydroxide; the soluble portion furnished the hydrated compound melting at 105° , described above.

The above reactions were repeated with 3:5'-dinitrobenzidine, and a third reaction, which consisted in adding the diazo-solution to hot concentrated sulphuric acid, was also carried out. From each of the three experiments a very small amount of a substance soluble in sodium hydroxide was obtained, the main product being brown, amorphous, and insoluble. The material soluble in alkali separated from dilute acetic acid as a yellow powder, which was apparently identical with the 3:5'-dinitro-4:4'-diphenol obtained by the action of light on diazotised 3:5'-dinitrobenzidine (see below).

Action of Light on the Diazo-solutions.

The diazotised solutions were submitted to the action of sunlight at the ordinary temperature until decomposition was complete (Orton, Coates, and Burdett, *loc. cit.*). The precipitates formed from each solution were soluble in sodium hydroxide, and were separated by means of alcohol into two portions, one being soluble and the other insoluble in this solvent. In the case of 3:3'-dinitrobenzidine, decomposition was complete in two weeks, and there were obtained a 3:3'-dinitro-4:4'-diphenol, which did not melt at 300° , and was soluble in alcohol:

0.1192 gave 10.4 c.c. N_2 at 23° and 764 mm. $N=10.1$.

$(C_{12}H_8O_6N_2)_x$ requires $N=10.1$ per cent.

and a tetranitro-4'':4'''-dihydroxybenzerythrene,

which did not melt at 330° , and was insoluble in alcohol:

0.2042 gave 19.5 c.c. N_2 at 19° and 763 mm. $N=11.2$.

$C_{24}H_{14}O_{10}N_4$ requires $N=10.8$ per cent.

Both the above substances were brown and amorphous.

In the case of 3:5'-dinitrobenzidine, decomposition was complete in three weeks, and there were obtained a 3:5'-dinitro-4:4'-diphenol, which separated from glacial acetic acid or alcohol as a brown, amorphous substance, melting at about 180° :

ABSORPTION SPECTRA AND CHEMICAL REACTIVITY. PART III. 2085

0.1152 gave 10.35 c.c. N_2 at 19.5° and 763 mm. $N=10.5$.

$C_{12}H_8O_6N_2$ requires $N=10.1$ per cent.,

and a *tetranitro-4'' : 4'''-dihydroxybenzerythrene*,

a brown, amorphous substance, which did not melt at 330° , and was insoluble in alcohol:

0.1646 gave 15.35 c.c. N_2 at 25° and 770 mm. $N=10.8$.

$C_{24}H_{14}O_{10}N_4$ requires $N=10.8$ per cent.

Whether this substance was identical or not with that described above could not be ascertained owing to their infusible nature.

The expenses of this work have been partly defrayed by grants from the Chemical Society and the Royal Society, for which the authors desire to express their grateful thanks.

24, AYLESTONE AVENUE,
BRONDESBURY PARK,
LONDON, N.W.

HACKNEY TECHNICAL INSTITUTE,
LONDON, N.E.