XLII.—*On a new series of bodies in which Nitrogen is substituted for Hydrogen.*

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I.

FOR a number of years I have been engaged in investigating a peculiar class of nitrogen-compounds, which are obtained by the action of nitrous acid upon amido-compounds, the latter exchanging 3 atoms of their hydrogen for 1 atom of nitrogen from the nitrous acid.

I have up to the present time prepared a large number of these compounds, many of which I have already minutely described.* They are all distinguished by remarkable physical and chemical properties, especially by their tendency to explode with great violence when heated, and by the facility with which they exchange 2 atoms of nitrogen for other atomic groups, thereby frequently forming substitution-products of great interest. It is on account of this property that I have given the name of "diazo-compounds" to this class of bodies. I purpose in this and in some future communications to give a short sketch of the most important representatives of this class.

Diazodinitrophenol.

On passing a current of nitrous acid gas into an alcoholic solution of picramic acid, $C_6H_3(NO_2)(NH_2)O$, the originally red colour of the solution is observed to change to yellow, a rise in the temperature taking place at the same time. Meanwhile the whole of the nitrous acid is absorbed, whilst scarcely a trace of nitrogen is evolved. After the gas has been passing some time, a few yellow plates of diazodinitrophenol

* Ann. Ch. Pharm. c. 201 ; cxvii. 1 ; cxxi. 257. Phil. Trans., Part III, p. 667.

appear in the solution. They rapidly increase, and are deposited in the form of a lustrous crystalline mass. The process is finished as soon as the separation of crystals has ceased. The new substance when separated from the mother-liquor and recrystallised several times from boiling alcohol, is sufficiently pure for analysis. Another, though less convenient method of preparing diazodinitrophenol consists in dissolving picramic acid in nitric acid, and passing a current of binoxide of nitrogen into the solution. The solution, after being concentrated, yields with water a yellow precipitate, which is purified by recrystallisation from alcohol. Analysis led to the formula—

$$C_6H_2N_4O_5 = C_6H_2(NO_2)_2N_2O.$$

The formation of the new body takes place according to the following equation :—

$$\underset{\text{Picramic acid.}}{C_6H_5N_3O_5} + NHO_2 = \underset{\text{Diazodinitrophenol.}}{C_6H_2N_4O_5} + 2H_2O.$$

Diazodinitrophenol crystallises in golden-yellow plates of great beauty; it is difficultly soluble in alcohol and in ether, insoluble in water. It has a slight bitter taste, and explodes at a high temperature with great violence. It has no action on litmus or turmeric.

Ordinary nitric acid, sulphuric acid, and hydrochloric acid dissolve diazodinitrophenol without alteration; it evinces, on the whole, very great stability in the presence of acids. It may be boiled for days with fuming nitric acid, without undergoing the slightest alteration, even fuming sulphuric acid destroys it only at a high temperature. It is not attacked by dry chlorine. It is, however, decomposed on boiling for a considerable time with water. In addition to a small quantity of a resinous substance, a reddish-brown powder is obtained, which, though soluble in alcohol, ether, and caustic potash, cannot be obtained in crystals.

Diazodinitrophenol suffers a most remarkable decomposition under the influence of alcohol, in the presence of alkalis. On treating an alcoholic solution of it with a solution of carbonate of potassium, and gently heating the mixture, an evolution of gas ensues, whilst the colour of the originally yellow solution turns to red. As soon as the evolution of gas has ceased, the excess of alcohol is distilled off; the residue on cooling yields brownish-red

needle-shaped crystals of a potassium-salt, which, when recrystallised and treated in solution with dilute nitric acid, give light yellow plates easily soluble in alcohol.

This acid, for the most part, forms beautifully crystallised salts. Its properties, as well as the analysis, establish its identity with dinitrophenylic acid $C_6H_4(NO_2)_2O$.

The gas evolved during the decomposition of diazodinitrophenol by alcoholic potassa was proved by analysis to consist of pure nitrogen. The reaction takes place thus:—

$$\underset{\text{Diazodinitrophenol.}}{C_6H_2N_4O_5} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Dinitrophenylic acid.}}{C_6H_4(NO_2)_2O} + N_2 + \underset{\text{Aldehyde.}}{C_2H_4O.}*$$

I have determined the quantity of nitrogen evolved. 0·237 grm. substance gave 26·6 c. c. nitrogen at 0°, and 760 m. m. Bar. weighing 0·0334 grm. = 14·1 p. c. The preceding equation requires 13·3 p. c.

If diazodinitrophenol is boiled with a solution of aqueous potash another compound is obtained, which may possibly be oxydinitrophenylic acid.

Diazodinitrophenol, as already stated, is prepared by dissolving picramic acid in alcohol, and passing nitrous acid into the solution. If this proceeding be reversed, and the picramic acid be added to the alcohol previously saturated with nitrous acid and slightly warmed, a different reaction takes place. In this case a powerful evolution of gas ensues, whilst not a trace of diazodinitrophenol separates. When the reaction is over, the alcohol is distilled off, and the residue treated with water, a copious separation of crystals is obtained, which, on further purification, exhibit all the properties of dinitrophenylic acid.

It may, however, be noticed that in the preparation of diazodinitrophenol traces of dinitrophenylic acid are invariably formed.

Diazonitrophenol.

This compound is obtained by treating amidonitrophenylic acid ($C_6H_4(NO_2)(NH_2)O$)† with nitrous acid. It is, however, not advisable to employ an alcoholic solution of the acid, on account of

* The aldehyde was recognised by its peculiar odour.

† Gerhardt and Laurent, when describing this acid under the name of dinitrodiphenamic acid (Compt. Rend. des trav. de Chim., 1849, p. 468) assigned to it a formula double of that given above. I, however, think that the simpler formula is preferable.

the solubility of the diazonitrophenol in that liquid. From an ethereal solution, on the other hand, it separates completely as soon as the nitrous acid has passed through for a short time, whilst not a trace of nitrogen is evolved. The product when only washed a few times with ether is already fit for analysis. Numbers were obtained leading to the formula

$$C_6H_3(NO_2)N_2O.$$

Diazonitrophenol, when separating from the ethereal solution, appears as a brownish-yellow granular mass. It is very soluble in alcohol. On allowing the solution to evaporate spontaneously it is deposited in the same granular form. Even in hot water it is very difficultly soluble, being at the same time partly decomposed, and converted into an amorphous red powder. The filtered solution on cooling deposits the greater part of the substance in the form of small yellow crystals, which appear as thick prisms under the microscope. These crystals have a sweetish bitter taste, and when ground yield a light yellow powder, which, on exposure to light, assumes a dark red colour. Diazonitrophenol has no action on vegetal colours. The dry compound cannot be heated up to 100°, as at that temperature it is decomposed with a violent explosion, exerting at the same time a destructive power which can only be compared to that of fulminate of mercury.

Diazonitrophenol is but slightly soluble in ether, but cold hydrochloric acid and sulphuric acid readily dissolve it without decomposition; addition of water precipitates it as a reddish flocculent mass. Ebullition with fuming nitric acid converts it into a substance which, on the addition of water, separates as a curdy precipitate.

Diazonitrochlorophenol $C_6H_2(NO_2)ClN_2O$.

This substance is obtained by acting with nitrous acid upon an alcoholic solution of amido-nitrochlorophenylic acid ($C_6H_3Cl(NO_2)(NH_2)O$*). It may be prepared with equal facility by first saturating the alcohol with nitrous acid and then introducing the amido-acid. In both cases it is separated from the mother-liquor by filtration and recrystallised from alcohol, from which it is obtained on cooling in large brownish-red prismatic crystals of perfect purity. When dried at 100°, they gave on analysis numbers corresponding with the formula given above.

* Ann. Ch. Pharm. cix. 290.

Diazonitrochlorophenol possesses great power of crystallisation. From alcohol, in which it is but slightly soluble, it separates in brownish-red prismatic crystals. It is also difficultly soluble in hot water and in ether. From the former it crystallises in greenish golden yellow plates; from the latter in needles, which are often grouped in sheaves. When dissolved in ordinary sulphuric acid and then treated with water, it is obtained in thread-like crystals which frequently attain the length of three inches.

In its other points, it exhibits great analogy with the preceding compounds. It is dissolved by acids without decomposition; it forms a yellow powder which acquires a red colour on exposure to the light. It is, however, capable of bearing a much higher temperature than diazonitrophenol, and may be dried at 100° without danger; at a higher temperature it also deflagrates with violence.

As far as my view of the rational constitution of the substances described in the preceding pages is concerned, I think I have already clearly expressed it by the names which I have chosen for them. I refer them to the type of phenylic acid, and assume that in these bodies two atoms of hydrogen are replaced by two monoatomic atoms of nitrogen, or perhaps better by one double atom.

$C_6H_2(NO_2)_2(N_2)''O$.	$C_6H_3(NO_2)(N_2)''O$.	$C_6H_2(NO_2)Cl(N_2)''O$.
Diazodinitrophenol.	Diazonitrophenol.	Diazonitrochlorophenol.

This view is supported by the transformation which diazodinitrophenol undergoes when boiled with alcoholic potash, in which case the two atoms of nitrogen are, in fact, exchanged for two atoms of hydrogen. It is self-evident that this view does not stand in opposition to the fact that these diazo-compounds arise through the substitution of three atoms of hydrogen by one atom of nitrogen, especially if we bear in mind the analogous reaction which takes place when nitrous acid acts upon ammonia:

$$NH_3 + NHO_2 = (N_2)'' + 2H_2O.$$

One glance at this equation shows that in this case also three atoms of hydrogen are replaced by one atom of nitrogen, and that the molecule of nitrogen produced is equivalent to two atoms of hydrogen.