LIII.—*Dyes Derived from Phenanthraquinone.*

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ON account of the close relationship between phenanthraquinone and anthraquinone, it may naturally be expected that suitable derivatives of phenanthraquinone will have valuable dyeing properties. This expectation is increased by the recorded properties of morpholquinone (3:4-dihydroxyphenanthraquinone), which dyes deep violet shades on alum mordant and blue on chrome, although the 4:5-dihydroxy-derivative is not a mordant colouring matter.

The present paper records some experiments made with the object of preparing colouring matters from phenanthrene through phenanthraquinone. The investigation may be divided into three parts:

(A) *Attempts to Prepare New Hydroxy-derivatives.*

2-Hydroxy- and 2:7-dihydroxy-phenanthraquinone can be readily prepared from phenanthrene. Attempts were made to

introduce additional hydroxyl groups into these compounds by methods of great value in the alizarin series, namely, by the action of sulphuric acid and manganese dioxide and by the action of fuming sulphuric acid, but these experiments did not give results of value. Probably the phenanthraquinone molecule was decomposed by the oxidising action of manganese dioxide and sulphuric acid. Fuming sulphuric acid gave *2-hydroxyphenanthraquinone-monosulphonic acid*, and apparently also a soluble sulphonic acid derivative of 2:7-dihydroxyphenanthraquinone. It seemed out of the question to fuse these products with potassium hydroxide in order to displace the sulphonic by hydroxyl groups, as apparently the phenanthraquinone molecule will not resist this treatment. Graebe (*Annalen*, 1873, **167**, 143) has recorded that phenanthraquinonedisulphonic acid on fusion with potassium hydroxide gives no substance like alizarin.

No definite product was obtained by heating 2:7-dinitrophenanthraquinone with fuming sulphuric acid and sulphur according to the method used in the preparation of anthracene-blue from 1:5-dinitroanthraquinone. The only new hydroxy-derivative prepared was 2:7-*?*-trihydroxyphenanthraquinone, obtained from 2:7-dihydroxyphenanthraquinone by acetylation, nitration, reduction, diazotisation, and boiling with water (P., 1913, **29**, 268). It gives a brown colour with potassium hydroxide, so that its dyeing properties are not very interesting. Judging from its colour it is probably 2:4:7-trihydroxyphenanthraquinone.

2:7-*Diacetylaminophenanthraquinone* was prepared with the idea that on its nitration the acetyl-amino-groups might direct the nitro-group into a more favourable position than happened on nitrating 2:7-diacetoxyphenanthraquinone, but up to the present this has not been tried.

(B) *Attempts to Prepare Anilino-derivatives of Phenanthraquinone and Closely Related Compounds.*

Owing to the exclusion of methods of producing phenanthraquinone dyestuffs through the sulphonic acids, nitration or bromination seemed the inevitable first steps. It was found that a number of bromo-nitro-derivatives could be prepared by nitrating bromo-derivatives and vice versa. *Dibromonitro-* and *bromo-dinitro-phenanthraquinone* were prepared by nitrating the dibromophenanthraquinone obtained by brominating phenanthraquinone in nitrobenzene solution, and *bromo-2-nitro-* and *bromo-4-nitro-phenanthraquinone* were obtained by brominating the corresponding mononitro-compounds. In the anthraquinone series

bromine atoms are easily displaced by anilino-groups by Ullmann's method (*Ber.*, 1901, **34**, 2174), and in this treatment nitro-groups are apparently reduced or displaced by anilino-groups (D.R.-P., 113011); some of the anilino-derivatives of anthraquinone have interesting dyeing properties (for example, alizarin-cyanine-green, which is 1:4-di-*p*-toluidinoanthraquinonedisulphonic acid; see also D.R.-P., 113011, 121155, 142512, etc.).

Led by these considerations to apply the same method to the bromonitro-derivatives of phenanthraquinone, we have obtained 2:7-dianilino-, 1:1-dianilino-, 2-nitroanilino-, 4-nitroanilino-, nitrodianilino-, and dinitroanilino-phenanthraquinone. These are all dyes giving dark green, blue, or black shades on wool (Eng. Pat. 9311 of 1915). Sulphonic derivatives of dianilino- and 2-nitroanilino-phenanthraquinone have also been prepared. In several cases it was found that it was advantageous to dye on chrome-mordanted wool, although it was difficult to give any reason for this.

Bromo-p-nitroanilinophenanthraquinone was obtained by the action of *p*-nitroaniline on dibromophenanthraquinone, but it has no dyeing properties. Equally uninteresting as to its dyeing properties was *dibenzidino*phenanthraquinone, prepared from the same dibromo-compound by the action of benzidine.

(C) Attempts to Prepare Phenanthraquinone Vat Dyes.

2-Benzoylamino-, 2-phthalylamino-, 2-oxalylamino-, 2:7-dibenzoyldiamino-, and 2:7-diphthalylldiamino-phenanthraquinone have been prepared by the action of acid chlorides on the corresponding amino-compounds. They are all dissolved by alkaline hyposulphite and precipitated from the solution on oxidation; 2-benzoylaminophenanthraquinone dyes pale pink shades on cotton; the 2-phthalylamino-derivative gives pale yellow shades, and the benzoyl derivative from 2:7-diaminophenanthraquinone brownish-orange shades.

Attempts to prepare more complex vat dyes were not very successful. A black product which dissolved in alkali hyposulphite was obtained by heating 2-aminophenanthraquinone with *p*-dibromobenzene in naphthalene solution in the presence of sodium acetate and copper chloride, but a pure substance was not isolated, nor could the brown product be purified which was obtained from dibromophenanthraquinone and 2-aminophenanthraquinone in the presence of sodium carbonate and copper oxide. An impure dye giving violet shades was prepared from dibromophenanthraquinone and *p*-phenylenediamine in nitrobenzene solu-

tion in the presence of copper chloride and fused sodium acetate. Dibromophenanthraquinone and β -naphthylamine in dimethylaniline solution in the presence of copper powder gave an impure, green substance. Almost colourless products were obtained on fusing 2:7-diaminophenanthraquinone with potassium hydroxide as in the preparation of indanthrene.

2:7-Diaminophenanthraquinone is deeply coloured, but apparently its dyeing properties had not been tested, it being too insoluble in all ordinary solvents. It dissolves, however, in alkaline sodium hyposulphite solution with a pale yellow colour, and is reprecipitated on oxidation, but the leuco-compound does not seem to possess any affinity for wool. Its *monosulphonic acid* was prepared, and dyed dull green shades on alum-mordanted wool. That dyestuffs can be prepared by coupling diazotised 2:7-diaminophenanthraquinone with phenolic substances had been already shown by Litthauer (*Ber.*, 1893, **26**, 848), but he did not crystallise his products and only described them very briefly.. We have obtained crystalline *phenanthraquinone-2:7-bisazophenol*. It dissolves in potassium hydroxide with a brown colour, and hence was not further examined.

EXPERIMENTAL.

Barium 2-Hydroxyphenanthraquinonesulphonate, $C_{14}H_6O_6SBa$.

Fifteen grams of fuming sulphuric acid ($SO_3=70$ per cent.) were added to 1.5 grams of 2-hydroxyphenanthraquinone in a small stoppered bottle, which was kept closed at $35-40^\circ$ for forty-eight hours. The product was then poured into 300 c.c. of water, when a deep red solution was obtained which gave no precipitate on boiling, as in the case of the preparation of alizarin-Bordeaux. To this solution was added excess of barium carbonate, the whole boiled and filtered, and the residue thrice boiled with 300 c.c. of water and filtered. The collected filtrate was allowed to remain in a tall cylinder for one day in order that the barium carbonate that passed through the filter-paper might settle down. The filtrate was of a reddish-violet colour, which turned to deep violet on concentration. The whole of the filtrate was evaporated to dryness. A violet substance was thus obtained, which was dissolved and reprecipitated from water, which process was thrice repeated in order to obtain the substance in a pure state. It dissolves readily in boiling water, but is quite insoluble in absolute alcohol. The substance was dried at 140° for one hour and analysed :

0.2512 gave 0.1263 BaSO₄. S=6.91.

0.1305 „ 0.0713 BaSO₄. Ba=32.13.

C₁₄H₆O₆SBa requires S=7.29; Ba=31.21 per cent.

Nitro-2:7-diacetoxyphenanthraquinone, C₁₄H₅O₂(OAc)₂·NO₂.

Three grams of 2:7-diacetoxyphenanthraquinone were added to 30 c.c. of cold nitric acid (D 1.39), and the mixture was warmed at 50–60° for one and a half minutes by plunging the containing vessel into boiling water. The mixture was then at once poured into water, and the nitro-compound, which was precipitated as a sandy, yellowish-brown powder, was crystallised from a mixture of acetic acid and acetone, and obtained in yellowish-brown, rhombic prisms which did not melt below 290°:

0.1100 gave 0.2367 CO₂ and 0.0307 H₂O. C=58.70; H=3.10.

0.1786 „ 6.2 c.c. N₂ (moist) at 24° and 758 mm. N=3.98.

C₁₈H₁₁O₈N requires C=58.53; H=2.98; N=3.79 per cent.

Nitro-2:7-dihydroxyphenanthraquinone, C₁₄H₅O₂(OH)₂·NO₂.

The above acetyl derivative was hydrolysed by boiling for a short time with glacial acetic acid and a few drops of concentrated sulphuric acid. On adding excess of boiling water to the mixture, the nitrodihydroxy-compound was precipitated as a brown powder which did not melt below 290°:

0.1215 gave 0.2628 CO₂ and 0.0284 H₂O. C=59.00; H=2.60.

0.1423 „ 6.4 c.c. N₂ (moist) at 30° and 757 mm. N=5.10.

C₁₄H₇O₆N requires C=58.93; H=2.45; N=4.91 per cent.

Amino-2:7-dihydroxyphenanthraquinone, C₁₄H₅O₂(OH)₂·NH₂.

One gram of nitrodiaacetoxyphenanthraquinone was heated on the water-bath with 2 grams of finely granulated tin and 15 c.c. of concentrated hydrochloric acid until all the tin had dissolved. The yellowish-brown nitro-compound did not dissolve, but turned at first deep brown and then became of a much paler brown colour. This pale brown, insoluble substance was collected and warmed with aqueous ferric chloride solution, when its colour became much deeper. It was finally boiled with dilute hydrochloric acid until free from inorganic matter, collected, and washed with water. The aminodihydroxy-compound thus obtained is a deep brown substance consisting of small, rectangular plates. It does not melt below 290°, is insoluble in all ordinary organic solvents, but dissolves in alkali hydroxide with a brown colour:

0.1210 gave 0.2897 CO₂ and 0.0403 H₂O. C=65.29; H=3.70.

C₁₄H₉O₄N requires C=65.88; H=3.53 per cent.

Acetyl-amino-2:7-diacetoxypheanthraquinone,
 $C_{14}H_5O_2(OAc)_2 \cdot NHAc$.

This was obtained by acetylating the preceding compound by boiling with acetic anhydride and a drop of pyridine. It was precipitated by adding alcohol to the acetylation mixture. It could not be crystallised, and did not melt below 295° :

0.1232 gave 0.2824 CO_2 and 0.0459 H_2O . $C=62.52$; $H=4.15$.
 $C_{20}H_{15}O_7N$ requires $C=62.99$; $H=3.93$ per cent.

2:7: ?-Trihydroxypheanthraquinone, $C_{14}H_5O_2(OH)_3$.

The aminohydroxy-compound was suspended in ice-cold 10 per cent. sulphuric acid and diazotised with the calculated amount of sodium nitrite. It dissolved almost entirely. The solution was filtered and boiled, when the trihydroxypheanthraquinone was precipitated as a reddish-brown substance which did not melt below 290° ; it can be dissolved in pyridine and precipitated by alcohol, and dissolves in alkali with a brown colour:

0.1236 gave 0.2951 CO_2 and 0.0368 H_2O . $C=65.11$; $H=3.31$.
 $C_{14}H_8O_5$ requires $C=65.62$; $H=3.12$ per cent.

2:7: ?-Triacetoxypheanthraquinone, $C_{14}H_5O_2(OAc)_3$.

This was obtained by acetylating 2:7: ?-trihydroxypheanthraquinone with acetic anhydride and a trace of pyridine. It was precipitated by alcohol from the solution in acetic anhydride, and was then recrystallised from glacial acetic acid, being obtained as a reddish-brown, microcrystalline powder melting at about 280° :

0.1130 gave 0.2590 CO_2 and 0.0373 H_2O . $C=62.51$; $H=3.67$.
 $C_{20}H_{14}O_8$ requires $C=62.83$; $H=3.66$ per cent.

2:7-Diacetylaminopheanthraquinone, $C_{14}H_6O_2(NHAc)_2$.

One gram of 2:7-diaminopheanthraquinone was heated with 1 gram of fused sodium acetate and 8 c.c. of acetic anhydride in a sealed tube at 160° for one hour. The contents of the tube were mixed with an equal volume of glacial acetic acid and poured into water. The precipitated acetyl compound was recrystallised twice from a mixture of acetic acid and alcohol. It is a chocolate-brown substance which does not melt below 295° , is readily soluble in acetic acid, and sparingly so in alcohol:

0.1150 gave 0.2821 CO_2 and 0.0450 H_2O . $C=66.90$; $H=4.35$.
 0.1255 „ 9.5 c.c. N_2 (moist) at 30° and 758 mm. $N=8.53$.
 $C_{18}H_{14}O_4N_2$ requires $C=67.08$; $H=4.31$; $N=8.69$ per cent.

Dibromonitrophenanthraquinone, $C_{14}H_5O_2Br_2 \cdot NO_2$.

Dibromophenanthraquinone (1 gram), obtained by brominating phenanthraquinone in nitrobenzene solution (D.R.-P., 222206), was boiled with nitric acid (35 c.c.; D 1.42) for half an hour and the solution poured into water. The new substance was deposited as a yellow precipitate, which crystallised from acetic acid in yellow, prismatic needles melting at 244—245°:

0.1644 gave 4.6 c.c. N_2 at 28° and 762 mm. $N = 3.19$.

$C_{14}H_5O_4NBr_2$ requires $N = 3.40$ per cent.

Bromodinitrophenanthraquinone, $C_{14}H_5O_2Br(NO_2)_2$.

A mixture of dibromophenanthraquinone (1 gram), fuming nitric acid (10 c.c.; D 1.51), and concentrated sulphuric acid (1.5 c.c.) was boiled for two minutes and the solution poured into water. The yellow precipitate crystallised from a mixture of acetic acid (2 parts) and nitrobenzene (1 part) in yellow, prismatic needles melting above 300°:

0.1530 gave 10 c.c. N_2 at 28° and 764 mm. $N = 7.49$.

$C_{14}H_5O_6N_2Br$ requires $N = 7.43$ per cent.

Bromo-2-nitrophenanthraquinone, $C_{14}H_6O_2Br \cdot NO_2$.

2-Nitrophenanthraquinone (1 gram), bromine (0.6 c.c.), and acetic acid (6 c.c.) were heated together in a sealed tube at about 140° for two hours. Shining, reddish-yellow plates, which were deposited in the tube, were washed out with acetic acid, collected, and washed with alcohol. The substance can be recrystallised from nitrobenzene, and melts above 300°:

0.1693 gave 6.5 c.c. N_2 at 25° and 763 mm. $N = 4.42$.

$C_{14}H_6O_4NBr$ requires $N = 4.22$ per cent.

Bromo-4-nitrophenanthraquinone, $C_{14}H_6O_2Br \cdot NO_2$.

One gram of 4-nitrophenanthraquinone was dissolved in as little nitrobenzene as possible at 110°, excess of bromine added, and the heating continued at the same temperature for one and a half hours. On cooling, the new substance was deposited in yellow prisms, which, when recrystallised from acetic acid, melted at 224—226°:

0.1501 gave 6 c.c. N_2 at 23° and 760 mm. $N = 4.62$.

$C_{14}H_6O_4NBr$ requires $N = 4.22$ per cent.

2:7-Dianilinophenanthraquinone, $C_{14}H_6O_2(NHPh)_2$.

A mixture of 2:7-dibromophenanthraquinone (1 gram), aniline (10 grams), and copper powder (0.25 gram) were boiled together for two and a half to three hours. The solution was then filtered hot and poured into excess of dilute hydrochloric acid, when the dianilinophenanthraquinone was precipitated. It was collected and purified by dissolving in a mixture of nitrobenzene and acetic acid and slowly precipitating with ether, when it was obtained as a non-crystalline, blue-black precipitate. It dyes mordanted or unmordanted wool in blue-black shades, and does not melt below 300° :

0.1050 gave 7 c.c. N_2 at 32° and 760 mm. $N=7.49$.

$C_{26}H_{18}O_2N_2$ requires $N=7.18$ per cent.

? : ?-Dianilinophenanthraquinone, $C_{14}H_6O_2(NHPh)_2$.

Dibromophenanthraquinone (D.R.-P., 222206) was boiled with aniline and copper powder in the same proportions as in the preceding case for the same length of time, and the substance isolated and purified in the same way. In this case, also, the substance could not be obtained crystalline. It is a bluish solid, which dyes chrome-mordanted or unmordanted wool in greenish-blue shades and does not melt below 300° :

0.1436 gave 9.4 c.c. of N_2 at 27° and 760 mm. $N=7.42$.

$C_{26}H_{18}O_2N_2$ requires $N=7.18$ per cent.

2-Nitroanilinophenanthraquinone, $C_{14}H_6O_2(NO_2) \cdot NHPh$.

This was prepared exactly in the above way from bromo-2-nitrophenanthraquinone. It is a blue-black substance, and dyes chrome-mordanted or unmordanted wool in fine, blue-black shades and does not melt below 300° :

0.1102 gave 0.2836 CO_2 and 0.0388 H_2O . $C=70.19$; $H=3.91$.

0.1089 „ 7.8 c.c. N_2 at 25° and 762 mm. $N=8.26$.

$C_{20}H_{12}O_4N_2$ requires $C=69.77$; $H=3.49$; $N=8.14$ per cent.

4-Nitroanilinophenanthraquinone, $C_{14}H_6O_2(NO_2) \cdot NHPh$.

This was prepared in the same way from bromo-4-nitrophenanthraquinone. It is a black, amorphous solid, which dyes wool in blackish shades and does not melt at 300° :

0.1200 gave 8.9 c.c. N_2 at 30° and 760 mm. $N=8.40$.

$C_{20}H_{12}O_4N_2$ requires $N=8.14$ per cent.

Nitrodianilinophenanthraquinone, $C_{14}H_5O_2(NO_2)(NHPh)_2$.

This was prepared exactly as above from dibromonitrophenanthraquinone. It dyes wool in black shades:

0.1012 gave 8.45 c.c. N_2 at 32° and 758 mm. $N=9.37$.

$C_{26}H_7O_4N_3$ requires $N=9.66$ per cent.

Dinitroanilinophenanthraquinone, $C_{14}H_5O_2(NO_2)_2 \cdot NHPh$.

This was obtained in the same way by the action of aniline on bromodinitrophenanthraquinone in the presence of copper powder. It is a black powder, and gives greenish-black shades on wool:

0.1128 gave 10.8 c.c. N_2 at 30° and 758 mm. $N=10.80$.

$C_{20}H_{11}O_6N_3$ requires $N=10.79$ per cent.

Dianilinophenanthraquinonesulphonic Acid.

One part of dry dianilinophenanthraquinone was heated with ten parts of sulphuric acid (D 1.84) at $110-120^\circ$ for one hour. The product was poured into water, boiled and filtered, and the sulphonated dyestuff salted out from the cold filtrate. It dyes greener shades than the parent substance, and the dyeings are faster to light.

2-Nitroanilinophenanthraquinonesulphonic Acid.

One part of dry 2-nitroanilinophenanthraquinone was heated with ten parts of sulphuric acid (D 1.84) at $125-130^\circ$ for two hours, and the product poured into water, when the sulphonated substance was precipitated. It can be dissolved in a large amount of boiling water, from which it separates on cooling, and can also be most conveniently salted out. It dyes chrome-mordanted wool in olive green shades.

Bromo-p-nitroanilinophenanthraquinone,

Dibromophenanthraquinone (1 gram), *p*-nitroaniline (1 gram), dimethylaniline (5 c.c.), and a trace of copper powder were heated together at 160° for three and a half hours. The product was poured into dilute hydrochloric acid, when the new substance was precipitated. It was purified by dissolving in acetone and precipitating with ether, when it was obtained as a reddish-violet substance, which did not melt at 280° . It does not dye wool:

0.1132 gave 6.2 c.c. N_2 at 32° and 759 mm. $N=6.15$.

$C_{20}H_{11}O_4N_2Br$ requires $N=6.62$ per cent.

Dibenzidino-phenanthraquinone, $C_{14}H_6O_2(NH \cdot C_{12}H_8 \cdot NH_2)_2$.

A mixture of dibromophenanthraquinone (1 gram), benzidine (1.5 grams), fused sodium acetate (2 grams), cupric chloride (0.35 gram), and nitrobenzene (20 grams) was heated to boiling for two hours. On cooling, ether was added to the solution to precipitate the new substance, which was collected and washed with alcohol. It was then boiled with water to free it from any inorganic impurity. It is a black powder which does not melt and does not dye wool:

0.1310 gave 12 c.c. N_2 at 30° and 758 mm. $N=10.34$.

$C_{38}H_{28}O_2N_4$ requires $N=9.80$ per cent.

2-Benzoylaminophenanthraquinone, $C_{14}H_7O_2 \cdot NHBz$.

Half a gram of 2-aminophenanthraquinone was dissolved in 20 c.c. of nitrobenzene, and 2 c.c. of benzoyl chloride were added to the solution. The mixture was heated at 100° for twenty minutes and allowed to cool, when needle-shaped crystals of the new substance were deposited. When crystallised from nitrobenzene it consists of fine, pinkish, needle-shaped crystals melting at 295° . It is a vat dye, and dyes cotton in pale pink shades:

0.1591 gave 6.6 c.c. N_2 at 31° and 747 mm. $N=4.59$.

$C_{21}H_{13}O_3N$ requires $N=4.28$ per cent.

2-Phthalylaminophenanthraquinone, $C_6H_4(CO \cdot NH \cdot C_{14}H_7O_2)_2$.

A solution of phthalyl chloride (2.5 grams) and 2-aminophenanthraquinone (0.5 gram) in nitrobenzene (20 c.c.) was heated for two hours at $100-105^\circ$. On cooling the mixture, orange-coloured crystals of the new substance were deposited. It was collected, washed with alcohol, and recrystallised from nitrobenzene, when it was obtained in pale orange, needle-shaped crystals, which did not melt at 295° . It behaves as a vat dye and gives pale yellow shades on cotton:

0.1931 gave 8.2 c.c. N_2 at 29° and 748 mm. $N=4.75$.

$C_{36}H_{20}O_6N$ requires $N=4.86$ per cent.

2-Oxalylaminophenanthraquinone, $(CO \cdot NH \cdot C_{14}H_7O_2)_2$.

Oxalyl chloride (1.5 c.c.) was added to a solution of 0.5 gram of 2-aminophenanthraquinone in 20 c.c. of nitrobenzene, and the solution heated at $80-90^\circ$ for two hours. A crystalline mass was

formed, which was collected, washed with alcohol, and recrystallised from nitrobenzene, from which it was deposited in clusters of reddish-brown needles. The substance does not melt at 295° . It dissolves in an alkaline solution of sodium hyposulphite and is reprecipitated on oxidation, but is not absorbed from the vat by cotton:

0.1484 gave 6.85 c.c. N_2 at 30° and 753 mm. $N=5.31$.

$C_{30}H_{16}O_6N_2$ requires $N=5.60$ per cent.

2:7-Dibenzoyldiaminophenanthraquinone, $C_{14}H_6O_2(NHBz)_2$.

To a solution of 2:7-diaminophenanthraquinone (0.5 gram) in 10 c.c. of boiling nitrobenzene 2 c.c. of benzoyl chloride were added, and the mixture was boiled for half an hour under a reflux condenser. On cooling, the substance was deposited in large needles. When recrystallised from nitrobenzene it forms brick-red needles, which do not melt at 295° . It behaves like a vat dye, giving brownish-orange shades on cotton:

0.0955 gave 5.2 c.c. N_2 at 28° and 760 mm. $N=6.20$.

$C_{28}H_{18}O_4N_2$ requires $N=6.28$ per cent.

2:7-Diphthalylldiaminophenanthraquinone,

A mixture of 2:7-diaminophenanthraquinone (0.5 gram), dissolved in nitrobenzene (15 c.c.), and phthalyl chloride (1 c.c.) was boiled under a reflux condenser for half an hour, and the solution filtered hot. On cooling, a brick-red precipitate was obtained, which crystallised from nitrobenzene in circular needle clusters. It does not melt at 295° . It dissolves in alkaline hyposulphite and is reprecipitated from the solution on oxidation, but is not absorbed from the vat by cotton:

0.1220 gave 8.1 c.c. N_2 at 22° and 761 mm. $N=7.72$.

$C_{44}H_{24}O_8N_4$ requires $N=7.61$ per cent.

2:7-Diaminophenanthraquinonesulphonic Acid,

An excess of fuming sulphuric acid ($SO_3=70$ per cent.) was mixed with 2:7-diaminophenanthraquinone in a bottle, when much heat was generated. The bottle was kept closed for forty-eight hours, after which the mixture was poured into water, when

the sulphonic acid was precipitated. The substance is insoluble in most organic solvents, but is sparingly soluble in alkali hydroxide. In the moist state it dyes alum-mordanted wool in dull green shades:

0.2222 gave 16.7 c.c. N_2 at 32° and 760 mm. $N=8.36$.

$C_{14}H_{10}O_5N_2S \cdot H_2O$ requires $N=8.80$ per cent.

Phenanthraquinone-2:7-bisazophenol, $C_{14}H_6O_2(N:N \cdot C_6H_4 \cdot OH)_2$.

One gram of 2:7-diaminophenanthraquinone was suspended in 5 per cent. sulphuric acid and diazotised by adding 0.58 gram of sodium nitrite. The solution of the diazo-compound was added to a solution of phenol, and the whole carefully rendered alkaline by sodium carbonate. The mixture was then acidified, and the insoluble substance collected and crystallised from a mixture of alcohol and nitrobenzene. It was obtained in brown, lenticular crystals, which did not melt at 295° and dissolved in alkali with a brown colour:

0.1134 gave 0.2890 CO_2 and 0.0367 H_2O . $C=69.51$; $H=3.60$.

0.1511 „ 16.0 c.c. N_2 (moist) at 25° and 759 mm. $N=12.21$.

$C_{26}H_{16}O_4N_4$ requires $C=69.64$; $H=3.57$; $N=12.50$ per cent.

Phenanthraquinone-2:7-bisazophenyl Acetate,

$C_{14}H_6O_2(N:N \cdot C_6H_4 \cdot OAc)_2$.

The preceding compound was acetylated by boiling with acetic anhydride and a drop of pyridine. On adding alcohol to the mixture, the acetyl derivative was precipitated; this crystallised from acetic acid in brick-red, rhombic prisms melting at 274° :

0.1660 gave 0.4126 CO_2 and 0.0589 H_2O . $C=67.84$; $H=3.94$.

0.2390 „ 21.8 c.c. N_2 (moist) at 25° and 761 mm. $N=10.46$.

$C_{30}H_{20}O_6N_4$ requires $C=67.67$; $H=3.76$; $N=10.52$ per cent.

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