CLXXI.—*Tetrazoline. Part III.*

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SEVERAL years ago, Ruhemann and Stapleton (Trans., 1899, **75**, 1131 ; 1902, **81**, 261) showed that the properties of tetrazoline,

differ most markedly from those of its *N*-aryl derivatives, which one of us (Ruhemann, Trans., 1889, **55**, 242 ; 1890, **57**, 50) obtained by the action of chloroform and caustic potash on phenylhydrazine and its homologues. Of especial interest is the difference in their behaviour towards methyl iodide. Whilst the action of this iodide on diphenyltetrazoline is normal and yields the methiodide,

it reacts with tetrazoline to form several products, two of which had been isolated and described previously (*loc. cit.*). From the analytical results, the composition $\text{C}_8\text{H}_9\text{N}_4\text{I}_3$ had been deduced for the dark blue compound, and $\text{C}_8\text{H}_7\text{N}_4\text{I}$ for the colourless substance. We now find that the former contains two atoms of hydrogen less, and therefore corresponds to $\text{C}_8\text{H}_7\text{N}_4\text{I}_3$, because it is formed directly from the

colourless iodide by its union with iodine. It has already been pointed out that the compound $C_3H_7N_4I$ cannot be the iodide of methyltetrazoline, $CH \begin{smallmatrix} \text{N} \cdot \text{N}(\text{CH}_3) \\ \text{NH} \text{---} \text{N} \end{smallmatrix} CH, HI$, because its aqueous solution in the presence of an alkali turns violet on exposure to the atmosphere, whereas such a reaction does not take place with tetrazoline; it therefore follows that the substance $C_3H_7N_4I_3$ cannot either be a derivative of methyltetrazoline. On further examination of the compound $C_3H_7N_4I_3$, we have been struck by its resemblance to the periodide of diazobenzene chloride; both crystallising in dark blue prisms, both being very unstable and readily decomposed by water with liberation of iodine. This fact seems to point to analogous formulæ and leads to the view that *a priori* the iodide, $C_3H_7N_4I$, should be represented either by the symbol

which fixes also the constitution of the coloured substance, $C_3H_7N_4I_3$. Either of those formulæ of $C_3H_7N_4I$ would allow of a ready explanation of the fact that alkaline solutions of this compound turn violet on oxidation. This reaction may be expressed thus :

and would be analogous to the formation of indigo from indoxyl.

According to the view which we have advanced concerning the constitution of the iodides $C_3H_7N_4I$ and $C_3H_7N_4I_3$, these compounds would appear as derivatives of a dihydrotetrazine, $\text{CH}_2 \begin{smallmatrix} \text{N}=\text{N} \\ \text{NH} \cdot \text{N} \end{smallmatrix} \text{CH}$, isomeric with bisdiazomethane and tetrazoline. Hantzsch and Silberrad (*Ber.*, 1900, **33**, 58) have shown that bisdiazomethane under the influence of hydrochloric acid undergoes isomeric change to tetrazoline; it may be assumed that this transformation takes place thus :

and is preceded by the formation of the dihydrotetrazine, which we regard as the parent substance of the compounds $C_3H_7N_4I$ and

$C_3H_7N_4I_3$. It would therefore follow that the formation of these derivatives is due to a regressive change of tetrazoline.

This view is supported by the behaviour of aldehydes towards tetrazoline. For instance, benzaldehyde reacts with tetrazoline in the presence of piperidine as a catalytic agent according to the equation:

and yields a compound which must be represented thus:

Its formation necessitates the isomerisation of tetrazoline. We have applied this reaction to a number of aldehydes, and have found that in most cases it takes place readily, yielding similar condensation products in almost theoretical quantities. Especially rapid is the action of salicylaldehyde on tetrazoline, being completed in a few minutes, but *o*-nitrobenzaldehyde condenses very slowly and incompletely with tetrazoline; this fact is probably to be attributed to the steric hindrance exercised by the ortho-position of the nitro-group in the aldehyde. These condensation products dissolve in mineral acids at the ordinary temperature with partial decomposition; nevertheless, their solutions in dilute hydrochloric acid yield with platinic chloride normal salts having the general formula $(C_2H_2N_4 : CHR)_2, H_2PtCl_6$.

The hydrolysis of the compounds which are formed by the action of aldehydes on tetrazoline is completed on digesting their solutions in hydrochloric acid. We have studied this decomposition in the case of benzyldenetetrazoline, $C_2H_2N_4 : CH \cdot C_6H_5$, with the view of ascertaining whether the base, which is thus produced along with benzaldehyde, is the dihydrotetrazine, $CH_2 \begin{smallmatrix} \text{N}=\text{N} \\ \text{NH} \cdot \text{N} \end{smallmatrix} \gg CH$. This inquiry has led to the result that the hydrolysis is accompanied by the isomerisation of the base to tetrazoline. This fact decides also the constitution of the iodides which are formed by the action of methyl iodide on tetrazoline. Since the dihydrotetrazine, $CH_2 \begin{smallmatrix} \text{N}=\text{N} \\ \text{NH} \cdot \text{N} \end{smallmatrix} \gg CH$, appears to exist only in such derivatives which exclude the change into the corresponding compounds of tetrazoline, it follows that the iodide, $C_3H_7N_4I$, has to be represented by symbol I, and that the corresponding formula should be attributed to the additive product, $C_3H_7N_4I_3$.

The fact that the condensation products which tetrazoline forms with aldehydes, although partially hydrolysed by cold dilute hydrochloric acid into tetrazoline and the aldehydes, yield the platinichlorides in a pure state, attracted our attention. For it had been shown (Ruhemann and Stapleton, *loc. cit.*; see also Hantzsch and

Silberrad, *Ber.*, 1900, 33, 83) that tetrazoline forms the sparingly soluble compound, $(C_2H_4N_4)_2PtCl_4$, and, therefore, we had expected that this substance would be precipitated along with the platinum chlorides of the condensation products. This circumstance has rendered it necessary to re-examine the behaviour of platinum chloride towards tetrazoline. We have been surprised to find that the hydrochloride, after crystallisation from alcohol, does not yield the sparingly soluble yellow precipitate, $(C_2H_4N_4)_2PtCl_4$, but orange crystals of the normal platinum chloride, $(C_2H_4N_4)_2H_2PtCl_6$, which are readily soluble in water. After many unsuccessful experiments to obtain, again, the yellow additive product, we have observed that it is formed from tetrazoline hydrochloride before recrystallisation. Although the salt before and after crystallisation has the same melting point (151–152°), yet the different behaviour of the two specimens leads to the view that they correspond to the tautomeric forms

The correctness of this explanation of the phenomenon is supported by the fact that the alcoholic mother liquor of the crystals of tetrazoline hydrochloride yields the yellow platinum compound, and that aqueous solutions of the orange platinum chloride very slowly deposit a solid which we have proved to be the additive product of platinum chloride with tetrazoline.

The results arrived at in the course of the study of tetrazoline have induced us to examine, on similar lines, dimethyltetrazoline,

We have found that this base behaves in many respects differently from tetrazoline. Whilst the latter compound reacts with mercuric chloride to yield the substance $2C_2H_4N_4, 3HgCl_2$ (see Ruhemann and Stapleton, *loc. cit.*), the additive product of dimethyltetrazoline with the metallic chloride has the composition $C_4H_8N_4, HgCl_2$. Aldehydes, which, in the presence of piperidine, so readily condense with tetrazoline, do not react with its dimethyl derivative.

Dimethyltetrazoline, however, yields with platinum chloride, besides the orange normal platinum chloride which is exceedingly soluble in water, a very small quantity of the insoluble yellow additive compound $(C_4H_8N_4)_2PtCl_4$.

The action of methyl iodide also seems to be similar to the behaviour of the iodide towards tetrazoline. We have not yet completed the study of this reaction, but can state already that a substance is formed which, like the iodide, $C_3H_7N_4I_3$, is decomposed by water with the liberation of iodine.

EXPERIMENTAL.

The tetrazoline required for this research has been prepared in the same way as before (Ruhemann and Stapleton, *Trans.*, 1899, **75**, 1132), with the exception that the solution which is produced by the action of ethyl formate on hydrazine hydrate has been freed from the water by warming it in a distilling flask at 40–50° under diminished pressure, and then continuing the heating to 200° under the ordinary pressure. This method recommends itself as being more expedient than the removal of the water from the solution of formylhydrazine in a vacuum at the ordinary temperature. For the purification of the tetrazoline, it is advisable to crystallise the residue which is left after heating from a mixture of chloroform and alcohol instead of adopting Hantzsch and Silberrad's plan (*Ber.*, 1900, **33**, 85) by transforming it into the hydrochloride, and then isolating the base by means of silver oxide. For, on boiling the solution of tetrazoline hydrochloride with the oxide, partial oxidation takes place and the filtrate contains silver; this fact renders it necessary to purify the residue which is left behind on evaporation by dissolving it in alcohol and precipitating the solution with ether.

Action of Platinic Chloride on Tetrazoline.

Ruhemann and Stapleton (*loc. cit.*), in studying the properties of tetrazoline, found that its hydrochloride yields a canary-yellow crystalline precipitate with the composition $(C_2H_4N_4)_2PtCl_4$. The same observation had been made by Hantzsch and Silberrad (*loc. cit.*). On repeating this reaction, we have been surprised to obtain, instead of the sparingly soluble yellow additive product, the normal platinichloride, $(C_2H_4N_4)_2H_2PtCl_6$. This separates in glittering, orange plates which are rather soluble in cold water; therefore concentrated solutions of tetrazoline hydrochloride and platinic chloride are necessary for the preparation of this salt. For analysis, it has been washed with alcohol and dried at 100°.

0.1873 gave 32.8 c.c. moist nitrogen at 22° and 746 mm. N = 19.45.

0.2248, on ignition, left 0.0791 Pt. Pt = 33.69.

$(C_2H_4N_4)_2H_2PtCl_6$ requires N = 19.38; Pt = 33.71 per cent.

This result became even more inexplicable when we ascertained that specimens of tetrazoline hydrochloride from former preparations also did not give the insoluble yellow platinum compound, but the soluble orange platinichloride. Light was thrown on this remarkable phenomenon when we found that tetrazoline hydrochloride, which is formed by evaporating a solution of the base in hydrochloric acid on

the water-bath, immediately yields with platinic chloride the yellow precipitate, identical in properties and composition with the product which we had previously described.

0.2378, on ignition, left 0.0918 Pt. Pt = 38.60.

0.2390 „ „ 0.0920 Pt. Pt = 38.49.

$(C_2H_4N_4)_2, PtCl_4$ requires Pt = 38.58 per cent.

But the hydrochloride, after crystallisation from absolute alcohol, although it melts at the same temperature ($151-152^\circ$) as the specimen obtained by evaporation, forms the orange normal platinichloride; on the other hand, the alcoholic mother liquor from the crystals of the hydrochloride yields the canary-yellow platinum compound. It therefore follows that tetrazoline hydrochloride exists in two isomeric forms which are interchangeable. This conclusion is supported by the fact that the aqueous solution of the orange platinichloride, on standing, very gradually deposits a yellow precipitate of the additive product.

0.0945, on ignition, left 0.0365 Pt. Pt = 38.62.

$(C_2H_4N_4)_2, PtCl_4$ requires Pt = 38.58 per cent.

The platinichloride, $(C_2H_4N_4)_2, H_2PtCl_6$, on heating in a melting-point tube, first darkens, and at about 220° becomes lighter in colour, being transformed most probably into the yellow additive product. This phenomenon is analogous to the behaviour of the platinichloride of pyrazole (see Balbiano, *Ber.*, 1890, **23**, 1107).

Hantzsch and Silberrad (*loc. cit.*) stated that the additive product $(C_2H_4N_4)_2, PtCl_4$ is formed on adding platinic chloride to the aqueous solution of tetrazoline; we find, however, that in this case also the orange normal platinichloride is produced, and we have verified its composition by a platinum determination.

0.2043, on ignition, left 0.0689 Pt. Pt = 33.72.

$(C_2H_4N_4)_2, H_2PtCl_6$ requires Pt = 33.71 per cent.

Action of Methyl Iodide on Tetrazoline.

This reaction furnishes a substance crystallising in dark blue prisms and a colourless compound. On account of the ease with which the coloured product is attacked by water, it is difficult to fix its composition by analysis. From the analytical results, Ruhemann and Stapleton (*Trans.*, 1902, **81**, 261) had deduced the expression $C_3H_9N_4I_3$. We have stated (see p. 1768) that this compound contains two hydrogen atoms less, and therefore is $C_3H_7N_4I_3$. The difference in the percentage compositions of those formulæ are only very slight, as shown in the following table :

$C_3H_9N_4I_3$ requires C = 7.47 ; H = 1.87 ; N = 11.62 ; I = 79.04 per cent.

$C_3H_7N_4I_3$ „ C = 7.50 ; H = 1.46 ; N = 11.67 ; I = 79.37 „

That the blue compound has the formula $C_3H_7N_4I_3$ is proved by the fact that on mixing the colourless substance, $C_3H_7N_4I$, and iodine dissolved in methyl alcohol and allowing the solution to remain in the desiccator for a short time, blue needles separate, which in melting point ($102-103^\circ$) and other properties are identical with the product of the action of methyl iodide on tetrazoline. These compounds, as has been stated (see p. 1768), should be represented thus :

Action of Aldehydes on Tetrazoline.

Benzylidenetetrazoline, $C_2H_2N_4 \cdot CH \cdot C_6H_5$.

This compound is formed by adding a few drops of piperidine to the mixture of tetrazoline (2 grams) dissolved in absolute alcohol and benzaldehyde (2.6 grams). In the course of a few hours, the whole sets to a semi-solid mass of crystals, which are sparingly soluble in carbon disulphide, readily so, however, in chloroform or alcohol, and which crystallise from the latter solvent in colourless needles melting at 171° .

0.2004 gave 0.4595 CO_2 and 0.0857 H_2O . C = 62.53 ; H = 4.74.

0.2024 „ 0.4659 CO_2 „ 0.0838 H_2O . C = 62.77 ; H = 4.60.

0.1776 „ 49.8 c.c. moist nitrogen at 17° and 756 mm. N = 32.35.

$C_9H_8N_4$ requires C = 62.79 ; H = 4.65 ; N = 32.55 per cent.

Benzylidenetetrazoline readily dissolves in dilute hydrochloric acid with partial hydrolysis, and the solution yields with platinic chloride a yellow platinichloride which is insoluble in water.

0.1840 gave 25 c.c. moist nitrogen at 23° and 743 mm. N = 14.95.

0.1371, on ignition, left 0.0356 Pt. Pt = 25.96.

$(C_9H_8N_4)_2, H_2PtCl_6$ requires N = 14.85 ; Pt = 25.85 per cent.

o-Nitrobenzylidenetetrazoline, $C_2H_2N_4 \cdot CH \cdot C_6H_4 \cdot NO_2$.

On adding piperidine to the alcoholic solution of the mixture of tetrazoline (1 gram) and *o*-nitrobenzaldehyde (1.8 grams), no solid deposits until it has been standing five to six days, and the separation, which is very small, ceases after about a week. The condensation product readily dissolves in boiling alcohol, and, on cooling, crystallises in colourless, stout prisms which melt at $121-122^\circ$.

0.1454 gave 40 c.c. moist nitrogen at 20° and 742 mm. $N = 32.22$.
 $C_9H_7O_2N_5$ requires $N = 32.25$ per cent.

The action of piperidine on a mixture of tetrazoline (1 gram) and *m*-nitrobenzaldehyde (1.8 grams) dissolved in alcohol takes place rapidly, the solution setting to a magma of crystals on standing overnight. The substance is sparingly soluble in chloroform; it dissolves with difficulty in boiling alcohol, and crystallises from this solution in colourless needles which melt at 225°.

0.2005 gave 0.3645 CO_2 and 0.0574 H_2O . $C = 49.58$; $H = 3.18$.
 0.1788 „ 50.2 c.c. moist nitrogen at 18° and 754 mm. $N = 32.15$.
 $C_9H_7O_2N_5$ requires $C = 49.77$; $H = 3.22$; $N = 32.25$ per cent.

This compound is formed by adding piperidine (5—6 drops) to the mixture of *p*-nitrobenzaldehyde (1.8 grams) and tetrazoline (1 gram) dissolved in alcohol. The reaction is complete after a few hours, and the yield of the solid which separates is almost theoretical. The substance is sparingly soluble in chloroform, but dissolves in a large quantity of boiling alcohol, and, on cooling, crystallises in slightly coloured needles which melt at 245°.

0.2018 gave 0.3673 CO_2 and 0.0586 H_2O . $C = 49.63$; $H = 3.22$.
 0.1889 „ 53.8 c.c. moist nitrogen at 20° and 754 mm. $N = 32.30$.
 $C_9H_7O_2N_5$ requires $C = 49.77$; $H = 3.22$; $N = 32.25$ per cent.

The platinichloride is precipitated in the form of light yellow needles on adding platinic chloride to the solution of the *p*-nitrobenzylidenetetrazoline in dilute hydrochloric acid. For analysis, it is washed with water, then with boiling alcohol, and dried on the water-bath.

0.1712 gave 24.8 c.c. moist nitrogen at 18° and 764.5 mm. $N = 16.82$.
 0.2318, on ignition, left 0.0535 Pt. $Pt = 23.08$.
 $(C_9H_7O_2N_5)_2, H_2PtCl_6$ requires $N = 16.60$; $Pt = 23.05$ per cent.

In the presence of piperidine, salicylaldehyde (1.5 grams) readily reacts with tetrazoline (1 gram) dissolved in alcohol, the whole setting to a semi-solid mass of crystals in the course of a few minutes. The compound freely dissolves in hot chloroform or alcohol, and crystallises

from its alcoholic solution in bunches of colourless needles which melt at 204°.

0·2020 gave 0·4257 CO₂ and 0·0775 H₂O. C=57·47 ; H=4·26.

0·1752 „ 45·4 c.c. moist nitrogen at 20° and 765·5 mm. N=29·86.

C₉H₈ON₄ requires C=57·44 ; H=4·15 ; N=29·79 per cent.

o-Hydroxybenzylidenetetrazoline readily dissolves in dilute hydrochloric acid, as well as in caustic potash and sodium carbonate, the acid solution being colourless, the alkaline yellow. On adding a little ferric chloride to the alcoholic solution, a purple coloration is produced which, by an excess of the chloride, is changed to yellowish-green.

The action of piperidine on the alcoholic solution of the mixture of *p*-hydroxybenzaldehyde and tetrazoline is slower than in the former case, and requires two to three days for completion. The substance is only sparingly soluble in cold alcohol, readily, however, when hot, and, on cooling, crystallises in yellow needles which melt at 240°.

0·2009 gave 0·4210 CO₂ and 0·0798 H₂O. C=57·15 ; H=4·41.

0·1786 „ 46·4 c.c. moist nitrogen at 21° and 765·5 mm. N=29·77.

C₉H₈ON₄ requires C=57·44 ; H=4·15 ; N=29·79 per cent.

The compound resembles in its properties the former substance, with the exception that its alcoholic solution gives a yellow coloration with ferric chloride.

The alcoholic solution of the mixture of tetrazoline (1 gram) and cinnamaldehyde (1·6 grams), when treated with a few drops of piperidine, begins to deposit a solid after a few hours, and the reaction is complete in two days. The substance which is formed is insoluble in ether or carbon disulphide, but dissolves readily in chloroform or boiling alcohol, and separates from the alcoholic solution in colourless needles which melt at 187°.

0·2008 gave 0·4904 CO₂ and 0·0913 H₂O. C=66·60 ; H=5·05.

0·1649 „ 40·8 c.c. moist nitrogen at 20° and 768 mm. N=28·04.

C₁₁H₁₀N₄ requires C=66·67 ; H=5·05 ; N=28·28 per cent.

Piperonaldehyde (1·8 grams) and tetrazoline (1 gram) react on adding piperidine (5 drops) to the alcoholic solution of the mixture.

The solid which separates is collected after two days ; it dissolves with difficulty in boiling alcohol and, on cooling, crystallises in colourless pyramids which melt at 185—186°.

0.2000 gave 0.4075 CO₂ and 0.0650 H₂O. C = 55.56 ; H = 3.61.

0.1736 „ 39 c.c. moist nitrogen at 20° and 765.5 mm. N = 25.89.

C₁₀H₈O₂N₄ requires C = 55.55 ; H = 3.70 ; N = 25.92 per cent.

This compound is produced from tetrazoline (1 gram) and vanillin (1.8 grams) under the influence of piperidine, and its formation is completed if the alcoholic solution of the mixture has been left for four days. The substance which separates is sparingly soluble in chloroform ; it dissolves with difficulty in boiling alcohol, and crystallises from the alcoholic solution in slightly pink prisms melting at 215—216°.

0.2002 gave 0.4035 CO₂ and 0.0838 H₂O. C = 54.96 ; H = 4.65.

0.1766 „ 39.6 c.c. moist nitrogen at 21° and 767.5 mm. N = 25.76

C₁₀H₁₀O₂N₄ requires C = 55.04 ; H = 4.59 ; N = 25.68 per cent.

The alcoholic solution of this compound yields with ferric chloride a yellowish-green coloration.

The alcoholic solutions of tetrazoline (1 gram) and protocatechuic aldehyde (1.7 grams) are mixed, and piperidine (6 drops) added, when in the course of a few hours the whole sets to a semi-solid mass of crystals, which are sparingly soluble in boiling alcohol, dissolve with difficulty in glacial acetic acid, and crystallise from either solution in groups of yellow needles ; these begin to blacken at about 250° and melt at 259° with decomposition.

0.1913 gave 0.3702 CO₂ and 0.0716 H₂O. C = 52.78 ; H = 4.15.

0.1726 „ 42.4 c.c. moist nitrogen at 20° and 740.5 mm. N = 27.36.

C₉H₈O₂N₄ requires C = 52.94 ; H = 3.92 ; N = 27.45 per cent.

This substance dissolves as well in dilute hydrochloric acid as in sodium carbonate, and the solutions are respectively colourless and deep yellow. The alcoholic solution gives with ferric chloride a deep green coloration.

4-Dimethylaminobenzylidenetetrazoline, $C_2H_2N_4 \cdot \overset{(1)}{CH} \cdot C_6H_4 \cdot \overset{(4)}{N}(CH_3)_2$.

This substance is deposited from the alcoholic solution of the mixture of tetrazoline (1 gram), *p*-dimethylaminobenzaldehyde (1·8 grams), and piperidine (5—6 drops), the separation being complete after five days ; it readily dissolves in boiling alcohol, and, on cooling, crystallises in yellow prisms which melt at 194—195°.

0·2002 gave 0·4494 CO_2 and 0·1112 H_2O . C = 61·22 ; H = 6·12.

0·1447 „ 40·9 c.c. moist nitrogen at 20° and 765 mm. N = 32·54.

$C_{11}H_{13}N_5$ requires C = 61·39 ; H = 6·05 ; N = 32·55 per cent.

Furfurylidenetetrazoline, $C_2H_2N_4 \cdot CH \cdot C_4H_3O$.

The condensation of tetrazoline (1 gram) with furfuraldehyde (1·2 grams) takes place readily on adding a few drops of piperidine to the alcoholic solution of the mixture. The solid which is formed on standing overnight is insoluble in carbon disulphide ; it dissolves with difficulty in chloroform, readily, however, in boiling alcohol and, on cooling, crystallises in light brown needles which melt at 207°.

0·2022 gave 0·3835 CO_2 and 0·0678 H_2O . C = 51·72 ; H = 3·72.

0·1574 „ 47·8 c.c. moist nitrogen at 23° and 769 mm. N = 34·61.

$C_7H_6ON_4$ requires C = 51·85 ; H = 3·70 ; N = 34·56 per cent.

The platinichloride is precipitated in the form of yellow needles on mixing the solution of furfurylidenetetrazoline in dilute hydrochloric acid with platinic chloride.

0·1910 gave 26·2 c.c. moist nitrogen at 21° and 743·5 mm. N = 15·25.

0·1533, on ignition, left 0·0406 Pt. Pt = 26·48.

$(C_7H_6ON_4)_2 \cdot H_2PtCl_6$ requires N = 15·26 ; Pt = 26·55 per cent.

Hydrolysis of Benzylidenetetrazoline.

The hydrolysis takes place on boiling the solution of benzylidenetetrazoline in dilute hydrochloric acid for 15—20 minutes. The liquid, when cold, is freed from benzaldehyde by extraction with ether, and the aqueous layer evaporated on the water-bath. The solid which is left crystallises from alcohol in transparent leaflets which, in melting point (151—152°) and other properties, are identical with tetrazoline hydrochloride. This identity has been further established by the preparation and analysis of the platinichloride.

0·2352, on ignition, left 0·0797 Pt. Pt = 33·88.

$(C_2H_4N_4)_2 \cdot H_2PtCl_6$ requires Pt = 33·71 per cent.

Dimethyltetrazoline.

We have prepared this substance by heating mono-acetylhydrazine (see Pellizari, *Atti R. Accad. Lincei*, 1899, [v], 8, 327). We have stated before (p. 1771) that it differs in some of its properties from tetrazoline.

Curtius and Lang (*J. pr. Chem.*, 1888, [ii], 38, 552), in the course of their researches on ethyl diazoacetate, obtained three isomeric compounds which they regarded as tripolymerides of diazomethane, $C_3H_6N_6$. Since Hantzsch and Silberrad (*Ber.*, 1900, 33, 58) have shown that two of these substances have the formula $C_2H_4N_4$ and are bisdiazomethane and tetrazoline, the composition, $C_3H_6N_6, 3HgCl_2$, which Curtius and Lang gave to the additive product of their so-called "trimethintriazimide" with mercuric chloride, cannot be correct. This conclusion follows already from the comparison of the percentage of nitrogen which they found—10·52—with the value—8·95—required for their formula. Ruhemann and Stapleton (*Trans.*, 1899, 75, 1133) have found that the composition of the additive product which is formed from tetrazoline and mercuric chloride is $2C_2H_4N_4, 3HgCl_2$, and have deduced it from two estimations of the mercury.* We have now verified this formula by the following nitrogen determination.

0·2002 gave 19·5 c.c. moist nitrogen at 17° and 765·5 mm. $N = 11·39$.
 $2C_2H_4N_4, 3HgCl_2$ requires $N = 11·41$ per cent.

Dimethyltetrazoline, however, yields the compound $C_4H_8N_4, HgCl_2$. This is formed as a white, crystalline solid, which is soluble in boiling water, on mixing aqueous solutions of tetrazoline and mercuric chloride; the white precipitate which is first produced dissolves, but becomes permanent, if an excess of the metallic chloride is added.

0·2065 gave 25·8 c.c. moist nitrogen at 17° and 762·5 mm. $N = 14·54$.
 0·3133 gave 0·1882 HgS. $Hg = 51·80$.
 $C_4H_8N_4, HgCl_2$ requires $N = 14·62$; $Hg = 52·22$ per cent.

Dimethyltetrazoline hydrochloride yields with platinic chloride the normal platinichloride. On account of the ease with which this salt dissolves in water, it is necessary to use solutions of the reagents in absolute alcohol, and to proceed as follows. Dimethyltetrazoline is dissolved in alcohol and mixed with alcoholic solutions of hydrogen chloride and platinic chloride, when, on cooling, the platinichloride separates in orange prisms which are scarcely soluble in cold alcohol and decompose at 256°.

* Owing to a misprint, HgI was indicated in the first record of the determination, instead of HgS .

0.1930 gave 29.4 c.c. moist nitrogen at 17° and 761.5 mm. $N = 17.70$.

0.2213, on ignition, left 0.0684 Pt. $Pt = 30.90$.

$(C_4H_8N_4)_2, H_2PtCl_6$ requires $N = 17.67$; $Pt = 30.73$ per cent.

The aqueous solution of the platinichloride, when left for a long time, deposits traces of a yellow solid. This substance, no doubt, is identical with the yellow prisms which are formed if the solution of dimethyltetrazoline in hydrochloric acid is evaporated on the water-bath and platinic chloride added to the aqueous solution of the residue. The yellow crystals which gradually separate are insoluble in water; but the yield is very small.

0.1260, on ignition, left 0.0437 Pt. $Pt = 34.68$.

$(C_4H_8N_4)_2, PtCl_4$ requires $Pt = 34.73$ per cent.

The behaviour of aldehydes towards tetrazoline has induced us to examine whether these compounds condense with dimethyltetrazoline in a similar manner. Our hope, however, that this base would be isomerised and then react with aldehydes, thus:

has not been realised. No reaction took place, even although the alcoholic solution of the mixture of the base, benzaldehyde and piperidine, was left for two weeks. But the isomerisation of dimethyltetrazoline seems to be effected by methyl iodide, for on heating the base in methyl-alcoholic solution with an excess of methyl iodide in a closed tube at 100° for five to six hours, an inflammable gas (probably methyl ether) is produced, and a brown solution is formed. If the latter is concentrated on the water-bath, a solid separates which dissolves in boiling chloroform and, on cooling, crystallises in brown needles melting at 101°. We have not yet completed the study of this compound, but have already ascertained that its behaviour is similar to that of the blue substance, $C_3H_7N_4I_3$, which is formed from tetrazoline, since it is decomposed by water with the liberation of iodine.

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