

XIV.—*Non-aromatic Diazonium Salts. Part V.* *Diazo-derivatives of Aminotriazoles.*

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THE aminotriazoles furnish an instance of a group of non-aromatic heterocyclic bases which undergo diazotisation, the researches of Thiele and Manchot having indicated that in hydrochloric acid solution these amines yield diazo-derivatives coupling with aromatic bases, such as β -naphthylamine (*Annalen*, 1898, **303**, 41).

Two points of interest were noted under these experimental conditions: first, that the diazo-compound was very unstable in the presence of hydrochloric acid, and secondly, that its coupling power disappeared when the solution was rendered alkaline. The first of these changes, which occurred rapidly even in ice-cold solution, led to the elimination of diazo-nitrogen and to the production of a chlorotriazole. The loss of coupling power which occurred on rendering the solution alkaline was assumed to be due to the formation of an *isodiazo*-compound, but this substance was neither identified nor isolated by the foregoing investigators.

In connexion with the general problem of the diazotisability of non-aromatic bases we have studied the behaviour of the aminotriazoles towards diazotising agents with the following results.

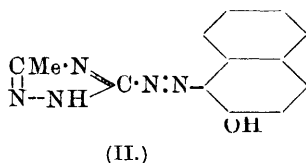
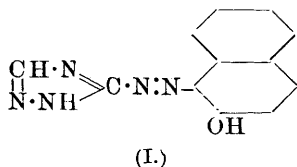
The work of Thiele and Manchot (*loc. cit.*) was in the main confirmed as regards the instability of the diazo-derivative in the presence of aqueous or alcoholic hydrochloric acid; the diazo-nitrogen is evolved at the ordinary temperature with the production of the corresponding chlorotriazole. A far more favourable result is obtained, however, by diazotising in the presence of an oxy-acid. When treated with sodium or ethyl nitrite, a cold dilute nitric acid solution of 5-amino-3-methyl-1:2:4-triazole yields a stable diazo-derivative coupling with β -naphthol, which can be isolated in the form of the sparingly soluble 5-*diazo-3-methyl-1:2:4-triazole aurichloride*, $C_3H_3N_5, H_2O, AuCl_3$. 5-Amino-1:2:4-triazole when similarly diazotised and treated with gold chloride yields 5-*diazo-1:2:4-triazole aurichloride*, $C_2HN_5, AuCl_3$.

A remarkable change occurs on evaporating at the ordinary temperature the nitric acid solution of 5-diazo-3-methyl-1:2:4-triazole. There is no loss of diazo-nitrogen during concentration, but the white, crystalline, soluble residue no longer couples with alkaline or alcoholic β -naphthol. This product still, however, contains the nitrogen requisite to form a diazonium salt, for when

dissolved in concentrated nitric acid or preferably sulphuric acid it is reconverted into a directly coupling diazo-derivative, which condenses quantitatively with β -naphthol.

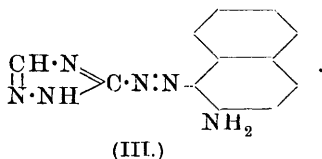
A similar result is observed on diazotising 5-amino-1:2:4-triazole, but in the case of the simpler base the products are less stable.

Unlike the purely aromatic azo- β -naphthols, 1:2:4-triazole-5-azo- β -naphthol (I) and 3-methyl-1:2:4-triazole-5-azo- β -naphthol (II)



are soluble in dilute aqueous alkali hydroxides.

This solubility in aqueous alkali is in all probability due to the presence in the triazole ring of an imino-group contiguous to the carbon atom bearing the azo-complex. That the hydroxylic hydrogen of the aromatic group is not involved in this salt formation is demonstrated by the fact that 1:2:4-triazole-5-azo- β -naphthylamine (III) is also readily soluble in aqueous alkali hydroxides:



The acidic character of the iminic hydrogen atom probably plays also an important part in determining the formation of the aurichlorides from the triazolediazonium salts and in the transformation of these diazonium compounds into isodiazio-derivatives.

The diazo- and isodiazio-derivatives of the triazole series are being further examined.

EXPERIMENTAL.

Diazotisation of 5-Amino-3-methyl-1:2:4-triazole.

The starting point in the preparation of 5-amino-3-methyl-1:2:4-triazole was aminoguanidine nitrate or the corresponding hydrochloride or carbonate, the two latter salts being converted into the nitrate by double decomposition with silver nitrate or nitric acid respectively.

Ten grams of aminoguanidine carbonate were converted into nitrate by evaporation to dryness on the water-bath with the calcu-

lated quantity of nitric acid. Excess of nitric acid led to destructive oxidation. The nitrate was heated with water (20 c.c.) and glacial acetic acid (10 c.c.) in a reflux apparatus, the product being kept in solution by adding water or dilute acetic acid. After twenty-four hours the reaction was completed, the solution evaporated to dryness, and the resulting anhydrous acetylaminoguanidine nitrate then melted at 144° , the hydrated salt melting at 85° . This salt was then dissolved in water, the solution evaporated to dryness with an equivalent amount of sodium carbonate (0.5 mol.), the residue extracted repeatedly with absolute alcohol, the alcohol distilled from the extract, and the residual, crude triazole purified by extraction with ethyl acetate in a Soxhlet apparatus. 5-Amino-3-methyl-1:2:4-triazole (m. p. 148°) was thus obtained in quantitative yield.

Diazotisation in Hydrochloric Acid.—On adding aqueous sodium nitrite to a solution of 5-amino-3-methyl-1:2:4-triazole in cold dilute hydrochloric acid, a diazonium chloride was obtained which decomposed rapidly even in solution, and on stirring the ice-cold liquid there was a rapid evolution of nitrogen.

Ethyl nitrite in moderate excess was added to 5-amino-3-methyl-1:2:4-triazole dissolved in cold alcoholic hydrochloric acid and the solution concentrated in a vacuum over potassium hydroxide and calcium chloride, when 5-chloro-3-methyl-1:2:4-triazole (m. p. 147°) slowly separated as a bulky, white precipitate (compare Thiele and Manchot, *loc. cit.*).

Diazotisation in Nitric Acid.—The substitution of nitric acid for hydrochloric acid in the diazotisation of 5-amino-3-methyl-1:2:4-triazole with sodium nitrite in aqueous solution led to the production of a much more stable diazonium salt. The solution, which was free from effervescence, was poured into alcoholic β -naphthol, when a brownish-red azo-compound separated. This substance was purified by four crystallisations from dilute ethyl alcohol (50 per cent.) and finally from absolute alcohol, when it was obtained in dark orange-brown plates and flattened needles melting at $213\text{--}215^{\circ}$:

0.0835 gave 20.4 c.c. N_2 at 20° and 737 mm. $N=27.74$.

$C_{13}H_{11}ON_5$ requires $N=27.67$ per cent.

3-Methyl-1:2:4-triazole-5-azo- β -naphthol was very readily soluble in ethyl acetate, chloroform, or in methyl or ethyl alcohol, less so in acetone or glacial acetic acid, and dissolved only sparingly in ether. With concentrated sulphuric acid it developed a purple coloration. Unlike the purely aromatic azo- β -naphthols, this mixed azo-derivative dissolved readily in cold dilute potassium hydroxide to a brownish-red solution.

5-Diazo-3-methyl-1:2:4-triazole Aurichloride.—A concentrated

aqueous solution of gold chloride was slowly added to 5-amino-3-methyl-1:2:4-triazole diazotised with sodium nitrite in dilute nitric acid; the aurichloride separated slowly as a heavy, crystalline precipitate consisting of rosettes of small, bright yellow prisms, the yield being almost quantitative. The salt, which was quite stable at the ordinary temperature, exploded on heating quickly to 100°. On raising the temperature slowly, it decomposed with brisk effervescence:

0.2300 gave 33.3 c.c. N_2 at 20° and 764 mm. $N=16.84$.

0.1639 „ 0.1616 AgCl. $Cl=24.30$.

0.1647 „ 0.075 Au. $Au=45.50$.

$C_3H_5ON_5, AuCl_3$ requires $N=16.26$; $Cl=24.73$; $Au=45.76$ per cent.

Although quite stable when dry, the sparingly soluble aurichloride changed in aqueous solution to an intensely red substance resembling an azo-derivative.

3-Methyl-1:2:4-triazole-5-isodiazohydroxide was obtained by diazotising 5-amino-3-methyl-1:2:4-triazole with excess of ethyl nitrite in dilute nitric acid, the solution being allowed to evaporate to dryness over potassium hydroxide at the ordinary temperature. The colourless, crystalline residue, which could be dried at 100° unchanged, but intumescd at 120°, dissolved readily in water and was less soluble in methyl or ethyl alcohol.

When crystallised from the latter solvent the isodiazio-derivative separated in colourless, prismatic needles, which after drying at the ordinary temperature in a vacuum desiccator contained 40.20 per cent. of nitrogen. This percentage is too low for the isodiaziohydroxide, $C_3H_5ON_5$, but corresponds approximately with this substance in combination with one molecular proportion of alcohol ($N=40.46$ per cent.).

This product did not couple with β -naphthol in alcoholic or alkaline solutions, but when dissolved in moderately concentrated nitric acid (2 vols. of acid of D 1.42 + 1 vol. of water) or preferably in cold concentrated sulphuric acid it became converted into a normal diazonium salt which on diluting the strong acid with cold water coupled with alcoholic β -naphthol, the formation of the azo-derivative being hastened by the addition of sodium acetate. This azo-compound, which was evidently 3-methyl-1:2:4-triazole-5-azo- β -naphthol, gave with concentrated sulphuric acid the same bluish-crimson coloration as that developed from the preparation obtained directly from 3-methyl-1:2:4-triazole-5-diazonium nitrate and alcoholic β -naphthol.

Diazotisation of 5-Amino-1:2:4-triazole.

The preparation of 5-amino-1:2:4-triazole from aminoguanidine nitrate followed the same course as that of its 3-methyl derivative, excepting that formic acid was substituted for acetic acid in the acylation. Formylaminoguanidine nitrate was similarly converted into 5-amino-1:2:4-triazole by the action of aqueous sodium carbonate.

Diazotisation in Hydrochloric Acid.—When treated in dilute hydrochloric acid with either sodium or ethyl nitrite, 5-amino-1:2:4-triazole was converted into an unstable diazonium chloride, readily losing nitrogen even in ice-cold solutions to yield 5-chloro-1:2:4-triazole (m. p. 167°).

Diazotisation in Nitric Acid.—Diazotisation of 5-amino-1:2:4-triazole in dilute nitric acid with either sodium or ethyl nitrite gave a stable diazo-solution, from which nitrogen was not evolved in the cold. The solution added to alcoholic β -naphthol (1 mol.) produced a copious precipitate of azo-derivative, which was washed with hot alcohol and crystallised from methyl alcohol, when it separated in acicular, orange crystals melting at 252—255°:

0.0578 gave 0.1284 CO_2 and 0.0222 H_2O . $\text{C}=60.55$; $\text{H}=4.25$.

0.0880 „ 23 c.c. N_2 at 20° and 737 mm. $\text{N}=29.64$.

$\text{C}_{12}\text{H}_9\text{ON}_5$ requires $\text{C}=60.25$; $\text{H}=3.76$; $\text{N}=29.30$ per cent.

1:2:4-Triazole-5-azo- β -naphthol was only sparingly soluble in the ordinary organic media; it gave a bluish-purple coloration with cold concentrated sulphuric acid and dissolved readily in cold dilute aqueous potassium hydroxide to a brownish-red solution.

1:2:4-Triazole-5-azo- β -naphthylamine was prepared by adding a solution of 1:2:4-triazole-5-diazonium nitrate free from excess of nitrous acid to alcoholic β -naphthylamine, when it separated as a dark red precipitate, rendered paler in colour by ammonia. This azo- β -naphthylamine was sparingly soluble in chloroform, benzene, and methyl or ethyl alcohol. When crystallised from ethyl acetate, it separated in dark brownish-red plates melting at 243—245°:

0.1585 gave 0.3527 CO_2 and 0.0672 H_2O . $\text{C}=60.68$; $\text{H}=4.73$.

0.0939 „ 29.1 c.c. N_2 at 19° and 737 mm. $\text{N}=35.28$.

$\text{C}_{12}\text{H}_{10}\text{N}_6$ requires $\text{C}=60.50$; $\text{H}=4.20$; $\text{N}=35.29$ per cent.

1:2:4-Triazole-5-azo- β -naphthylamine developed an intense brownish-yellow coloration with cold concentrated sulphuric acid, becoming red on dilution. In cold dilute aqueous potassium hydroxide, it dissolved readily to a brownish-yellow solution.

5-Diazo-1:2:4-triazole Aurichloride.—Slightly more than the calculated quantity of gold chloride was slowly added to 5-amino-1:2:4-triazole diazotised with sodium nitrite in dilute sulphuric

acid. The aurichloride, which separated in opaque, yellow, granular crystals, was washed repeatedly with cold water and dried on a porous tile in a desiccator over sulphuric acid:

0.2088 gave 0.2265 AgCl. Cl=26.81.

0.2158 „ 33.2 c.c. N₂ at 21° and 756 mm. N=17.72.

0.1786 „ 0.0884 Au. Au=49.45.

C₂HN₅,AuCl₃ requires Cl=26.71; N=17.55; Au=49.46 per cent.

Evidence was obtained of the formation of 1:2:4-triazole-5-*isodiazohydroxide*, although the substance was not isolated in a purified condition. 5-Amino-1:2:4-triazole was diazotised in dilute nitric acid and sodium acetate was added to the solution, when a yellowish-white precipitate was slowly produced which was less crystalline than its homologue from 5-amino-3-methyl-1:2:4-triazole. After washing and drying at the ordinary temperature the substance contained 60.31 per cent. of nitrogen, the calculated proportion for 1:2:4-triazole-5-*isodiazohydroxide* being 61.8. Further experiments on the foregoing *isodiazo*-derivatives are in progress.

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