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I.—*On some new Colouring Matters, Derivatives of Dinitrobenzole, Dinitronaphthaline, &c. &c.*

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By the action of nascent hydrogen upon dinitrobenzole, its homologues and analogues, red or purple colouring matters of great intensity are produced. At present we can give an account of the preparation, composition, and properties of two only of these interesting bodies; but, as we shall show towards the conclusion of this communication, the number of similar bodies producible is very great.

I. *Action of nascent hydrogen on Dinitrobenzole.*—When an alcoholic solution of dinitrobenzole is treated with zinc and hydrochloric acid, the evolution of hydrogen, at first energetic, soon ceases almost entirely, and then the liquid in the immediate neighbourhood of the zinc assumes a rich crimson colour. When the reaction is complete, the liquid must be separated from any excess of zinc, and after complete neutralisation with an alkali, thrown upon a filter and washed with water. The dark-coloured oxide of zinc on the filter must be exhausted repeatedly with strong alcohol. The residue left on evaporation to dryness at 100° C. of this alcoholic solution, may be completely purified by washing with water and exhaustion with absolute alcohol, in which the colouring matter is extremely soluble. This solution evaporated in the water-bath ultimately deposits the whole of the colouring matter in a state of perfect purity. We have examined

the properties of the substance as obtained from its solution in absolute alcohol. For considerations which will shortly be apparent, we have named this substance NITROSOPHENYLINE. Besides the general outlines of the method for the preparation of nitrosophenyline, the following precautions may be noted. If the acid solution of the colouring matter be evaporated to dryness in the presence even of a trace of chloride of zinc, the substance then no longer gives with strong acids the characteristic magnificent crimson tint of nitrosophenyline. Again, the action of the zinc must not be too energetic, nor must the solution get too hot. A saturated cold solution of dinitrobenzole may be taken; the zinc should be perfectly pure, and in the form of a long strip, which, when occasion requires, may be conveniently and rapidly withdrawn. The hydrochloric acid should be strong, and added carefully, drop by drop, until the whole of the dinitrobenzole has been converted: when the reaction is complete, a drop of the coloured solution will not produce any turbidity with water.

Properties of Nitrosophenyline.—As obtained by the evaporation of its alcoholic solution, nitrosophenyline occurs in the form of a black, shining film, brittle, and easily removed from the containing vessel. Although when pure it stands a temperature considerably higher than 100° C. without undergoing any change, yet it is not volatile without decomposition. On the application of heat, it fuses, then evolves a white vapour, leaving a very bulky carbonaceous residue, which may be completely burnt in a stream of oxygen or by prolonged ignition in the air. The new body is almost insoluble in water, but very soluble in acids and in alcohol. To benzole, &c., it imparts scarcely a trace of colour. Heated strongly with soda lime, all the nitrogen of nitrosophenyline appears in the forms of ammonia and aniline. The formation of aniline was detected by its well-known reaction with hypochlorite of lime. Nitrosophenyline appears to have, if any, a very slight claim to the basic character.

The alcoholic solution of nitrosophenyline exhibits some remarkable optical properties. Perfectly transparent to transmitted light, it presents, when viewed in reflected light, a most extraordinary degree of opacity. A solution of 0.01 of a gramme dissolved in 5 grammes of alcohol, the solution thus containing only 0.2 of a per cent. of nitrosophenyline, exhibits this phenomenon in a very marked manner: a brilliant orange-red light illuminates the surface of the liquid, and descends to a slight depth beneath it; while the liquid itself appears as if finely

powdered vermilion were suspended in it. The flame of alcohol saturated with a baryta-salt is suitable for exhibiting the curious properties of this solution: but they are best seen when examined with the solar spectrum, the *red* ray producing no effect.

The colouring matter is acted upon by acids and by alkalis. The strongest hydrochloric acid and dilute nitric and sulphuric acids dissolve it with a magnificent crimson tint; ebullition with nitric acid produces a yellow colour; and solution in Nordhausen sulphuric acid, an intense brown, which nearly disappears on addition of water. Potash, soda, and ammonia partly precipitate the colouring matter from its acid solutions in brownish-yellow flakes; but if the action of the alkali be not prolonged, the original crimson tint of the solution reappears on the addition of an acid. From a solution of nitrosophenylene in hydrochloric acid, the colouring matter gradually separates as a reddish film, having the brilliant metallic lustre of copper. If nitrosophenylene be dissolved in the strongest hydrochloric acid, and the solution be exposed to the air, a gummy mass is formed after some time, while a portion of the nitrosophenylene separates: the hydrochloric acid in this compound does not exist in any definite proportion.

By the prolonged action of nascent hydrogen, nitrosophenylene loses its colorific properties, possibly passing into a substance containing no oxygen (and possessing the basic character?). The difficulty of preparing pure nitrosophenylene in sufficient quantity has prevented us from inquiring into the exact nature of this new product, but the inquiry would not be without interest. We have not as yet succeeded in regenerating from this colourless compound, by the action of oxidising agents, the original nitrosophenylene. All the analogues of nitrosophenylene which we have obtained suffer further reduction, producing colourless compounds by the prolonged action of hydrogen.

It was not surprising to find that dinitrobenzole is not the only substance of the benzole type from which a colouring matter may be produced in the way described. In the following table is a list of substances, homologous with dinitrobenzole, all of which give similar reactions with nascent hydrogen:—

1. Dinitrobenzole	$C_{12}H_4 2NO_4$
2. Dinitrotoluole	$C_{14}H_6 2NO_4$
3. Dinitroxylene	$C_{16}H_8 2NO_4$
4. Dinitrocumole	$C_{18}H_{10} 2NO_4$
5. Dinitrocymole	$C_{20}H_{12} 2NO_4$

The hydrocarbons from which the above-mentioned substances were produced had been obtained from very various sources. On account of the sparing solubility of *dinitroxylole*, &c., the compounds corresponding to nitrosophenyline in the higher terms of the series, are produced but sparingly by the method above given.

Composition of Nitrosophenyline.—Unlike most colouring matters, nitrosophenyline offers no difficulties in its analysis. In burning it, a stream of oxygen was employed towards the close of the combustion; in this way, the carbonaceous residue which it leaves on ignition was rapidly consumed. The nitrogen was determined by igniting the substance with soda-lime and precipitating the mixed hydrochlorates of aniline and ammonia with bichloride of platinum. As each equivalent of platinum corresponded to 1 eq. of nitrogen, the percentage of this latter element in the original substance was calculated from the amount of metal left on the ignition of the platinum-salts just mentioned. The following are the details of our analyses:—

- I. 0.293 grm. of nitrosophenyline gave
 0.634 „ „ carbonic acid, and
 0.1235 „ „ water.
- II. 0.2825 „ „ nitrosophenyline burnt with soda-lime gave
 0.454 „ „ platinum.

In 100 parts:

	I.	II.
Carbon	59.04	
Hydrogen	4.68	
Nitrogen		22.80

These percentages lead to the formula

as may be seen in the following table:—

		Theory.	Experiment.
12 equiv. of carbon . .	72	59.01	59.04
6 „ „ hydrogen . .	6	4.92	4.68
2 „ „ nitrogen . .	28	22.95	22.80
2 „ „ oxygen . .	16	13.12	—
1 equiv. of nitrosophenyline .	122	100.00	

This formula is confirmed by the mode in which nitrosophenyline is formed from dinitrobenzole, $\text{C}_{12} \text{H}_4 2\text{NO}_2$, or from nitra-

niline, $C_{12}H_6N_2O_4$, and by the decompositions which it undergoes. As it forms no salts, the formula could not be controlled.

The relations of nitrosophenyline to dinitrobenzole and to nitraniline becomes simple and intelligible if we arrange the crude formula of nitrosophenyline as derived from the foregoing analyses, thus—

or thus—

consequently, it differs from dinitrobenzole by containing 6 equiv. oxygen less, and 2 eq. hydrogen more; and from nitraniline by containing 2 eq. oxygen less. Thus, in the production of nitrosophenyline from dinitrobenzole, 1 eq. of NO_4 is replaced by 1 eq. NH_2 , while the 2nd eq. loses 2 eq. of oxygen; the 1 eq. NO_4 in nitraniline is similarly reduced to NO_2 . Nitrosophenyline may, in fact, be viewed as aniline in which 1 eq. of hydrogen is replaced by 1 eq. of NO_2 ; to such replacements Laurent has applied the terms "*substitutions nitrosées*." From this expression we have constructed the name of the new colouring matter; but as this substance presents but a very equivocal basic character, we have preferred to call it nitrosophenyline rather than nitrosaniline. We are not without an example of a partial reduction of NO_4 , somewhat similar to the present case. For, in the formation of azoxybenzole from nitrobenzole, we may imagine, with Laurent, that the reaction may be described in the following manner:—

The following list presents in a tabular form the derivation of nitrosophenyline, and the composition of those members of the benzole series which are related to it:—

1. Benzole	$C_{12}H_6, H.$
2. Nitrobenzole	$C_{12}H_5, NO_4.$
3. Dinitrobenzole	$C_{12} \begin{matrix} H_4 \\ NO_4 \end{matrix}, NO_4 + 8H = C_{12} \begin{matrix} H_4 \\ NO_2 \end{matrix}, NH_2 + 6HO.$

It is perhaps worthy of remark that nitrosophenylene presents considerable resemblance to the *red indigo* of Berzelius.

II. As we have said before, not only the homologues but the *analogues* of dinitrobenzole produce remarkable colouring matters when acted upon by nascent hydrogen. In order to ascertain the true nature of the new bodies thus produced, we have submitted to a detailed inquiry a beautiful red substance obtained by reducing *dinitro*-naphthaline with hydrogen. But a colouring matter perfectly identical may be procured by acting upon naphthalamine with nitrous acid, or upon the hydrochlorate of naphthalamine with nitrite of potash. By this last method we have obtained it in considerable quantities. This new substance resembles nitrosophenylene in its properties, and is perfectly analogous with it in composition, as we shall shortly show. We have termed it NITROSONAPHTHYLINE.

Properties of Nitrosonaphthylene.—When nitrite of potash is added to hydrochlorate of naphthalamine, nitrosonaphthylene is precipitated, nearly pure. It then merely requires washing with water, drying, and exhaustion with boiling spirits of wine. From this alcoholic solution, by slow evaporation in the water-bath, the colouring matter is gradually precipitated in minute crystals, very dark in colour, and having a green metallic lustre, similar to that of murexide. It imparts to alcohol a rich red tint, which is changed to a magnificent violet by acids, and restored to its original colour by alkalis. Water precipitates it from its alcoholic solution of a scarlet colour. Cotton, linen, paper, &c., may be permanently dyed of an orange tint by immersion in the alcoholic solution of nitrosonaphthylene. Materials so dyed, if plunged in acids, become of an intense purple hue, but in a stream of water the original orange tint speedily returns. Nitrosonaphthylene is insoluble in water. It may be fused without decomposition. Heated strongly, a portion sublimes unchanged; white fumes are afterwards given off, and a residue of carbon remains. Nitrosonaphthylene is not dissolved by dilute acids; strong nitric acid destroys it, but it is soluble in Nordhausen sulphuric acid, with a bluish-purple colour. Alkalis do not change the colour of

nitrosonaphthylene: but by the prolonged action of nascent hydrogen it is destroyed.

Composition of Nitrosonaphthylene.—The determinations of carbon, hydrogen, and nitrogen in this substance were made with the usual precautions, and gave the following numbers:—

- I. 0.301 grm. of substance gave
 0.77 „ „ carbonic acid, and
 0.13 „ „ water.
 II. 0.3205 „ „ substance burnt with soda-lime, gave
 0.37 „ „ platinum.

These numbers correspond in 100 parts to

Carbon	.	.	.	I. 69.76	II. —
Hydrogen	.	.	.	4.80	—
Nitrogen	.	.	.	—	16.39

These percentages lead to the formula

as may be seen by the following table:—

				Theory.		Experiment.
20 equiv. of carbon	.	.	.	120	69.77	69.76
8 „ „	.	.	.	8	4.65	4.80
2 „ „	.	.	.	28	16.28	16.39
2 „ „	.	.	.	16	9.30	—
				<hr/>		
1 „ „ nitrosonaphthylene	.			172	100.00	

Nitrosonaphthylene is quite analogous to nitrosophenylene: if the former be *aniline* in which 1 equiv. of hydrogen has been replaced by NO_2 , the latter is naphthalamine, in which a similar substitution has taken place. The following equations sufficiently explain the various methods for the formation of nitrosonaphthylene:—

A fourth method, which might be successful, suggests itself,

viz. the action of nascent hydrogen upon nitronaphthalamine. The reaction of aniline and NO_3 produces carbolic acid $\text{C}_{12}\text{H}_6\text{O}_2$, and not *nitrosophenylene*.

Nitrosonaphthyline dissolved in alcohol appears gradually to suffer partial decomposition. In the altered substance thus produced, the carbon amounts to 75 per cent.

The results of the present inquiry indicate the existence of an almost entirely new type of substitution-products,—bodies, too, remarkable alike for their physical properties and their chemical relations.