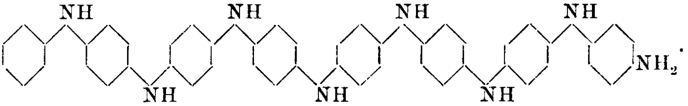
CCXLIII.—*Aniline-black and Allied Compounds. Part I.*

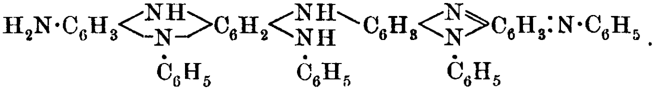
By Arthur George Green and Arthur Edmund Woodhead.

Although the recent researches of Willstätter and his pupils (Willstätter and Moore, *Ber.*, 1907, **40**, 2665; *J. Soc. Dyers*, 1908, **24**, 4; Willstätter and Dorogi, *Ber.*, 1909, **42**, 2147, 4118) have added much of value to our knowledge of the complex oxidation products of aniline, the constitution of aniline-black and of its intermediate products still cannot be regarded as completely elucidated. The view advanced by Willstätter, that these compounds are all to be regarded as indamine-like derivatives of the eight-nucleal chain compound (leucoemeraldine):



will scarcely gain acceptance without further evidence. As Bucherer has pointed out, it might a priori be expected that substances of such a type would exhibit a high degree of instability, and would readily decompose into simpler compounds under the influence of acids, etc.

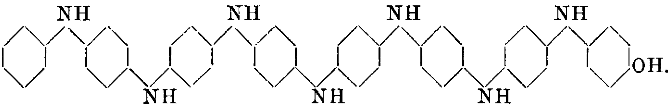
Amongst other arguments in support of the chain structure, Willstätter has shown that the quantitative conversion into *p*-benzoquinone is only compatible with the existence of di-para-connexions, and is entirely opposed to an azine structure, such as that suggested by Bucherer (*Ber.*, 1909, **42**, 2931):



$$H_2N\cdot C_6H_3{<}\begin{array}{c}NH\\N\\\dot{C}_6H_5\end{array}{>}C_6H_2{<}\begin{array}{c}NH\\NH\\\dot{C}_6H_5\end{array}{>}C_6H_3{<}\begin{array}{c}N\\N\\\dot{C}_6H_5\end{array}{>}C_6H_3{:}N\cdot C_6H_5.$$

In respect to the validity of this argument, it is, however, necessary to point out that a sharp distinction must be made between the primary oxidation products of aniline (emeraldine, nigraniline, etc.) and the condensation products of these with aniline ("ungreenable aniline-black"), which latter alone can be properly regarded as true aniline-black. Willstätter's experiments refer only to the former class of compounds, and it yet remains to be shown what yield of *p*-benzoquinone is obtainable from the latter. It is quite conceivable, and in fact probable, that whilst the former possess a di-para chain or ring structure, the "ungreenable aniline-black," that is, true aniline-black, is an azine (Green, *The Chemical Technology of Aniline-black*, 7th Internat. Congress of Applied Chemistry, London, 1909; *J. Soc. Dyers*, 1909, **25**, 188). Only the "ungreenable aniline-black" can be correctly regarded as a highly stable compound; the primary oxidation products probably owe much of their apparent stability to their insolubility in water and aqueous solvents, for when dissolved in pyridine, etc., they exhibit a much greater tendency to undergo change.

The view held by Willstätter that "ungreenable aniline-black" is a compound of the same type as the primary oxidation products (that is, contains an eight-nucleal chain, and only differs from the primary products in the degree of oxidation and the replacement of the terminal NH by O), is opposed, in our opinion, to the experimental facts. Were this view correct, the behaviour with sulphurous acid of the two oxidation stages he describes should be the same, that is to say, both compounds should be reduced to the green monoquinonoid stage, and by the application of a stronger reducing agent all should be reduced to the mother substance, that is, to the oxygen analogues of leucoemeraldine:



Furthermore, this reduction-product, like leucoemeraldine itself, would certainly be a tolerably stable substance, giving, on air oxidation, only the lowest quinonoid stage, and requiring the application of a strong oxidising agent to reconvert it into the original tri- or tetra-quinonoid compound. These properties are not exhibited either by the preparations described by Willstätter as "hydrolysed triquinonoid and tetraquinonoid blacks," or by the "ungreenable aniline-black" produced on the fibre. The latter is not reduced at all by sulphurous acid, and by stronger reducing agents, such as hyposulphites, it is converted into a leuco-compound which is rapidly re-oxidised by air to the original "black," and that apparently without passing through any lower stage of oxidation. Moreover, the facts known respecting the conditions of formation of "ungreenable aniline-black" clearly show that it cannot be a product of further oxidation alone, but is a condensation product with aniline of a different type to the simpler oxidation products from which it is formed (Green, *loc. cit.*).

In order to throw more light on this complicated subject, it has appeared to us necessary to obtain, in the first instance, further evidence for the molecular weight and constitution of the primary oxidation products (emeraldine and nigraniline), and we have attempted to do this by determining, on the one hand, the quantity of hydrogen required to reduce these products to leucoemeraldine, and, on the other, the quantity of oxygen necessary to oxidise each stage into the next. The data obtained in this manner, combined with the fact that we have been able to recognise four distinct stages of oxidation of leucoemeraldine, support Willstätter's view of an eight-nucleal molecule, but do not agree with the constitution assigned by Willstätter and Dorogi to the compounds they prepared.

Assuming the correctness of the eight-nucleal structure for the primary oxidation products, it still remains an undecided question whether the aniline residues are to be regarded as united in an open or in a closed chain, but without attempting to decide this point we shall make use of the open-chain formulæ to express provisionally the analytical results. The constitution of "ungreenable aniline-black" we reserve for discussion in a later communication.

Before proceeding to a consideration of the results obtained, it is desirable to attempt to clear up some of the existing confusion regarding the various oxidation products of aniline and their nomenclature. Much of the obscurity in this subject arises from the fact that no criterion of purity has hitherto existed, and that the products obtained have been doubtless largely mixtures. Unsuitable nomenclature has still further added to the confusion. Thus the name "emeraldine," which properly belongs to the first acid-oxidation product of aniline—a violet-blue base giving green salts, and well known to dyers of aniline-black—has been transferred by Willstätter and Moore to an entirely different compound, namely, the blue imide obtained by polymerisation of phenylquinonedi-imide, which was apparently first mistaken for emeraldine by Caro. On the other hand, for the true emeraldine, originally so-called by Crace-Calvert and Lowe, the name "triquinonoid aniline-black" is now proposed by Willstatter and Dorogi, although emeraldine is neither black nor (as will be shown later) is it triquinonoid. In justification for this confusing and unnecessary transfer of names, Willstätter and Dorogi advance the incomprehensible plea that "technisches Emeraldine langst nicht mehr existirt."

The various oxidation products which have been described under the name of aniline-black by the earlier authors (Müller, Nietzki, Kayser, Guyard, etc.) are lacking in any criterion of purity or individuality beyond that furnished by elementary analysis, which in this case is quite inconclusive and valueless. The discovery that the primary oxidation products (emeraldine and nigraniline bases) are readily soluble in somewhat diluted organic acids, such as 80 per cent. acetic acid and 60 per cent. formic acid (the former base giving a green solution, and the latter a blue), whilst the higher condensation products are insoluble in these solvents, has provided us with a valuable means for diagnosis and separation, by means of which we have been able to show that all the above-mentioned so-called "aniline-blacks" consist mainly of emeraldine and nigraniline mixed with varying proportions of higher condensation products. These "blacks" prepared in substance therefore do not properly correspond with the aniline-black produced on the fibre, since in the latter case the higher condensation products are either exclusively present (ungreenable blacks) or largely predominate (greenable blacks).

In order to simplify the nomenclature, we propose that the term "aniline-black" should be restricted to the higher condensation products (ungreenable black), whilst the original names "emeraldine" and "nigraniline" should be retained for the primary oxidation products. As, however, there is a stage of oxidation below emeraldine and one above nigraniline, we propose for these the names "protoemeraldine" and "pernigraniline." All four substances, protoemeraldine, emeraldine, nigraniline, and pernigraniline, are quinonoid derivatives of the same parent substance, to which we have given the name "leucoemeraldine." Into this compound they are all converted on reduction, and from it they can all be produced by oxidation. At present the protoemeraldine stage has only been obtained in the *o*-toluidine series, whilst pernigraniline is too unstable to isolate in a dry state.

Emeraldine.

This compound is the first clearly defined stage in the oxidation of aniline in an acid medium, whatever the oxidising agent employed. When a chlorate is used, the reaction tends in part to at once proceed further with production of more or less nigraniline, but with hydrogen peroxide, if not used in excess, the oxidation stops at the emeraldine stage. If the reaction is effected in the cold and in the presence of an excess of acid, emeraldine and nigraniline are nearly the sole products, but if the mixture is neutral or only slightly acid, a certain quantity of condensation products (ungreenable black) is also produced. An excess of acid is therefore a necessary condition for preparing emeraldine in a pure state. As the result of a series of experiments, proportions corresponding with 1 mol. of aniline hydrochloride to 1·33 mols. of oxygen and 1 mol. of hydrochloric acid were found the most suitable.

Emeraldine is also produced by the further oxidation of the blue imide, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NH$, of Willstätter and Moore (termed "emeraldine" by these authors).

I. A solution of 100 grams of aniline hydrochloride, 42 grams of sodium chlorate, and 46·5 c.c. of hydrochloric acid (33 per cent. HCl) in 1800 c.c. of water, to which 2 drops of syrupy vanadium chloride are added, is kept in the cold for from two to three days. The precipitate is then collected, washed thoroughly with water, basified by mixing the paste with dilute ammonia in a mortar, finally washed with alcohol and with water, and dried at 35—40°. The product thus obtained contains a varying amount of nigraniline, which may be readily converted into emeraldine by warming the precipitate with dilute hydrochloric acid before basifying. Pure emeraldine may also be obtained by dissolving the crude base in 50 parts of 80 per cent. acetic acid, filtering from any insoluble matter, reprecipitating by addition of dilute hydrochloric acid, collecting the hydrochloride, and finally basifying the precipitate with ammonia. During this process the nigraniline present is converted into emeraldine.

II. A solution of 50 grams of aniline hydrochloride in 2½ litres of water, to which is added 135 c.c. of hydrochloric acid (33 per cent. HCl), 380 c.c. of hydrogen peroxide solution (4·6 per cent.), and 0·5 gram of ferrous sulphate, is kept in the cold for twenty-four hours. The precipitated emeraldine is collected, washed, and basified with ammonia.

III. Ten grams of *p*-aminodiphenylamine are dissolved together with 27 c.c. of hydrochloric acid (33 per cent. HCl) in 1 litre of water. After cooling to 0—5° by addition of ice, 78 c.c. of hydrogen peroxide (4·7 per cent.), followed by 0·1 gram ferrous sulphate, are added. The hydrogen peroxide used was rather more than twice the quantity required to convert the aminodiphenylamine into Willstätter and Moore's blue imide. On adding the iron salt, a voluminous indigo-blue precipitate of the imide was first produced, which, after about twelve to twenty-four hours, slowly lost its blue colour and became green, while the excess of peroxide disappeared and an odour of *p*-benzoquinone was apparent. The mixture was warmed on the water-bath, and the precipitate collected, washed, and basified with ammonia.

When prepared by either of these methods, the emeraldine base forms an indigo-blue powder, which, when purified by the acetic acid method, has a bronzy lustre. When dried at a low temperature it retains a remarkably large amount of water (about 30 per cent.). It is insoluble in alcohol, benzene, chloroform, etc., but dissolves readily in cold pyridine, giving a bright blue solution. This solution is, however, very unstable, for in a short time the greater part of the product separates out again as a colloidal precipitate. This precipitate consists of a condensation product of quite different properties to the original emeraldine. In concentrated sulphuric acid, emeraldine dissolves with a reddish-violet colour, and on addition of water a bright green precipitate of the sulphate is obtained. Towards acetic and formic acids the behaviour of emeraldine and nigraniline is very remarkable. These bases are insoluble in glacial acetic acid or in concentrated formic acid, and are also insoluble in these acids when fairly dilute, but in acids of medium concentration, that is, in acetic acid of about 80 per cent. or in formic acid of about 60 per cent., they dissolve readily. The solutions obtained with emeraldine are yellowish-green, and give a green precipitate on the addition of mineral acids or salts. By means of such a solution, the various stages of oxidation can be very effectively demonstrated, for on addition of a very dilute solution of chromic acid the green colour of the solution first changes to pure blue (nigraniline), and then, as more oxidising agent is added, to violet (pernigraniline), finally giving a violet precipitate (pernigraniline chromate). If to the violet solution of the pernigraniline a very weak solution of sodium hydrogen sulphite is added, these colour changes occur in the opposite direction, namely, from violet to blue, and from blue to green. Stronger reducing agents, such as phenylhydrazine, sodium hyposulphite, or titanium trichloride, convert emeraldine into leucoemeraldine.

In order to determine the quantity of hydrogen required for conversion of emeraldine into leucoemeraldine, the acetic acid solution was titrated with titanium trichloride according to Knecht's method, the analysis being carried out as follows. One gram of emeraldine in fine powder is weighed into a 250 c.c. flask containing 50 c.c. of water, and well shaken to prevent any of the powder agglomerating into lumps. Glacial acetic acid is then added until the flask is about three-quarters full, the contents well shaken, and heated on the water-bath for fifteen minutes to about 90° to ensure conversion of all nigraniline present into emeraldine. The solution is then cooled, and made up to the mark with glacial acetic acid. For each titration, 25 c.c. of this solution ($=0{\cdot}1$ gram of substance) are transferred, by means of a pipette, to a conical flask, and mixed with 25 c.c. of water and a measured excess of titanium trichloride, the strength of which is re-determined each day. The mixture is kept in the cold for ten to fifteen minutes, air being excluded by a slow stream of carbon dioxide. At the end of this time the solution is quickly filtered from the precipitated leuco-emeraldine, employing a funnel and filter paper enclosed in a vessel filled with carbon dioxide. An aliquot portion of the whole (50 c.c.) is then transferred to another flask also containing carbon dioxide, and at once titrated with a standard ferric alum solution, employing ammonium thiocyanate as indicator. In calculating the results, the percentage of water, chlorine, and ash is allowed for, and a further small correction, determined by parallel blank experiments made under exactly the same conditions, is introduced for the loss of titanium trichloride oxidised by air during the operation. The first preparation analysed (obtained by method I) contained 31·9 per cent. of water, 1·1 per cent. of chlorine, and 0·1 per cent. of ash. The following results were obtained:

No. of experiment.	Vol. of $TiCl_3$ run in, c.c.	Vol. of $TiCl_3$ unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Hydrogen value of 1 litre $TiCl_3$, gram.	Percentage of hydrogen on pure dry emeraldine.
1	25	13·70	1·77	0·0374	0·533
2	25	14·15	0·92	0·0366	0·543
3	25	14·15	0·92	0·0366	0·543
4	25	13·23	1·30	0·0358	0·560
5	25	13·65	1·34	0·0358	0·536
6	25	13·55	1·33	0·0358	0·542
7	25	13·47	1·29	0·0358	0·545
8	25	13·47	1·29	0·0358	0·545
				Mean.........	0·543

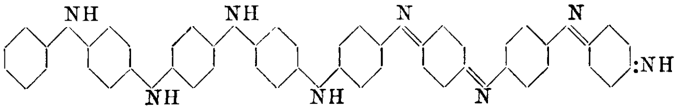
A second series of estimations was made with a larger excess of titanium trichloride and another preparation of emeraldine containing 30·65 per cent. of water, 1·0 per cent. of chlorine, and 0·1 per cent. of ash. Using 0·1 gram for each titration, the following results were obtained:

No. of experiment.	Vol. of $TiCl_3$ run in, c.c.	Vol. of $TiCl_3$ unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Hydrogen value of 1 litre $TiCl_3$, gram.	Percentage of hydrogen on pure dry emeraldine.
1	50	40·69	0·87	0·0442	0·547
2	50	40·59	0·87	0·0442	0·553
3	50	40·80	0·88	0·0442	0·540
4	50	40·69	0·87	0·0442	0·547
				Mean.........	0·547

Figures of the same order were also obtained by direct titration of the acetic acid solution with titanium trichloride, although, owing to the uncertain end-point, the results were not as trustworthy as those obtained by the indirect method.

The mean value of the two series of determinations was 0·545 gram of hydrogen for 100 grams of pure dry emeraldine.

A diquinonoid compound of the formula:



would require 0·555 per cent. of hydrogen for complete reduction to the leuco-compound.

In order to estimate the quantity of oxygen consumed in the conversion of emeraldine into nigraniline, two methods have been adopted. The first consists in titrating an acetic acid solution of emeraldine with a standard solution of chromic acid until the pure blue colour of the nigraniline is reached. The second consists in separately titrating emeraldine and nigraniline until the violet pernigraniline chromate is completely precipitated. Deduction of the quantity of chromic acid required to reach this point for nigraniline from the quantity required to reach the same point for emeraldine gives the quantity consumed in oxidising emeraldine into nigraniline. Owing to the more definite end-point, the latter method is the more trustworthy.

I. Twenty-five c.c. of emeraldine solution, containing 0·1 gram of substance dissolved in 80 per cent. acetic acid, were diluted with 25 c.c. of water, and titrated with a solution of chromic acid containing 3·52 grams of chromium trioxide per litre (equal to 0·845 gram of oxygen per litre). The emeraldine employed contained 31·9 per cent. of water, 1·1 per cent. of chlorine, and 0·1 per cent. of ash and 1·5 c.c. of chromic acid (several experiments) were required to give a pure blue colour. Correcting for contents of water, chlorine, and ash, this is equivalent to a consumption of 1·9 grams of oxygen per 100 grams of pure dry emeraldine for oxidation to nigraniline.

II. (*a*) Twenty-five c.c. of emeraldine solution, containing 0·1 gram of substance dissolved in 80 per cent. acetic acid, were diluted with 25 c.c. of water, and titrated with a solution of chromic acid containing 0·704 gram of chromium trioxide per litre (equal to 0·169 gram of oxygen per litre) until the precipitation of the violet pernigraniline chromate was complete, and no further change of colour took place. The emeraldine employed contained 30·65 per cent. of water, 1 per cent. of chlorine, and 0·1 per cent. of ash.

No. of experiment.	Weight of emeraldine, gram.	Vol. of CrO_3 required, c.c.	Percentage of oxygen on pure dry emeraldine.
1	0·1	24·5	6·07
2	0·1	25·0	6·19
3	0·1	25·0	6·19
4	0·1	24·5	6·07
		Mean.........	6·13

(*b*) A weighed quantity of nigraniline (preparation see later) was added in a state of fine powder to 5 c.c. of water. The whole was cooled in ice, 20 c.c. of glacial acetic acid added, the mixture shaken until dissolved, and then at once titrated with chromic acid as above. The nigraniline employed contained 11·28 per cent. of water, 1·12 per cent. of chlorine, and 1·3 per cent. of ash:

No. of experiment.	Weight of nigraniline, gram.	Vol. of CrO_3 required, c.c.	Percentage of oxygen on pure dry nigraniline.
1	0·0950	19·5	4·02
2	0·0983	20·0	3·98
3	0·1257	25·0	3·89
4	0·1017	21·0	4·04
		Mean.........	3·98

Deducting 3·98 from 6·13 gives 2·15 as the percentage of oxygen required to oxidise pure dry emeraldine into nigraniline. If emeraldine has the above formula, it would require, theoretically, 2·20 per cent. of oxygen for the removal of two hydrogen atoms, that is, to introduce one quinonoid group.

Nigraniline.

The best method for the preparation of nigraniline in substance was found to be the oxidation of emeraldine base (or the mixture of emeraldine and nigraniline obtained by the chlorate oxidation), using an excess of hydrogen peroxide in an ammoniacal solution. For instance, the precipitate obtained by oxidising 40 grams of aniline hydrochloride and 18·6 c.c. of hydrochloric acid with 16·8 grams of sodium chlorate in presence of vanadium, as already described, is basified with ammonia, and the washed product, without being dried, is evenly suspended in 6 litres of water, to which 400 c.c. of hydrogen peroxide (3 per cent.) and 40 c.c. of concentrated ammonia are added. After keeping overnight, the precipitate is collected, washed well, and dried at 35°. The product contained 11·28 per cent. of water, 1·12 per cent. of chlorine, and 1·30 per cent. of ash.

Nigraniline base forms a bluish-black powder with a bronzy lustre. Like emeraldine, it is insoluble in most solvents, but dissolves in cold pyridine with a bright blue colour. The salts are blue, not dark green as stated in the literature. This error arises from the fact that nigraniline salts are very unstable, and both in substance and on the fibre are readily converted into salts of emeraldine. The change takes place slowly in the cold, but more rapidly on heating, and is accompanied by the production of *p*-benzoquinone. One part of the nigraniline is oxidised to *p*-benzoquinone, whilst another part is reduced to emeraldine, a fact which affords an explanation of the well-known "greening" of certain blacks on the fibre when exposed to an acid atmosphere. Similarly, when nigraniline is dissolved in concentrated sulphuric acid, it gives a violet solution of rather bluer shade than that of emeraldine, but on pouring into water, decomposition occurs, and a bright green precipitate of emeraldine sulphate is produced. Nigraniline dissolves readily and completely in cold 80 per cent. acetic acid or in 60 per cent. formic acid, giving pure deep blue solutions. These solutions, on warming, quickly change in colour to the green of the emeraldine salt. In contrast to the instability of the salts, nigraniline base is quite stable.

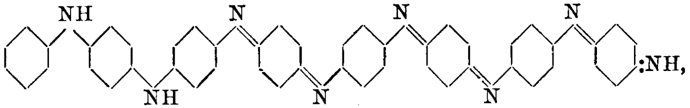
In performing the quantitative reduction of nigraniline, it is essential for the above reasons to avoid all heating in making the solution, and to effect the reduction as rapidly as possible. The operation is therefore carried out as follows. A weighed quantity of nigraniline (about 0·1 gram), which must be very finely powdered to ensure quick and complete solution, is suspended in 5 c.c. of water contained in a small flask. The flask is then cooled in ice for ten minutes, 20 c.c. of glacial acetic acid added, and the mixture shaken for half a minute, by which time the substance should have dissolved completely. Before the addition of the acetic acid, the air in the flask is expelled by carbon dioxide. The titanium trichloride solution is then added, and the titration effected in the same manner as with emeraldine:

No. of experiment.	Weight of nigraniline taken, gram.	Vol. of $TiCl_3$ run in (1 litre = 0·0307 gram of hydrogen), c.c.	Vol. of $TiCl_3$ left unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Percentage of hydrogen on pure dry nigraniline.
1	0·1009	40	17·3	0·87	0·771
2	0·0673	40	23·85	1·20	0·791
3	0·1089	40	15·62	0·78	0·772
4	0·1320	50	20·47	0·63	0·781
5	0·1198	50	23·38	0·72	0·770
6	0·1108	50	24·35	0·75	0·801
				Mean.........	0·781

Another series of titrations made with a stronger titanium solution (1 litre = 0·0442 gram of hydrogen) gave the following results:

No. of experiment.	Weight of nigraniline taken, gram.	Vol. of $TiCl_3$ run in (1 litre = 0·0307 gram of hydrogen), c.c.	Vol. of $TiCl_3$ left unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Percentage of hydrogen on pure dry nigraniline.
7	0·1386	50	27·98	0·51	0·797
8	0·0900	50	35·06	0·63	0·816
9	0·1090	50	32·10	0·58	0·816
10	0·1035	50	32·95	0·60	0·816
				Mean.........	0·811

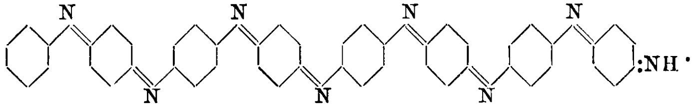
A triquinonoid compound of the formula:



would require 0·835 per cent. of hydrogen for complete reduction to leucoemeraldine. This formula is also supported by the oxidation numbers given under emeraldine.

Although the above formula is the same as that given by Willstätter and Dorogi to the preparation which they term "triquinonoid aniline-black," yet the compound described and analysed by them can scarcely be identical with nigraniline, for the properties do not correspond. If these authors originally had nigraniline in hand, it must have suffered conversion into emeraldine, and probably into further decomposition products by the process of purification employed.

Pernigraniline.



When a solution of emeraldine or nigraniline in acetic or formic acid is treated with an excess of a powerful oxidising agent, such as chromic acid or ammonium persulphate, the oxidation proceeds beyond the nigraniline stage, giving rise to a violet precipitate, which, on basifying with ammonia, yields a purple-brown compound, "pernigraniline." This substance is exceedingly unstable, decomposing slowly on drying, or even if kept in the paste form, with reproduction of nigraniline and formation of other products. This decomposition occurs still more rapidly in the presence of acids, following a similar course to nigraniline, which, together with *p*-benzoquinone, is first formed. The change is brought about by a few drops of dilute hydrochloric acid, and also more slowly by acetic acid. Reducing agents, if applied at once, convert pernigraniline first into nigraniline, then into emeraldine, and finally into leucoemeraldine. The base is soluble in pyridine, with a purple colour, and apparently undergoes decomposition in this solvent in the same manner as do emeraldine and nigraniline. In concentrated sulphuric acid, it dissolves with a bluish-violet colour. On pouring this solution into water, a green precipitate of emeraldine sulphate is produced.

On account of its instability, pernigraniline cannot be obtained pure in the dry state; an almost complete reversion to nigraniline occurs during drying. An attempt was therefore made to submit it, without drying, to analysis by reduction, employing a paste which contained 8·45 per cent. of dry product. This was prepared as follows. Five grams of the mixture of emeraldine and nigraniline base obtained by the chlorate method were dissolved in 500 c.c. of 80 per cent. acetic acid. To the ice-cold solution was added 5 grams of ammonium persulphate dissolved in a little water, when a violet precipitate at once separated. The whole was then immediately stirred into an excess of dilute ammonia mixed with crushed ice, the temperature being kept as low as possible. After adding a little salt, the precipitate was collected, washed with several litres of water, and brought to a uniform consistency, in which the percentage of water was estimated. The following results were obtained on analysis:

No. of experiment.	Weight of pernigraniline paste (8·45 per cent.) grams.	Vol. of $TiCl_3$ run in (1 litre $=0·0507$ gram of hydrogen), c.c.	Vol. of $TiCl_3$ left unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Percentage of hydrogen on dry pernigraniline.
1	0·9565	50	34·7	0·28	0·949
2	1·1782	50	31·8	0·25	0·914
3	0·8900	50	36·4	0·29	0·896
4	1·8010	50	24·9	0·20	0·830

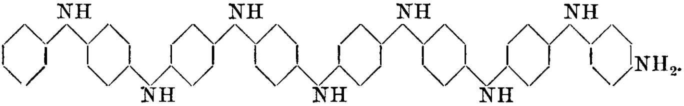
A tetraquinonoid compound of the above constitution would require for reduction to leucoemeraldine 1·11 per cent. of hydrogen. It will therefore be seen that, whilst the first titration gives a value approaching that required by this formula, there is a steady diminution in the consumption of hydrogen in the later analyses. The last titration, which was made after the paste had been kept a day, gives a hydrogen value almost corresponding with that of nigraniline (theory, 0·835 per cent.).

The above formula for pernigraniline is also supported by the figures given on p. 2396 for the consumption of chromic acid required to oxidise emeraldine and nigraniline to pernigraniline chromate. Thus, calculating the whole chromic acid as oxygen, the results are:

	Oxygen consumed, per cent.	$C_{48}H_{34}N_8+\frac{1}{2}CrO_3$ requires, per cent.
From emeraldine.........	6·13	5·96
,, nigraniline	3·98	3·79

It will be seen that the above formula for pernigraniline is the same as that assigned by Willstätter and Dorogi to the preparations which they call "tetraquinonoid aniline-black." The great instability of pernigraniline is, however, entirely inconsistent with the assumption that these products are identical, since the treatment to which Willstätter and Dorogi's preparations were subjected would have completely decomposed pernigraniline, and even the drying alone, without treatment with acid, would have converted it into nigraniline.

Leucoemeraldine.



This product is readily prepared by reducing either emeraldine or nigraniline with a strong reducing agent. For instance, the mixture of emeraldine and nigraniline bases obtained by the chlorate oxidation was moistened with alcohol in a mortar, and then ground to a paste with a concentrated solution of sodium hyposulphite and a little ammonia. The precipitate was collected, washed, and dried in a vacuum.

A better method consists in moistening the dry base with pure dry ether, and grinding the paste with an equal weight of phenylhydrazine. It is then thrown on a filter, and washed with dry ether until the excess of phenylhydrazine is removed, after which the product is dried quickly on a porous plate.

Leucoemeraldine forms a pale brown, amorphous powder, probably colourless when pure, which does not melt below 350°. It is fairly stable when dry, but when exposed to air in a damp state it becomes blue. It is insoluble in most solvents, but dissolves to a slight extent in pyridine. In 80 per cent. acetic acid or in 60 per cent. formic acid, it is sparingly soluble.

The constitution assigned to leucoemeraldine above is supported by the fact that four atoms of hydrogen are required for its formation from emeraldine, and six atoms for its formation from nigraniline.

Willstätter and Dorogi's Blacks.

In order to ascertain how far the products examined by these authors, and termed "triquinonoid aniline-black" and "tetraquinonoid aniline-black," compare in properties with the foregoing compounds, we have prepared them by following exactly the prescriptions given. The properties of the products we obtained are given in the following table:

Product.	80 per cent. acetic acid.	60 Per cent. formic acid.	Pyridine.
Persulphate Black. (W. & D.)	Considerable portion soluble with bright bluish-green colour.	Partly soluble with bright green colour.	Considerable portion soluble with deep blue colour.
Bichromate Black. (W. & D.)	As above.	As above.	As above.
Chlorate Black: triquinonoid, 6 hours. (W. & D.)	Small part soluble with dull greenish colour.	Nearly insoluble.	Trace only soluble with pale blue colour.
Chlorate Black: triquinonoid, 23 hours. (W. & D.)	Trace soluble with dull greenish colour.	Insoluble.	Very sparingly soluble with pale blue colour.
Chlorate Black: tetraquinonoid, 6 hours. (W. & D.)	Small part soluble with dull greenish colour.	Insoluble.	As above.
Chlorate Black: tetraquinonoid, 22 hours. (W. & D.)	Sparingly soluble with greenish colour.	Very sparingly soluble.	As above.

It will thus be seen that these products differ entirely from the emeraldine, nigraniline, and pernigraniline described above. They appear to be mixtures containing emeraldine, together with further condensation products. Three of them were submitted to successive extractions with cold 80 per cent. acetic acid until nothing further dissolved. The following were the results obtained:

	Persulphate Black (W. & D.), per cent.	Bichromate Black (W. & D.), per cent.	Chlorate Black: triquinonoid (W. & D.), per cent.
Soluble portion	51·5	60·0	80·0
Insoluble portion ...	48·5	40·0	20·0

Oxidation of o-*Toluidine.*

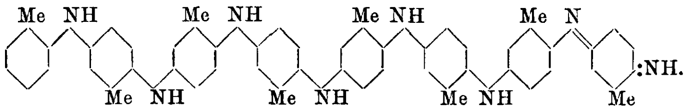
It has long been known to technologists that *o*-toluidine, when oxidised on the fibre, gives rise to a black which is not so brilliant as aniline-black, but which has less tendency to "green." No attempt has apparently been made to prepare this dye or its intermediate compounds in substance.

We have found that under the same conditions as employed for aniline the oxidation proceeds in an analogous manner, giving corresponding products. It appears, however, that the primary oxidation products are rather less stable than in the aniline series, being more prone to undergo polymerisation, and that the higher quinonoid products are less easily formed, and more readily revert to the lower. The best results were obtained by conducting the oxidation without any excess of mineral acid. Thus, 33 grams of *o*-toluidine and 34 grams of hydrochloric acid (33 per cent.) were dissolved in 700 c.c. of water, with the addition of 16·8 grams of sodium chlorate and 2 drops of syrupy vanadium chloride. After being kept for three days at the ordinary temperature, the greenish-blue precipitate was collected, washed with water, basified with ammonia, and then repeatedly extracted with 90 per cent. alcohol in order to remove a soluble by-product (? homologue of Willstätter's blue imide). It was then dried at 30—35°. The product is a violet-blue powder of indigo-like appearance. It is insoluble in most solvents, but dissolves readily in pyridine with a blue colour, and in 80 per cent. acetic acid or 60 per cent. formic acid with a dull yellowish-green colour. It contains 4·6 per cent. of water and 2·0 per cent. of chlorine.

The analysis by reduction was effected in the same manner as employed for emeraldine.

No. of experiment.	Vol. of $TiCl_3$ run in, c.c.	Vol. of $TiCl_3$ unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Hydrogen value of 1 litre $TiCl_3$, gram.	Percentage on pure dry substance.
1	50	45·43	0·36	0·0506	0·228
2	50	45·15	0·36	0·0506	0·243
3	50	44·71	0·36	0·0506	0·267
4	50	44·89	0·36	0·0506	0·257
5	50	45·88	0·37	0·0506	0·203
6	50	45·25	0·36	0·0506	0·238
				Mean.........	0·239

A monoquinonoid compound of the constitution:



would require 0·24 per cent. of hydrogen for reduction to the leuco-compound. It therefore appears that the product of the oxidation of *o*-toluidine is the protoemeraldine of this series.

Another preparation in which an excess of acid was used in the oxidation gave as the average consumption of hydrogen for reduction 0·360 per cent. This preparation was therefore apparently a mixture of the tolu-protoemeraldine with tolu-emeraldine.

Attempts to oxidise tolu-protoemeraldine into a higher oxidation stage by means of hydrogen peroxide and ammonia, employing the same conditions as those used for nigraniline, gave a negative result. The product still dissolved in acetic acid with a green colour, and afforded the same reduction figures as before. On the other hand, on addition of chromic acid or persulphate to the acetic acid solution, the colour first becomes blue and then violet, as in the aniline series. It therefore appears that the formation of the tolu-nigraniline does not take place with the same facility as with the lower homologue, a conclusion which is supported by the fact that no tolu-nigraniline was ever produced in our experiments with the chlorate and vanadium oxidation.

Oxidation of Other Amines.

The oxidation of various primary amines was studied under the same conditions as employed in the preparation of emeraldine. *o*-Chloroaniline gave emeraldine-like products; *m*-chloroaniline gave none. *o*-Anisidine underwent oxidation in a different direction, apparently through elimination of the methyl groups. Dimethylaniline remained unattacked.

Conclusions.

1. There are four quinonoid stages derived from the parent compound leucoemeraldine.
2. The minimum molecular weights of these primary oxidation products of aniline are in accordance with an eight-nucleal structure.
3. The conversion of emeraldine into nigraniline consumes one atom of oxygen.
4. The conversion of emeraldine into pernigraniline consumes two atoms of oxygen.
5. The conversion of nigraniline into pernigraniline consumes one atom of oxygen.
6. The reduction of emeraldine to leucoemeraldine consumes four atoms of hydrogen.
7. The reduction of nigraniline to leucoemeraldine consumes six atoms of hydrogen.
8. The reduction of pernigraniline to leucoemeraldine consumes eight atoms of hydrogen.
9. The reduction of tolu-protoemeraldine consumes two atoms of hydrogen.
10. None of these products are properly entitled to be considered as aniline-black, but are intermediate products in the formation of the latter.

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