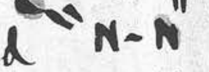
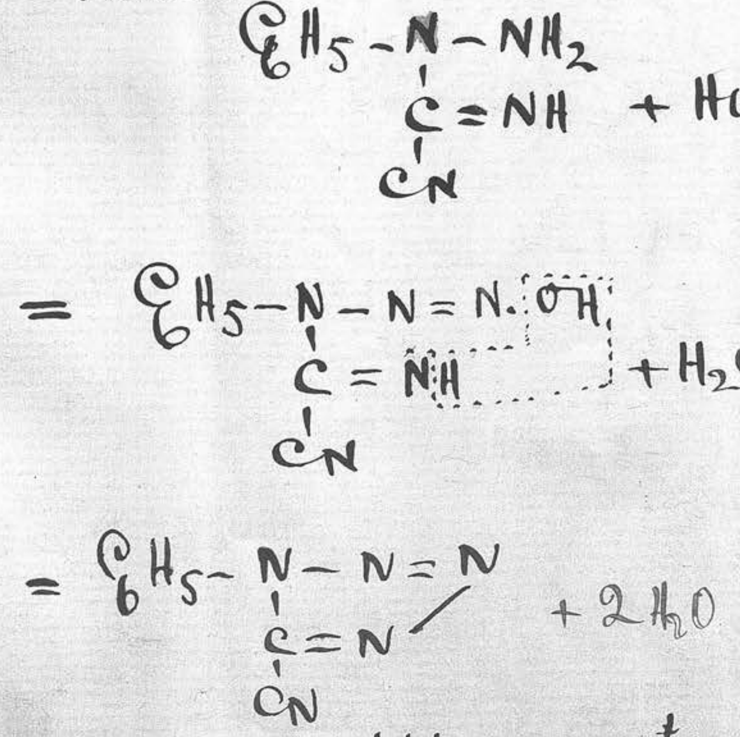
Azol compounds which contain four atoms of Nitrogen in the five-membered Azol-ring have become known and been investigated only recently. They are the so-called Tetrazols.

By allowing Nitrous Acid to act on Dicyanphenyl-Hydrazin Bladin(x) obtained a compound in which the formation of the Tetrazol ring  had taken place. This body he called "Phenyl-cyan-Tetrazol". The reaction is represented as follows: At first the Amido-group is diazotised; then a molecule of water (or acid resp.) splits off, the free bonds of the end Nitrogen atoms join together, and form the closed 5-membered ring: Thus:



$$\begin{array}{l} C_6H_5-N-NH_2 \\ \qquad\quad | \\ \qquad\quad C=NH \quad + HONO \\ \qquad\quad | \\ \qquad\quad CN \end{array}$$

$$= \begin{array}{l} C_6H_5-N-N=N.OH \\ \qquad\quad | \\ \qquad\quad C=NH \qquad\qquad + H_2O \\ \qquad\quad | \\ \qquad\quad CN \end{array}$$

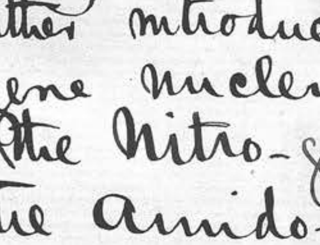
$$= \begin{array}{l} C_6H_5-N-N=N \\ \qquad\quad | \qquad\quad / \\ \qquad\quad C=N \qquad + 2H_2O \\ \qquad\quad | \\ \qquad\quad CN \end{array}$$

(x) Berichte 18, 666a + 1544a
+ " 18 II 2907b.

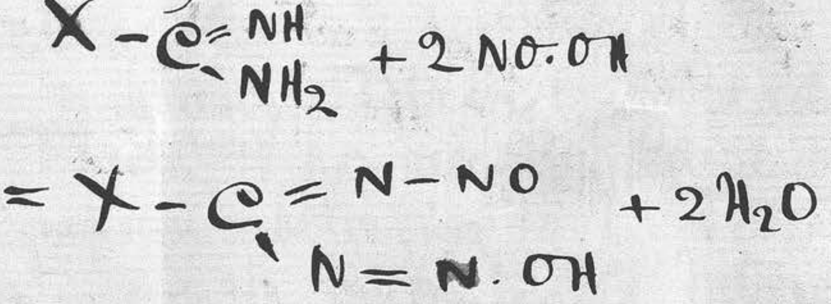
By the conversion of the CN-group into Carbonyl COOH, and ~~the~~ heating the so-obtained ~~Phyn~~ Phenyl-Tetrazyl-Carbone acid to 150°C he obtained Phenyl-Tetrazo

For the sake of avoiding circumscriptio we shall denote a radical which replaces the H of attached to the Carbon atom of the ring by prefixing a small o, that which replaces the H. of the Nitrogen atom by a small ~~n~~ n. The last-named compound is, thus denoted-n-Phenyl-Tetrazol.

Bladin further introduced a Nitro-group into the Benzene nucleus of the above compound; the Nitro-group was then reduced to the amido-group, and the amido-phenyl radical replaced by Hydrogen by means of Potassic Per-manganate in alkaline solution. The resulting compound, which is the "Mother-substance" of all the Tetrazyl derivatives, is Tetrazol:



Lossen(x) has recently investigated another class of Tetrazyl derivatives where the non-acidic or C-Hydrogen is replaced by radicals. He shewed that Nitrous acid acts on the Amidines, whose Amid- and Imid-Hydrogens are not replaced by Alkyls, in such a manner that the Amido-group is diazotised, and the Imid-group at the same time converted into a Nitrosamine group. The compounds thus obtained have the common formula $X-CN_4O_2H$, and are acids, dioxy-Tetrazolic acids:



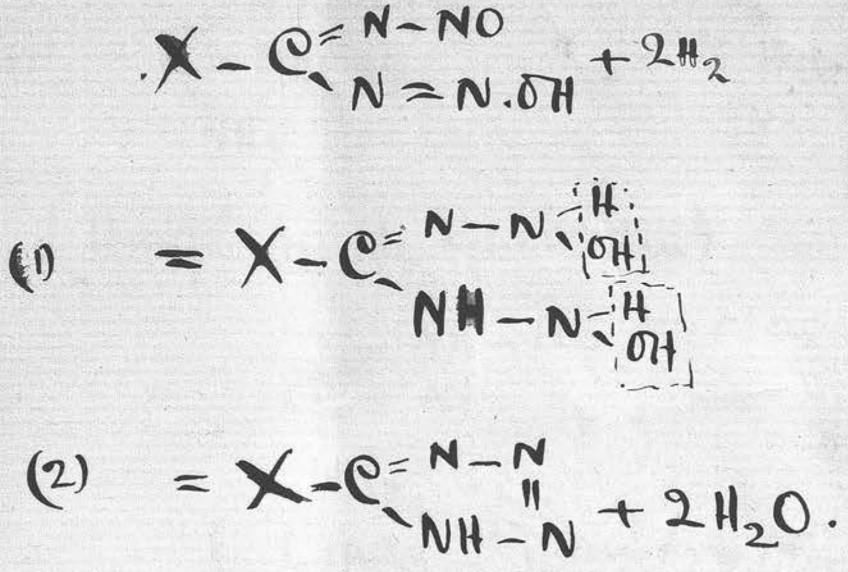
$$X-C\begin{array}{l}=NH\\ -NH_2\end{array} + 2NO.OH$$

$$= X-C\begin{array}{l}=N-NO\\ -N=N.OH\end{array} + 2H_2O$$

Sodium-Amalgam reduces this class of bodies with the formation of two new classes of Acids, by the loss of one and two atoms of Oxygen respectively. These two new classes of acids have the empirical formulae $X-CN_4OH$, and $X-CN_4H$ resp. — Oxytetrazolic and Tetrazolic acids.

The formation of Oxy-tetrazolic acid has not been explained constitutionally but for Tetrazolic acid he gives the following explanation, which is evidently the correct one, though the reaction is a remarkable one:

(x) Annalen 263, 73/77.

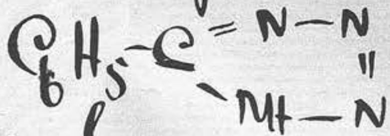


$$X-C\begin{array}{l}=N-NO\\ \diagdown N=N.OH\end{array}+2H_2$$

$$(1)\quad =X-C\begin{array}{l}=N-N\begin{array}{l}\boxed{H}\\ \boxed{OH}\end{array}\\ \diagdown NH-N\begin{array}{l}\boxed{H}\\ \boxed{OH}\end{array}\end{array}$$

$$(2)\quad =X-C\begin{array}{l}=N-N\\ \diagdown NH-N\end{array}+2H_2O.$$

Thus in the case of Benzenyl-dioxytetrazolic acid, the acid ~~will~~



$$C_6H_5-C\begin{array}{l}=N-N\\ \diagdown NH-N\end{array}$$

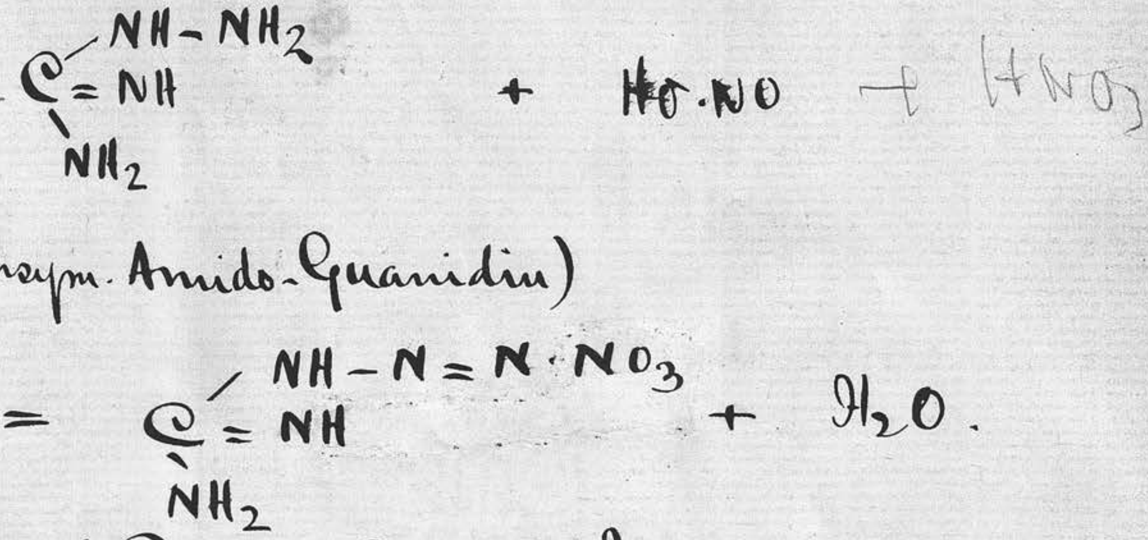
results, that is o-Phenyl-Tetrazolic acid, which is isomeric with the n. Phenyl-Tetrazol of Bladin.(*)

Thiele(**) has recently described a new Compound belonging to the Tetrazols. ~~He~~ On acting with concentrated Nitric acid on Guanidin he shewed that Nitro-Guanidin and not Nitroso-Guanidin (according to Jousselin) is obtained. This nitrobody he reduced with Zn-dust and acetic acid to Amido-Guanidin, which in its turn he diazotised and isolated the Diazo-Guanidin nitrate. By the action of Acetates or Carbonates on this last body Nitric acid is split off, and the end Nitrogens combine forming the closed Tetrazol ring:

(*) Note: One could also distinguish these two classes of Isomers, by affixing the word "acid" after those whose o-Hydrogen has been replaced by Radicals, the remaining n-Hydrogen being acidic.

(**) Añalen 270 Bd. pg 1-62.

(1)



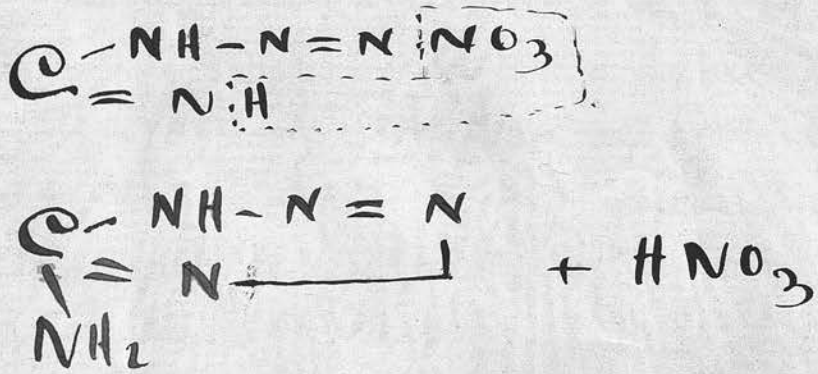
$$C\begin{cases}-NH-NH_2\\=NH\\-NH_2\end{cases} + HO\cdot NO + HNO_3$$

(Unsym. Amido-Guanidin)

$$= C\begin{cases}-NH-N=N\cdot NO_3\\=NH\\-NH_2\end{cases} + H_2O.$$

(Diazo- Guanidin Nitrate)

(2)



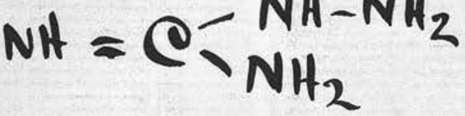
$$C\begin{cases}-NH-N=N\,NO_3\\=N\,H\end{cases}$$

$$= C\begin{cases}-NH-N=N\\=N\text{———}\rfloor\\-NH_2\end{cases} + HNO_3$$

This Compound Thiele called <u>Amido-Tetrazolic acid</u>. It is o-Amido-Tetrazol, and has the group NH_2 in the place of C_6H_5 in Losten's o-Phenyl Tetrazol.

Constitution of Amido-Tetrazolic Acid

Thiele assigns to Amido-Guanidin the unsymmetrical formula



$$NH=C\begin{matrix}-NH-NH_2\\-NH_2\end{matrix}$$

on the following grounds:

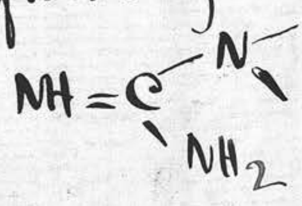
By hydrolitic decomposition Amido-Guanidin splits into Carbonic acid, Ammonia and Hydrazin, which points to the fact that it is a Substituted Hydrazin.

One atom of Hydrogen is replaceable by Cu, Amido-Guanidin-Copper salts resulting for instance Amido-Guanidin Copper nitrate: $[(CH_5N_4)_2Cu](NO_3H)_2$, This property ~~the~~ Amido-Guanidin has in common with Biguanid, dicyandiamidin and Biuret, all of which contain ~~the~~ an imid-group attached to the rest $-C-NH\cdot NH_2$, respectively $-CO-NH_2$.

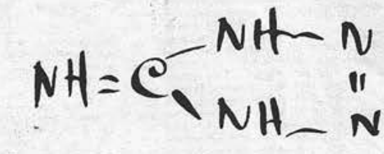
As Substituted Hydrazin Amido-Guanidin combines with aldehydes, by the loss of a molecule of water.

By diazotising Amido-Guanidin, a diazo-derivative is obtained which must contain the open chain $NH-N=N$, because "Stickwassestof" N_3H is given off under the action of NaOH.

If Amido-Guanidin has the unsymmetrical formula $NH=C\begin{matrix}\diagup NH-NH_2\\ \diagdown NH_2\end{matrix}$, then the body resulting from its Nitric acid Salt by the loss of $H \cdot NO_3$ under the action of Acetates or Carbonates, can be constituted according to one of the following three ways:



I



II

III

From a body of the formula I, one would expect ~~NH_3~~ N_3H to be easily split off; but amido-tetrazolic acid in no way gives this decomposition-product. It must also shew strongly basic properties, as it would belong to the Amidines — Amido-tetrazolic acid however is a strong acid, and shews only weak basic properties.

It has been shewn by Gerlach that Amido-Guanidin and its derivatives, when treated according to Kjeldahl for determining their percentage of Nitrogen, yield in the form of Ammonia only those atoms of Nitrogen which are not directly bound to each other in the molecule. Amido-tetrazolic acid only yields one-fifth of its Nitrogen in the form of Ammonia; four-fifths go off as Nitrogen gas

Hence formula I does not hold for Amido-Amido-Tetrazolic acid.

By the action of Nitrous acid on Amido-Tetrazolic acid, a Substance is obtained which explodes even in moderately concentrated Solution at 0°C. This Solution also gives azo-derivatives with amines e.g. with Methyl-Aniline and β-Naphthyl-Amine, like the Aromatic diazo-bodies.

Accordingly formula II is also excluded because Nitrous acid would convert a body of that constitution into a Nitro-, and not into a Diazo-body.

Hence only formula III is tenable for Amido-Tetrazolic acid:

Theoretical Part.

The object of the present research, which I undertook at the suggestion of Herrn Dr. Thille, Privat Docent at the University of Halle, whose kind and valuable advice I here gratefully acknowledge, was the investigation of the derivatives of Amido-Tetrazolic acid. Thiele had already diazotised this compound, and found that the solution so obtained explodes in solution at 0°C, unless ~~largely~~ very dilute. To prove the existence of diazo-tetrazol in the Sol^{n}. he made use of the action of amines on diazo-bodies, and found that β-Naphthylamine produces a magnificent rose-red azo-derivative, whose composition as a derivative of diazo-tetrazol was confirmed by analysis.

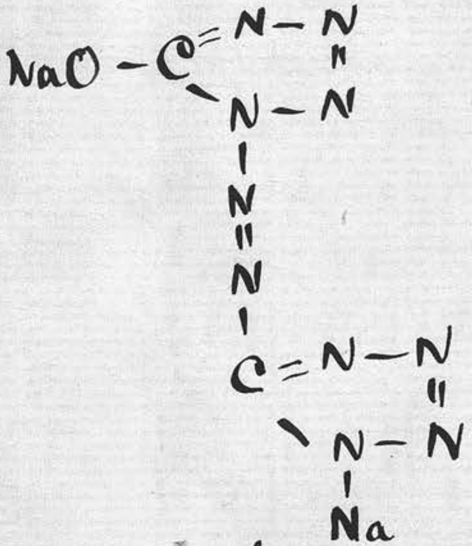
The conversion of this diazo-tetrazol into oxy-tetrazol was the first task I set myself. On boiling the Sol^{n}. of diazo-tetrazol a remarkable result was got. Instead of exchanging the group $-N=N\cdot OH$ for OH as in the case of diazo-benzol, diazo-tetrazol decomposes almost quantitatively into Cyanogen gas and Nitrogen. This entire breaking up of the ring is all the more remarkable, because the Tetrazol ring has shewn itself to be very stable and not easily attacked by reagents.

For instance in the conversion of amido-Phenyl-Tetrazol into Tetrazol, Bladin subjected the former to the action of Potassic Permanganate in alkaline Soln.; and in converting diazo-tetrazol into Tetrazol-Hydrazin (see below), I acted with ~~the~~ Stannous Chloride and Hydrochloric acid on diazo-tetrazol. And yet diazo-tetrazol decomposes even in the cold on standing, into CN gas and Nitrogen. In alkaline solution however Diazo-Tetrazol is quite stable, and can even be ~~boiled~~ heated to boiling without decomposing — its Sodium salt, though exceedingly difficult to get perfectly pure, can even be isolated. That the acid of this Sodium salt is identical with Diazo-Tetrazol is confirmed by the fact that β-Naphthyl-amine gives with it in Acetic acid solution the same rose-red azo-derivative, as with the free diazo-tetrazol in solution.

Oxyazo-Tetrazol:

On boiling a solution of Sodium diazo-tetrazolate ~~in~~ and passing a current of Carbonic acid through, or under certain conditions by evaporation ~~the~~ alone, Sodium diazo-tetrazolate is converted into a remarkably explosive compound of the composition $C_2N_{10}ONa_2$. Comparing the class of compounds under consideration with their analogues in the Aromatic Series, it seems evident that this body belongs to the

Oxy-azo-derivative of the diazo-compounds, having the following constitution:



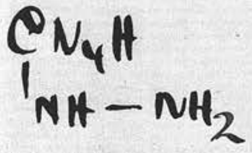
Oxy-azo-benzol results when diazo-benzol acts on Phenol, as a rule in alkaline Solution. In this way the formation of oxy-azo-tetrazol according to the Second of the above methods can be explained: Thus on boiling the Solution of Sodium-diazo-tetrazolate, part is converted into Sodium-oxy-tetrazolate. This oxy-tetrazolate then reacts with more diazo-tetrazolate forming oxy-azo-tetrazolate. — Oxy-azo-benzol is also formed when diazo-benzol is warmed with $BaCO_3$. This ~~explains~~ is analogous to the first of the above method of formation of the oxy-azo-tetrazolate.

When Sulphuretted Hydrogen is led through a Solution of Sodium-oxy-azo-tetrazolate Sulphur is precipitated after Some time, & the yellow colour of the Solution disappears. Stannous Chloride decolorises the Solution at once. In both cases a reduction evidently has taken place, as is the case with

Oxy-azo-benzol.
Its intense yellow colour too agrees with that of other azo-bodies.
The Barium Salt, $C_2N_{10}OBa$, is obtained in a similar manner as the Na-salt, when the solution of Diazo-Tetrazol is neutralised with $Ba(OH)_2$ and evaporated.

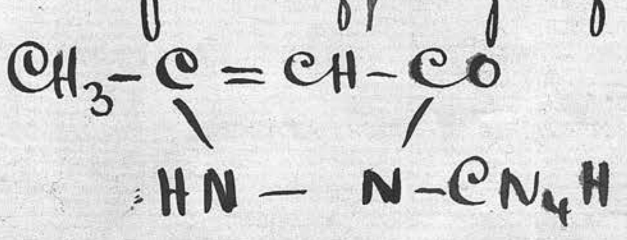
Tetrazyl-Hydrazin.

When the solution of diazo-tetrazol is at once reduced with Stannous Chloride & Hydrochloric acid, a body is obtained with the composition CN_6H_4 having all the properties of a hydrazin. It combines with aldehyds to form insoluble compounds; it reduces Fehling's solution in the cold; and is oxidised to a violet-reddish body in solution by the action of the air. By the action of Aceto-acetic ester, tetrazyl-Pyrazolone is obtained from it, $C_5N_6H_6O$. Hence the constitution of Tetrazyl-Hydrazin is:



$$\begin{array}{l} CN_4H \\ | \\ NH-NH_2 \end{array}$$

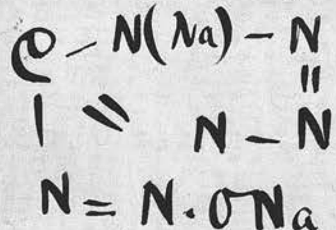
And that of Tetrazyl-Pyrazolone:



Tetrazyl Hydrazin suffers no decomposition into Hydrazin itself, on boiling with concentrated solutions of either acids or alkalies. This fact shews also that it is a primary Hydrazin.

Experimental Part.

I. Sodium-diazo-tetrazolate.



The great solubility of this compound in water, and its insolubility in alcohol and other ordinary solvents makes the diazotising in acid solution (mineral acid) impracticable, because it cannot be separated from the mineral salt present. Diazotising in acetic acid solution with nitrite makes the reaction take a different direction. To overcome these difficulties a solution of ~~t~~ Nitrous acid ~~dissolved~~ in Chloroform was used to diazotise the Amido-Tetrazolic acid.

20.6 gr. Amido-tetrazolic acid is dissolved in hot water. This is added in portions(*) to about a litre of water kept cool by ice. Into the ice-cold solution the solution of Nitrous acid is slowly run under stirring. At the

---

(*) If the whole of the hot Amido-Tetrazolic acid is at once ~~added~~ to the ice-cold water, it would separate out again.

At the end of the operation the volume should be about 2 litres, a little less than ~~abt~~ half a Kgr. ice having been added during the operation. The end point is ascertained by placing a drop of the liquid time after time on paper soaked in Starch and Potassium Iodide. The Solution is now filtered from the Chloro=form into a concentrated Solution of the Calculated quantity of NaOH. Here the liquid assumes an intense yellow Colour. The liquid is next evaporated to about 100 cc. under reduced pressure at a temperature of about 70° – 80°, while a current of air (freed from Carbonic acid) is led through to prevent bumping.

When the nitrous acid has not been added in excess, and the right quantity of alkali added, a yellow Salt crystallises out which will be described later on. – To the filtered liquid absolute Alkohol is now slowly added, when ~~a~~ the Na-diazo-tetrazolate Separates out as oil which soon becomes crystalline on adding more alcohol. The slightly yellowish Salt ~~thus~~ obtained is next dissolved in the Smallest quantity of water, and this time absolute alcohol dropped in till the Salt just begins to fall out. On Standing the greater part crystallises out ~~in~~ in colourless needles.

I have only once Succeeded in obtaining it perfectly pure. As a rule it contains traces of Nitrite and of some body richer in Carbon.

I 0.0888 gr. yielded 40.6 cc N at
17.4° & 762 m.m. Pressure.

0.3040 gr yielded 0.2720 gr. Na_2SO_4
equal to 0.088112 Na.

Calculated for $CN_4Na.N_2ONa$		Found.
N	53.76	53.08
Na	29.11	28.99

In order to prove beyond doubt that this Sodium Salt is the Salt of diazo-tetrazol, a portion of the Na-Salt was dissolved in water and a solution of β-Naphthyl-amine added. The rose-red precipitate was filtered off and recrystallised from hot alkohol.

I 0.1239 gr gave 43.7 cc N at
15.2° and 761 mm Pressure.

Calculated for $CN_4H-N_2-C_{10}H_6NH_2$		Found
N	41.0	41.29

The melting Point also agrees with the

compound obtained by the action of β-Naphthyl-amine on the Solution of diazo-tetrazol, being 181°C. — Sodium-diazo-tetrazolate reacts strongly alkaline. When heated it ~~detonates~~ explodes with a slight report; dropped into strong Sulphuric acid it takes ~~fire~~ fire.

Decomposition of Diazo-Tetrazol.

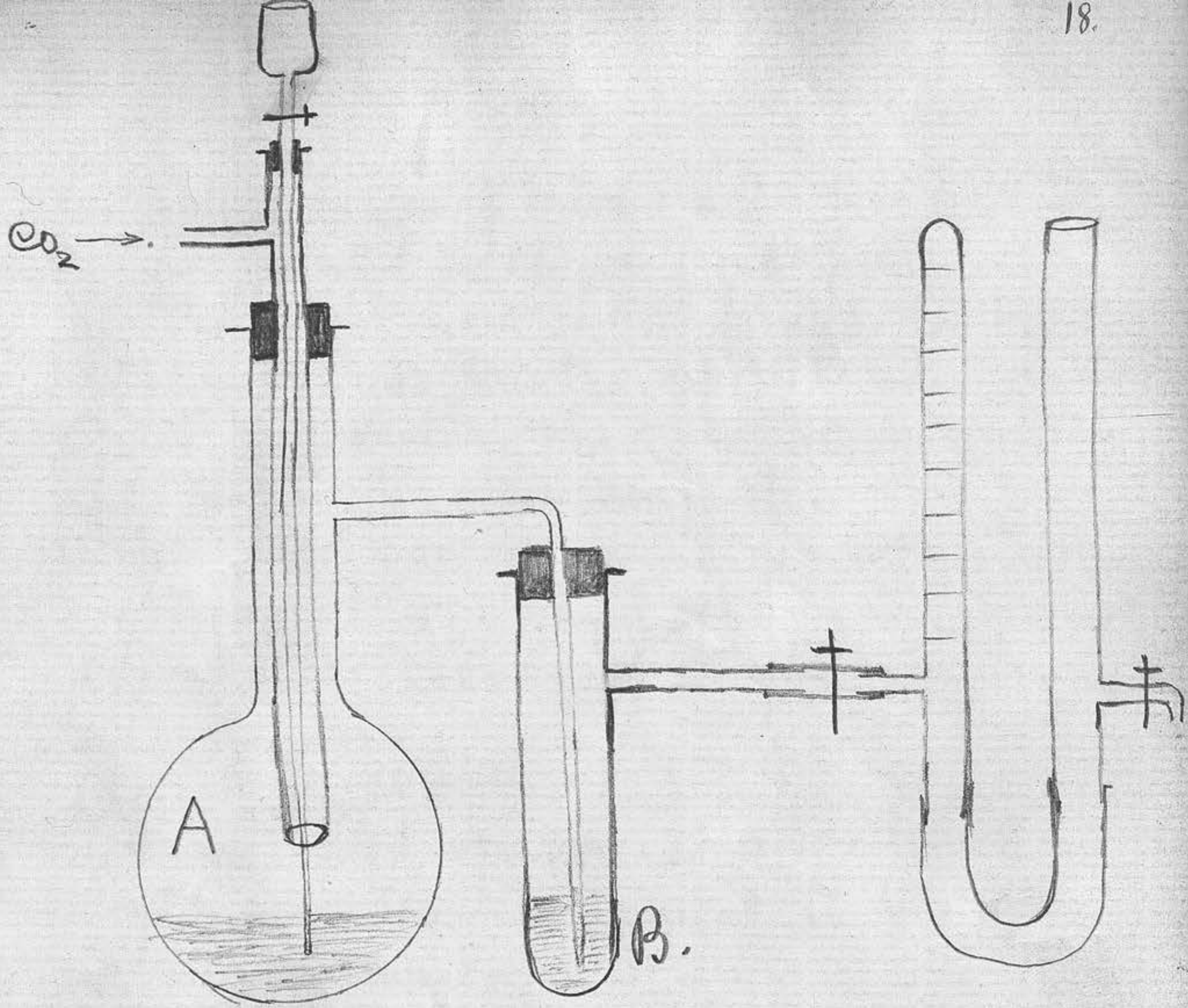
10 gr. of Amido-Tetrazolic acid was diazotised with mineral acid and $NaNO_2$. The Solution was then boiled. A copious evolution of gas took place, possessing a very pungent odour and attacking the eyes very strongly. The Solution was however evaporated to dryness, the residue extracted with acetone, (which left only mineral salt), and the acetone solution allowed to evaporate. Here a very small quantity of a syruppy mass was left. It acts acid & gives ~~the~~ a green Copper Salt ~~and~~ in acetic acid solution, and a yellowish-white Silver Salt, which are characteristic of all the Compounds Containing the Tetrazol ring. This body is probably c-Oxy-tetrazol, but the yield was so small that it did not suffice for an analysis.

Identification of the gas evolved.

In order to prove the presence of CN in the gas given off, a solution of diazo-tetrazol was boiled in a flask and the escaping gas led over heated (to melting) K_2CO_3 in a current of Hydrogen gas. This Potassic Carbonate was then dissolved in water, Caustic Potash added, then slightly oxidised Ferrous Sulphate, heated, and acidified. A greenish colour was visible in the acidified Solution, which on standing gave a precipitate of Prussian blue.

Extent of Decomposition.

In order to measure the extent of the decomposition, the amount of Nitrogen gas evolved from a known weight of Amido-Tetrazolic acid was determined. If diazo-tetrazolic acid decomposed according to the Equation $CN_4H-N=N\cdot Cl + H\cdot OH = CN_4H\cdot OH + HCl + N_2$ then for every molecule of Amido-Tetrazolic acid taken two atoms of Nitrogen must be given off. If however the decomposition of the ring takes place at the same time, every molecule of Amido-Tetrazolic acid diazotised will yield one Cyanogen and five atoms of Nitrogen. In order now to measure the evolved Nitrogen the following apparatus was constructed:



0.1806 gr. Amido-Tetrazol Hydrochloride, ($CN_5H_3 \cdot HCl + H_2O$), was dissolved in water and placed in the flask A.

0.096 gr $NaNO_2$ (Slight excess) dissolved in water was run in by a tapfunnel, after all the air in the apparatus was replaced by Carbonic acid from a Kipp's apparatus. Next the flask (A) was slowly heated, and the escaping gas, after being washed in water in tube B, was collected in a Zulkowsky's apparatus. At the end of the operation, the remaining Nitrogen gas ~~is~~ was driven out by Carbonic acid.

The above quantity of Amido-Tetrazol Hydrochloride yielded 84.1 cc N gas at 19.5° and 757 mm Pressure, equal to 76.17cc at 0°, 760 mm Pressure, and dryness.

As a slight excess of Nitrous acid was present, the gas collected had to be freed from any NO that might have been formed. For this purpose the gas was transported into an Orsat's apparatus, where the NO was absorbed by a Solution of Ferrous Sulphate.

Before ~~app~~ absorption the gas measured 82.9cc at 17.8° and 750 mm Pressure; equal to 75.01 cc at 0°, 760 mm. Pressure and dryness.

After the absorption had taken place the gas measured 76.8cc at 18.2° and 746 mm Pressure; equal to 68.97 cc at 0° & 760 mm Pr., and dryness.

Hence the of the original 76.17 cc gas at 0° & 760 mm Pr. 70.04 cc were Nitrogen, that is 48.67% of the Amido Tetrazol Hydrochloride taken.

Pure Amido-Tetrazol-Hydrochloride must yield 20.09% Nitrogen when only the 2 diazo-atoms of Nitrogen escape, and 50.22% when the ring likewise breaks up into Nitrogen and Cyanogen gases. Hence under complete decomposition it would yield 30.13% Nitrogen which is not diazo-Nitrogen, but derived from the broken up Tetrazol ring. Now by experiment 48.67% Nitrogen was obtained as total ie from both the ring and the 2 diazo-atoms of Nitrogen. Of the 48.67% 20.09% must come from the diazo-Nitrogen. Hence 48.67 − 20.09 = 28.58% of Nitrogen came from the

Splitting of the Tetrazol ring. But on the ~~complete~~ decomposition of every molecule 30.13 % Nitrogen must be given off besides the 30.09 % from the diazo-Nitrogen. Hence $\frac{28.58}{30.13}$ % of the Amido-Tetrazol-Hydrochloride employed had suffered ~~complete~~ decomposition of the ring.
i.e. 94.85 %.

The residue in flask A was evaporated further, and then acidified with acetic acid & $CuSO_4$ added, when only traces of a green Copper salt was got. The wash-water in B gave the reaction for Cyanogen — Prussian blue.

Sodium and Barium Salts of Oxy-azo-tetrazol.

When Nitrous acid has not been added in excess in diazotising Amido-tetrazolic acid, a yellow salt crystallises out when the solution of ~~the~~ diazo-tetrazolate is concentrated by evaporation at ~~[illegible]~~ 70°-80°.
The Na salt can also be prepared by boiling a solution of Sodium-diazo-tetrazolate, ~~with~~ and passing a current of Carbonic acid gas through. The operation must however not be too long continued for instance till all the diazo-tetrazolate has disappeared (which can be

ascertained by the β-naphthylamine reaction), because the oxy-azo body gets further decomposed on continued boiling with evolution of NH_3. It is better to take out small portions time after time, ~~and~~ to ~~concentrate and~~ cool the same, and observe ~~the~~ how much crystallises out.— The salt obtained in either way is recrystallised from hot water and dried by exposure to the air. It crystallises in large prisms and has a neutral reaction.

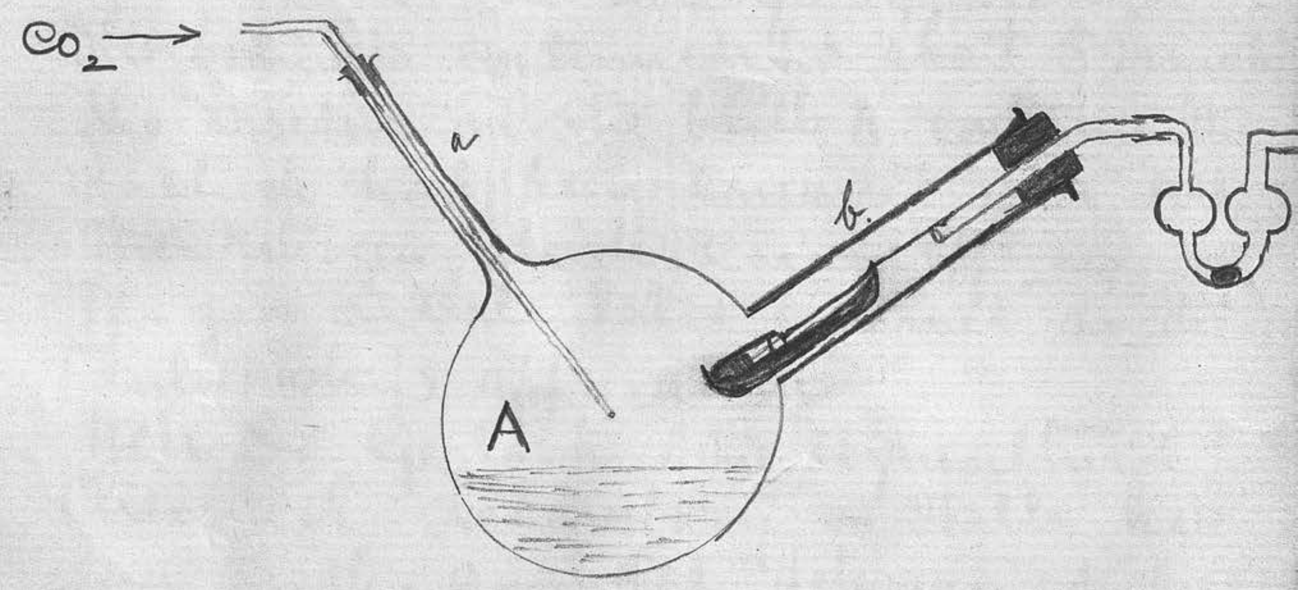
The corresponding Ba salt is obtained in larger quantity when the diazo-tetrazol solution is neutralised with $Ba(OH)_2$. The excess of Barium is removed by pasing Carbonic acid gas through, then a current of air, and ~~then~~ filtered. The Solution is evaporated in the same way as that of the Na-salt, at about 70°–80° in a partial vacuum. The yellow salt which here falls out contains ~~two~~ Ba-salts one very difficultly soluble in hot water the other more easily soluble. Both salts are exceedingly explosive. The one which is the more easily soluble is the ~~corresponding~~ Ba-salt of Oxy-azo-~~tetrazol~~: $C_2N_{10}OBa + 4H_2O$, corresponding to the above Sodium salt.

The analyses of these oxy-azo-bodies have been attended with great difficulty. Their enormous explosive power render them exceedingly dangerous. Percussion ~~&~~ or friction does not affect them, but when heated they explode with terrible force. On heating a small portion on a platinum spoon, ~~&~~ it seemed to melt first in its water of crystallisation and then to explode. This led to an attempt ~~to~~ at determining its melting point. About 0·3 to 0·5 mgr. was heated in the ordinary way in a Sulphuric acid ~~bath~~ bath. When the temperature had risen to somewhere between 170° – 180° the Substance exploded, without any sign of previous melting, pulverising glass beaker and thermometer, and blowing a shower of acid into the Operator's face and eyes.

Of the several analyses done in the ordinary way only one Nitrogen determination succeeded. On all other occasions dangerous explosions resulted; although the Substance was in every case intimately mixed beforehand in a mixing-tube with about a 20 cm long cylinder of Copper Oxide, and not more than 0.15 gr taken for each combustion.

Analyses in the wet way had therefore to be resorted to.

The method invented for the determination of the Nitrogen depended on the fact that several derivatives of Amido-Guanidin, when subjected to Kjeldahl's way of determining the Nitrogen, yielded only those nitrogen-atoms in the form of NH_3, which are not directly bound to each other, the rest escaping as Nitrogen. — For the purpose of estimating both forms of Nitrogen the following apparatus was made use of:—



A is a small bulb with two necks. Through the one (a) a current of carbonic acid gas is led from a Kipp's apparatus. Into the other (b) a tube is inserted which leads to a Zulkowsky's Nitrogen apparatus, and which has attached to its other end a small platinum boat. This ~~boat~~ boat serves to hold the tube containing the substance to be analysed.

10 cc concentrated Sulphuric acid, Ammonia free, are brought into A, the boat with the load inserted, and the air in the apparatus replaced by Carbonic acid gas. When this is done, the tube with Substance is made to drop into the Sulphuric acid by either tapping gently or turning the boat round its axis by means of the tube to which it is attached. As soon as the Substance is thoroughly wetted by the acid, <u>and not before</u>, the bulb A is slowly heated till the acid boils, the Nitrogen being collected in Lulkowsky's apparatus. The boiling is continued for about 5 minutes. The residue in the bulb A contains the N which had been converted into NH_3; the Nitrogen which came off as N-gas is ~~calculated~~ contained in the Lulkowsky's apparatus.

Herr Dr. Gerlach of the Agricultural Chemical Laboratory in Halle has ~~been~~ kindly ~~analysed~~ determined the amount of Nitrogen in the residue according to Kjeldahl's method.

This method was first applied to compounds of known composition, viz. Amido-tetrazolic acid & Hydrazin Sulphate.

A.

I 0.1094 gr. Amido-Tetrazolic acid gave 50.75 ccm N. at 15.4° & 760 m m Pr. The residue gave 0.0147 gr N. in the form of NH_3.

II 0.1536 gr. gave 69.9 ccm N. at 16.5° and 759 m m Pr. The residue gave ~~0.028~~ 0.0218 gr N. in the form of NH_3.

Calculated for $CN_4H \cdot NH_2 + H_2O$		Found I	Found II
Nitrogen-bound nitrogen, 4 atoms	54.36	54.19	52.85
Carbon-bound nitrogen, 1 atom	13.59	13.44	14.20
Total Nitrogen	67.95	67.63	67.05

B.

I. 0.2321 gr. ~~gave~~ Hydrazin Sulphate gave 43.3 ccm N. at 16.5° & 759 m m Pr. The residue contained no Nitrogen.

II. 0.2290 gr. gave 43.05 cc N at ~~15~~ 18.3° & 758.5 m m Pr. The residue contained no Nitrogen.

Calculated for $NH_2-NH_2+2H_2SO_4$		Found I	Found II
Nitrogen-bound nitrogen	21.46	21.65	21.63
Carbon-bound Nitrogen	0.00	0.00	0.00

The method was next applied to the explosive compounds. Though not very exact it at any rate gives approximate results, except in the case of Sodium-oxy-azo-tetrazolate.

A. Sodium salt of oxy-azo-tetrazol

$C_2N_{10}ONa_2+4H_2O$

I. 0.0958 gr gave 30.8 cc N at 16.6° and 761.0 mm Pr.
The residue gave 0.0053 gr N in the form of NH_3.

II. 0.1446 gr. gave 51.3 cc N at 20.1° & 761 mm Pr.
The residue gave 0.0087 gr N in the form of NH_3.

III. 0.1008 gave 37.6 cc N at 20.0° & 761 mm Pr.
The residue gave 0.0054 gr N, as NH_3.

Calculated for $C_2N_{10}ONa_2+4H_2O$		Found I	Found II	Found III
As Nitrogen gas:	—	37.42	40.69	42.71
As Ammonia:	—	5.53	6.02	5.36
Total Nitrogen	44.30	42.95	46.71	48.07

B. Barium salt of oxy-azo-Tetrazol

I. 0.2076 gr. gave 52.5 cc N at 17.6° and 761 mm Pr.
The residue gave 0.0131 gr N as Ammonia

II. 0.1961 gr gave 50.1 ~~gr~~ cc N
at 17.6° and 761 mm Pr.
The residue gave 0.0115 gr N in the form of NH_3

	Calculated for $C_2N_{10}OBa + 4H_2O$	Found I	Found II.
As Nitrogen gas —		29.29	29.60
As Ammonia —		6.31	5.87
Total Nitrogen	35.99	35.60	35.47

The method was also applied to the other Ba-Salt which is less soluble in water than the ~~last~~ above one, but whose composition has not been made out yet.

I 0.2024 gr gave 47.5 cc N at 16.6° & 761 mm Pr.
In the form of Ammonia, 0.0082 gr N.

II 0.2330 gr gave 55.45 cc N at 16.9° and 761 mm Pr
In the form of Ammonia, 0.0094 gr N.

	Calculated for	Found I	Found II
As Nitrogen gas —		27.32	27.65
As Ammonia —		4.05	4.00
Total —		31.37	31.65

It contains 40.64 % Ba.

Determination of Carbon in the wet way in the above explosive compounds.

The method employed was that described by Messinger (x). The substance is oxidised by a mixture of Chromic acid and concentrated Sulphuric acid. Here too difficulties ~~were~~ arose, which at first seemed unsurmountabl Although the method was closely followed, far too high results, which did not even agree among themselves, were repeatedly obtained. At the end of the operation a cloud was produced in the oxidising flask long before the Sulphuric acid had reached its boiling temperature. This cloud was due to the generation of Sulphur dioxide. To prevent this gas getting into the Potash bulbs, a U-tube filled with glass beads and a concentrated solution of Chromic acid, was placed in front of the Calcium chloride tube (xx). Still the results remained too high and did not agree among themselves.

The formation of Sulphur dioxide at the end of the operation seemed to

---

(x) Berichte

(xx) This same U-tube had previously been tried and found to absorb all the SO_2 led through it. Solid Chromic acid did not answer the purpose.

to prove that the Tetrazol ring escapes oxidation at comparitively low temperatures at which a Chromic mixture evolves its oxygen, and only suffers decomposition at a temperature where all the Chromic acid has been already reduced, at the Same time reducing the Sulphuric acid. This ~~however~~ however Seemed very improbable ~~; and~~ on arresting the Sulphur dioxide vapours by the Sol^n. of Chromic acid, the results were still far too high. It was only after making a blind experiment ~~that~~ the true cause of these ~~inexplicable~~ faulty results was discovered. On using 50 cc of the Sulphuric acid and 8 grs CrO_3, and performing as before with the exception of adding any Substance, the potash bulbs soon shewed the formation of Potassic Carbonate on the inner sides of the first bulb. On weighing the Same an increase of 0.1802 gr had taken place. - Pure Chromic acid was then prepared; and on heating this with the Same Sulphuric acid, the gas after washing gave a white precipitate with Baryta water. It was the Sulphuric acid which contained organic ~~Substan~~ impurities, though it had a perfectly clear & colourless appearance and marked "Purissimum". Sulphuric acid derived from another Source was next tested and proved to be not much better. In order therefore to get Sulphuric acid free from organic impurity, it was heated for some time with some Chromic acid. On employing the acid so treated satisfactory results were obtained.

Analysis of Sodium salt of oxy-azo-tetrazol.

I (1) 0.1028 gr. gave 38.5 cc N at 11.2° & 757 mm Pr.
(2) 0.4079 gr gave 0.1818 gr Na_2SO_4, ie 0.058921 gr Na, and 0.1133 H_2O at 120°.

II (1) 0.3278 gr. gave 0.1483 gr Na_2SO_4 ie 0.048029 gr Na, and 0.0924 H_2O at 120°.

III (1) 0.6133 Subst. gave 0.1690 gr CO_2 ie 0.0460909 gr C.
~~0.3278 gr gave 0.1~~
(2) 0.3200 gr. gave 0.0900 gr H_2O at 120°.
(3) 0.6929 gr. gave 0.1953 gr CO_2 ie 0.053263 gr C.

IV. 0.5520 gr. gave 0.1592 gr CO_2 ie 0.043418 gr C.

Calculated for $C_2N_{10}ONa_2+4H_2O$		Found			
		I	II	III	IV
C.	7.59	—	—	7.49 7.68	7.86
N	44.30	(x) 44.41	—	—	—
Na.	14.56	14.67	14.66	—	—
H_2O	28.48	28.18	28.13	28.13	—

Nos. I & III were two different preparations from Sodium-diazo-tetrazolate by the action of Carbonic acid; Nos. II & IV two different preparations obtained in the evaporation of the Solution of Sodium diazotetrazolate.

(x) Analysed in the dry way with CuO, the only case where no explosion ensued.

Though the product in the two cases was proved to be identical by analysis, and is further confirmed by the following reactions, ~~yet~~ they differ considerably in the intensity of their colours, that obtained ~~by~~ in the evaporation of the diazo-tetrazolate solution having a much deeper yellow colour than the other. Determination of their melting points is here altogether out of the question.

Action of reagents on the Sodium Salt of Oxy-azo-tetrazol:

	(1) Light yellow salt.	(2) Deep yellow salt
$BaCl_2$	gives a light yellow precipitate, easily soluble hot water; crystallises in rectangular tablets.	The same, except that the crystals are slightly ~~more~~ deeper yellow.
$CaCl_2$	After some time separation of almost colourless needles.	The same.
$AgNO_3$	Gelatinous yellow precipitate, soluble in Ammonia, insoluble in Nitric acid	The same, except that the precipitate is slightly deeper yellow.
$HgNO_3$	Yellow gelatinous, difficultly soluble in Nitric acid	The same.

	(1) Light yellow salt	(2) Deep yellow salt
$HgCl_2$	No precipitate —	The same. —
$CuSO_4$	Light green precipitate, insoluble in Ammonia, soluble in acids.	The same. —
SH_2	Decolorises after some time, Sulphur separating	The same.
$SnCl_2$ in HCl	Decolorises at once	The same.

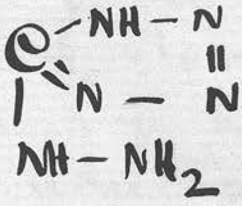
Analysis of Barium salt of Oxy_azo_tetrazol.

I 0.3018 gr. gave 0.1812 gr. $BaSO_4$ ie 0.1065 Ba, and 0.0565 gr H_2O at 110°.

Calculated for $C_2N_{10}OBa+4aq$		Found I	II	III
Ba	35.22	35.32	—	—
H_2O	18.57	18.72	—	—
(x) N	35.99	—	35.60	35.47

(x) As done in the wet way, See pg 27.

Tetrazyl-Hydrazin.



This body is obtained when the dilute Solution of diazo-tetrazol is reduced by Stannous Chloride and Hydrochloric acid.

25.8 grs Amido tetrazolic acid is mixed with 13.6 gr. Sodium Carbonate, previously dried, To this mixture hot water is added, when the resulting Sodium Salt goes in Solution under the escape of Carbonic acid. To this liquid is now added 17.65 gr Sodium Nitrite, and filled up to 250 cc with water.

Next dissolve 130 grs Stannous chloride in 200 cc fuming Hydrochloric acid. Now allow the 250 cc of the Nitrite and Amido-Tetrazol Solution to run slowly into 250 cc of 12 per cent Hydrochloric acid, under stirring, and continual cooling by the addition of ice. To start with, the 250 cc of 12 per cent Hydrochloric acid should be diluted to a litre. If the Solution be not very dilute, an explosion may ensue. The beakers &c in which the "diazotisation" has been performed must also be washed out at once, as any drops which remain would dry up and on explosion destroy the vessel.

As soon as the diazotising is complete the ~~cooled~~ resulting liquid is poured into the Solution of Stannous chloride, which is kept cold by adding ice freely during the reduction. Here evolution of gas takes place and a pinkish transient coloration is produced.

The reduced diazo-tetrazol is now filtered if clear (to get rid of dirt got in with addition of ice), if not clear it is warmed for a while till clear & then filtered. To get the Tetrazyl-Hydrazin out of the great bulk of water, the solution is shaken up with small quantities at a time of Benzaldehyd, which forms a white precipitate with the Hydrazin. As soon as the smell of Benzaldehyd is still pronounced after vigorous shaking and standing for a while, the precipitate is filtered off, washed with water, then with alcohol and dried at 100°C.

The filtrate contains small quantities of another tetrazol derivative, the isolation of which has however not been successful.

To get the free base from the above Benzaldehyd combination, the ~~dried substance above~~ latter is ~~was~~ suspended in a solution of 25 per cent Hydrochloric acid, and a rapid current of

Steam passed ~~pass~~ through. A weaker solution of the acid decomposes the Benzaldehyd-combination very slowly.

After an hour or an hour and a half all the Benzaldehyd is distilled over. The solution is concentrated, and Sodium acetate (solid) added — 22 grs for every 25 grs Benzaldehyd-combination used — Here The Hydrochloride of Tetrazyl Hydrazin is decomposed into free base and Sodium Chloride, ~~the~~ its acetate being unstable. If the solution be not concentrated enough, it must now be boiled in a narrow-necked flask, since it ~~because~~ gets oxidized to a reddish violet compound by the action of the air. The cooling of the solution is made to take place in an atmosphere of Carbonic acid; the Hydrazin crystallises out in hard warty masses. It forms a supersaturated solution, from which the base crystallises at once on the addition of a crystal of the same substance.

It can be more easily obtained by saturating the concentrated solution by Hydrochloric acid gas, when a white crystalline pp precipitate of the dihydrochloride falls out. On adding to this precipitate the calculated quantity of Sodium acetate, the free base crystallises out.

The free base so obtained is once more crystallised from hot water, and dried in a vacuum exsiccator.

I (1) 0.1043 gr. gave 77.6 ccm N. at 16.[illegible]° and 739.5 mm Pr.

(2) 0.4422 gr. gave 0.2013 gr. CO_2, equal to 0.05481 gr C; and 0.1656 gr. H_2O, equal to 0.0184 gr H.

II (1) 0.0953 gr. gave 68.6 ccm N. at 16.5° and 764.5 mm Pr.

(2) 0.4117 gr gave 0.1836 gr CO_2, equal to 0.05007 gr. C; and 0.1513 gr H_2O, equal to 0.01681 gr. H.

III 0.3640 gr gave 0.1628 gr CO_2, equal to 0.0444 gr C; and 0.1392 gr H_2O, equal to ~~0.05~~ 0.015466 H

	Calculated for	Found		
	CN_6H_4	I	II	III
C	12.00	12.41	12.16	12.19
H	4.00	4.16	4.08	4.24
N	84.00	84.30	84.15	—

Nos. I II + III were from three different preparations.

It may be remarked here ~~that~~ of all these bodies containing such a high percentage of Nitrogen, are very difficult to analyse. Unless one lays in front

Of the combustion tube Copper spirals to the length of about 20 cm, and combust very slowly and carefully. The Carbon and Nitrogen always fall out too high.

Tetrazyl Hydrazin is richer in Nitrogen than any hitherto known Organic compound. – It is not very difficultly soluble in water, but insoluble in alcohol, benzene, acetone &c. It is very readily oxidised; a solution in water becomes pink in a few minutes when exposed to the air. Ferric Chloride oxidises it to a deep violet solution; attempts at isolating this product of oxidation have not been successful. It resists the continued action of strong solutions of acids and alkalies, shewing ~~that~~ it is a primary Hydrazin. Its melting point is 199°; it melts under evolution of gas.

Tetrazyl-Hydrazin Dihydrochloride

$CN_6H_4 + 2HCl$.

When a solution of Tetrazyl-Hydrazin is saturated with Hydrochloric acid gas, a white crystalline precipitate falls out; this is the dihydrochloride of Tetrazyl Hydrazin. It melts at 179°.
Dried in vacuum exsiccator and analysed according to Carius's method

I 0.3242 gr gave 0.5354 gr AgCl, equal to 0.1325 gr Cl.

II ~~0.2815~~ 0.1760 gr. gave 0.2897 gr AgCl, equal to 0.0716 gr Cl.

Calculated for $CN_6H_4 \cdot 2HCl$		Found I	II
Cl	41.04	40.88	40.71

The oxidation must take place at 250° at least, otherwise it is not complete.

§ When the dihydrochloride is repeatedly evaporated on a waterbath, Hydrochloric acid is given off. The residue dissolved in the smallest qt. of water & placed in a vacuum exsiccator, crystallises in colourless prisms. This salt on analysis proved to be still a mixture of di- and mono-Tetrazyl Hydrazin.

Benzal-Tetrazyl Hydrazin.

$$CN_4H.NH-N=CH.C_6H_5.$$

The preparation of this compound has already been described. It is difficultly soluble in alcohol in the cold, but fairly soluble in ~~the~~ hot alcohol, from which it crystallises in fine colourless needles. It is insoluble in Chloroform, almost insoluble in Benzol, slightly more soluble in ~~Gr~~ Glacial acetic acid and Acetone, but ~~b~~ more soluble in Nitrobenzene than in Alcohol. It dissolves in Sodium Carbonate solution and in Ammonia, forming the Sodium and Ammonium Salts of Benzal-Tetrazyl-Hydrazin. The Ammonium Salt decomposes on evaporation.

It melts at 140°.

I (1) 0.1612 gr gave 62.4 ccm N. at 16°. and 758.5 mm Pr.

(2) 0.2558 gr. gave 0.4828 gr CO_2, equal to 0.13167 gr C; and 0.0994 H_2O, equal to 0.01104 H.

II (1) 0.2475 gr gave 0.4637 gr CO_2, equal to 0.12646 gr C; and 0.0978 gr H_2O, equal to 0.010866 gr H.

	Calculated for $CN_4H-NH-N=CH.C_6H_5$	Found I	 II
C.	57.06	57.47	57.09
H.	4.25	4.31	4.39
N.	44.68	44.40	—

Nos. I & II were from different preparations.

Sodium Salt of Benzal-Tetrazyl Hydrazin

$C_8N_6H_7Na + 3aq.$

Benzal-Tetrazyl-Hydrazin is added to the calculated quantity of Sodium Carbonate, & enough hot water added to dissolve the resulting Sodium Salt. This is allowed to cool, when the Salt separates in prisms. It is recrystallised from hot water. On boiling it suffers slow decomposition, Benzaldehyd escaping. It reacts ~~slight~~ weakly alkaline. Heated in the solid ~~sal~~ state, it begins to decompose even at 95°.

I. 0.4707 gr. gave 0.1265 Na_2SO_4, equal to 0.040978 gr Na.

II 0.1571 gr gave 43.6 ccm N at 14° & 749.5 mm Pr.

Calculated for $C_8H_7N_6Na + 3H_2O$		Found I	Found II
Na	8.71	8.71	—
N	31.81		32.18

Nos I + II were from different preparation

Calcium Salt — $(C_8N_6H_7)_2Ca + 6H_2O$.

On the addition of Calcium chloride to the Sodium Salt, a white precipitate of the above Calcium Salt is got. It is almost insoluble in cold water, but soluble in hot water, from which it is crystallised and then dried in the air. On too long exposure to the air it loses water of crystallisation

I 0.3576 gr gave 0.0377 gr CaO, equal to 0.026642 gr Ca.

II 0.1407 gr gave 39.6 ccm N at 15.2° and 751 mm Pr.

Calculated for $(C_8N_6H_7)_2Ca + 6H_2O$		Found	
		I	II.
Ca.	7.66	7.66.	—
N.	32.18	—	32.52

Nos. I + II were from different preparation.

Barium Salt. $(C_8N_6H_7)_2Ba + 6H_2O$.

This Salt is prepared in the same way as the Calcium Salt, by Barium chloride on the Sodium Salt.

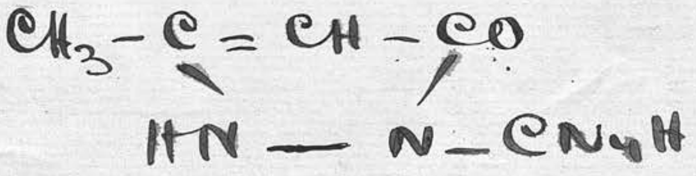
I 0.1985 gr. gave 46.5 ccm N. at 15.2° & 761 mm Pr.

II 0.4137 gave 0.1297 gr $BaCO_3$ equal to 0.08512 Ba

Calculated for $(C_8N_6H_7)_2Ba + 6H_2O$	Found II	I
Na 21.81	22.12	—
N 27.14	—	27.43

Silver nitrate produces a gelatinous yellowish white precipitate with the Sodium Salt, which soon becomes brown when in the dry state. It does not explode on heating.
Lead acetate gives a bluish white precipitate which is soluble in hot water.

Tetrazyl-Pyrazolone.



10 grs. Tetrazyl-Hydrazin is boiled with an excess of Aceto-acetic ester (about 20 grs). An energetic reaction sets in which is soon completed. The resulting liquid is then poured into cold water, when Tetrazyl-Pyrazolone crystallises out in silky needles. The filtered off crystalline mass is once dissolved in hot water, , boiled with some

Animal charcoal filtered off, washed, and allowed to crystallise.
Dried in air at 105°.

0.1093 gr gave 47.7 ccm N. at 17°.4 and and 761 mm Pr.
0.2708 gr gave 0.3600 gr CO_2, equal to 0.098172 gr C.; and 0.0905 gr H_2O, equal to 0.01005 gr H.

Calculated for $C_5N_6OH_6$		Found
C.	36.14	36.25
H.	3.61	3.71
N.	50.60	50.60.

On the addition of ferric chloride, it gives an intense violet-brown coloration, which on much dilution, becomes violet. This reaction is a very delicate one. It melts at 216.5°.C