XCVIII.—*Studies on Citrazinic Acid. Part V.*

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INTRODUCTION.

ALTHOUGH its genesis from citric acid by various methods renders it probable that the hydroxyl groups in citrazinic acid occupy the $\alpha\alpha'$ position, there is still wanting direct evidence on this point. With the view of supplying this evidence, it was determined to prepare a quantity of the compound in which the hydroxyl groups are replaced by chlorine, with the object, if possible, of replacing the latter by cyanogen of methyl, and thus obtaining by the well-known methods one of the

tricarboxy-acids whose constitution has been established. At the outset of the investigation, however, it was found that such a number of interesting products presented themselves that it was deemed advisable to publish this part of the work separately, leaving the second portion for a further communication. The present paper deals exclusively with the interaction of phosphorus pentachloride on citrazinic acid together with the properties of the products. To some extent this reaction has been studied by Behrmann and Hofmann (*Ber.*, 1884, 17, 2694) who failed to obtain any definite products without recourse to sealed tubes and a very high temperature, when they obtained a compound in which both hydroxyl groups are replaced by chlorine, together with a small quantity of an oil which, beyond a chlorine determination on what was undoubtedly a mixture, was not further examined. Mention is also made in their communication of crystals which separated out from this oil, as to the nature of which, as will be shown below, they were entirely mistaken.

Briefly summarised, the chief substances isolated in this investigation are :—

1. Chlorhydroxyisonicotinic acid and its derivatives.
2. Dichlorisonicotinic acid and its derivatives.
3. Tetrachlorisonicotinic acid and its derivatives.
4. $\alpha\beta\alpha'\beta'$ -Tetrachlorpyridine and its derivatives.
5. Pentachlorpyridine.
6. Pentachlorpicoline.

EXPERIMENTAL.

The experimental part may be conveniently considered under the following heads :—

- I. The action of phosphorus pentachloride (*a*) in a reflux apparatus, (*b*) in sealed tubes.
- II. The isolation of the products formed (*a*) non-volatile in steam, (*b*) volatile in steam.
- III. Description of the above products and their derivatives.
- IV. The conversion of chlorisonicotinic acids into chloro- and amido-chloro-pyridine, and description of the latter.

I.—(*a*) *The Interaction of Citrazinic Acid with a Saturated Solution of Phosphorus Pentachloride in Phosphorus Oxychloride in a Reflux Apparatus.*

The interaction under these conditions was studied by Behrmann and Hofmann (*loc. cit.*), who state that, after long heating and pouring into water, the acid chloride produced was reconverted into the original citrazinic acid,

A repetition of these experiments, using the same proportions of materials, and heating for six hours, showed that a certain amount of chlorhydroxyisonicotinic acid had been formed, but that the greater part of the citrazinic acid had not gone beyond the acid chloride, and could be recovered by treatment with water. A further repetition in which the heating was kept up for seventy-five hours continuously proved, however, that a more deep-seated change had been effected, and that, not only had the hydroxyl groups of the acid been replaced by chlorine, but that, to some extent, the hydrogen atoms of the original pyridine nucleus had also been replaced, no citrazinic acid being left after treatment of the product with water. The method pursued in general in this part of the investigation was to heat the acid with from 3 to 6 molecules of phosphorus pentachloride and some oxychloride to the boiling point of the mixture in a flask provided with a reflux condenser. Where a large excess of pentachloride had been used, a little amorphous phosphorus was added, and the mixture of phosphorus trichloride and oxychloride distilled off. The acid chlorides were then poured into cold water and the whole distilled with steam, until nothing more was carried over by the steam. The residual liquid in the flask was filtered while hot, and on cooling deposited brownish crystals consisting of a mixture of acids containing respectively 1 and 2 atoms of chlorine replacing the hydroxyl groups of the citrazinic acid together with a small quantity of a more highly chlorinated product since identified as tetrachlorisonicotinic acid.

The oily or semi-solid product collecting at the bottom of the aqueous distillate consisted of a mixture of the acid chloride of tetrachlorisonicotinic acid and pentachloropicoline. Without quoting the actual experiments, it may be stated generally that the yield of more highly chlorinated products increased with the proportion of phosphorus pentachloride used and the length of time the heating was continued, although after 168 hours' uninterrupted boiling in presence of a large excess of phosphorus pentachloride, the amount of dichlorisonicotinic acid which had not been further chlorinated reached 40 per cent. of the weight of citrazinic acid used. The maximum yield of the latter product was obtained when 3 molecules of phosphorus pentachloride were employed, and reached 80 per cent. of the weight of acid taken.

The order of replacement by chlorine appears to be :

1. The acid chloride is formed.
2. The hydroxyl groups of the nucleus are replaced.
3. When the dichlorisonicotinic acid chloride has been thus formed, the reaction proceeds in one of two directions ; either the remaining hydrogen atoms are attacked, or the second oxygen atom of the carboxyl group is replaced by two chlorine atoms, the proportion in which the reaction takes the former direction being by far the greater.

(b) Interaction in Sealed Tubes.

In order to examine the effects of a higher temperature than could be obtained in open vessels, recourse was had to heating in sealed tubes. The proportions of materials used in this part of the work varied from 3 to 6 molecules of the pentachloride to 1 of the acid. Without, however, going into minute details, it may be stated that according to the relative weights of pentachloride to acid employed, the *proportion* of the products differs to a greater extent than does their *nature*. When 3 molecules to 1 of acid were used, the results differ in some important particulars from those described by Behrmann and Hofmann (*loc. cit.*), who used about these proportions. In their paper, a temperature of 250° is recommended for the preparation of the *aa'*-dichloro-derivative. From a large number of experiments, it was found that such a high temperature is not only unnecessary, but gives a much less satisfactory yield of this substance than when the operation is conducted at 170°. In the latter case, the yield of the dichloro-derivative reaches 80 per cent. of the citrazinic acid taken. In the paper referred to above, it is stated that after heating the mixture of acid and pentachloride, treating the product with water and distilling with steam, crystals separate from the oily distillate consisting of the *aa'*-dichlorisonicotinic acid which has been carried over as the acid chloride, and subsequently decomposed by water. The only proof cited that these crystals are the dichlorisonicotinic acid seems to rest on a melting point determination. The great instability of the acid chloride of this substance in presence of water renders this statement inexplicable, and frequent repetition of the experiment failed to give the least trace of the dichloro-derivative in the steam distillate. That crystals not infrequently separate on a slight fall of temperature there is no question, but these are the acid chloride of the tetrachloro-derivative which, together with a small but variable quantity of pentachloropicoline, constitute the oily liquid. These substances when mixed have a remarkably low fusing point, so low, indeed, that a freezing mixture is necessary to cause complete solidification. When the proportion of phosphorus pentachloride is increased to 5 or 6 molecules for 1 of the acid and the temperature maintained at 170° for some hours, the chief product is the tetrachlorisonicotinic acid chloride and some pentachloropicoline which distils over with steam, very little of the dichloro-derivative being recovered. Experiments in which the temperature was pushed up to 250° gave a similar result, except that the proportion of pentachloropicoline formed was higher.

II.—*Isolation of the Products Formed.*

An attempt was made to isolate the products of the reaction by fractional distillation under reduced pressure, but it was found that, with the exception of the acid chloride of dichlorisonicotinic acid, which, at a pressure of 25 mm. in a gentle current of air, distilled over at 156—157°, all the products came over between 170° and 180°. It was evident, therefore, that much more material than was available would be required in order to effect complete separation by this method.

(a) *Products Non-volatile in Steam.*

The contents of the flask, after being distilled in a current of steam until nothing further was carried over, were immediately filtered and allowed to cool, when a plentiful crop of brownish-yellow crystals was deposited, consisting of a mixture of chlorhydroxyisonicotinic, dichlorisonicotinic, and tetrachlorisonicotinic acids. After drying, the crystals were exhausted with ether, which readily dissolves the two latter, leaving the chlorhydroxyisonicotinic acid behind. The latter was further purified by recrystallisation from boiling water, in which it is sparingly soluble.

The ether was distilled off from the extract, and the two constituents separated by taking advantage of the fact that the tetrachlorisonicotinic acid will not give an ethereal salt when treated with alcohol and hydrochloric acid in the usual way, whereas the dichlorisonicotinic acid gives an almost quantitative yield of its ethylic salts under the same conditions. To test the applicability of this method of separation, an experiment was carried out using 0.5 gram of the pure tetrachlorisonicotinic acid, when it was found that mere traces of the salt had been formed. The resistance to etherification in the diortho-substituted aromatic acids was first pointed out in the case of benzoic acid by V. Meyer, Gümbel and Sudborough (*Ber.*, 1894, 27, 510). The application of this principle to the diortho-substituted acids of pyridine is interesting, and constitutes a further resemblance between pyridine and benzenoid compounds.

Accordingly, the mixture of acids was dissolved in absolute alcohol, and saturated with hydrochloric acid gas. After standing some hours, the mass was poured into water, and the water shaken with ether. The lower layer was then run off, and the ethereal solution washed once with water, and then with a solution of sodium carbonate. By this means, the tetrachlorisonicotinic acid was removed from the ethereal solution as the sodium salt. The lower layer was removed, heated to expel dissolved ether, and acidified with sulphuric acid, when the

tetrachlorisonicotinic acid was precipitated. This was recrystallised once or twice from water or dilute alcohol.

In many cases, when the amount of tetrachlorisonicotinic acid in the mixture was known to be small, the dichlorisonicotinic acid was purified from it by several recrystallisations from boiling water.

(β) *Products Volatile in Steam.*

The oily distillate consists of the acid chloride of tetrachlorisonicotinic acid and pentachloropicoline, the amount of each substance varying with the conditions of the experiment. Frequently, on standing, the whole mass became semi-solid. At other times, a fall in the temperature of the laboratory resulted in the separation of large crystals, whilst occasionally the mass remained liquid until placed in a freezing mixture.

The first crop of crystals which separated out invariably consisted of the almost pure acid chloride, which was recrystallised from ether. Subsequent crops were contaminated with increasing amounts of pentachloropicoline.

Several methods of isolation were tried, of which the one yielding the most satisfactory results was as follows.

The oily or semi-solid distillate was digested at about 70–80° with excess of aqueous ammonia to which an equal volume of alcohol had been added. The greater part of the pentachloropicoline remained undissolved, whilst that taken up was deposited as the first crop as the solution cooled. Subsequent crops consisted of pure tetrachlorisonicotinamide, from which the acid is conveniently prepared by the nitrite method, using sulphuric acid of 70–80 per cent. as the solvent (Bouveault's method, *Bull. Soc. Chim.*, 1892, [iii], 9, 368).

It was found possible to separate the tetrachlorisonicotinic acid chloride from the pentachloropicoline by boiling with water in a flask with a reflux condenser, changing the water from time to time, filtering and evaporating to small bulk, when the acid was obtained. This method, however, is not recommended on account of the length of time required for complete separation, and the risk of loss from the violent bumping to which the mixture is liable after a time.

III.—Description.

Chlorhydroxyisonicotinic Acid.—This compound, freed from other substances by extraction with ether as described above, and recrystallised from boiling water, gave the following numbers on analysis :

- I. 0.2225 gave 0.3385 of CO_2 and 0.0470 H_2O . C = 41.50 ; H = 2.34 %.
 - II. 0.1253 „ 0.1030 AgCl . Cl = 20.33 per cent.
- $\text{C}_6\text{H}_4\text{O}_3\text{NCl}$ requires C = 41.52 ; H = 2.30 ; Cl = 20.38 per cent.

As prepared in this way, the acid has a brownish colour, which is only partially removed by boiling with animal charcoal. The colour can be entirely removed, and a very pure product obtained by converting the crude acid into the methylic salt, recrystallising, and saponifying with soda. It is also obtained in colourless crystals when prepared from ethylic dichlorisonicotinate as described below.

Chlorhydroxyisonicotinic acid is moderately soluble in boiling water, from which it separates on cooling in tufts of small needles. It is sparingly soluble in cold water, alcohol, and ether; readily soluble in alkalis and alkaline carbonates, from which solutions it is reprecipitated on neutralisation. The substance is unacted on by strong boiling nitric acid. Its colourless aqueous solution has a strong blue fluorescence which is not destroyed by the addition of mineral acids. This is a distinction from citrazinic acid, which is not fluorescent, although its alkaline salts are remarkably so. When heated, chlorhydroxyisonicotinic acid chars, but does not melt. It effervesces freely with alkaline carbonates, and forms two series of salts with monad metals. When titrated with normal potash, using litmus as indicator, the neutral point is reached when only one equivalent of potash has been added; with phenolphthalein as indicator, however, two equivalents of potash are necessary to effect a change of colour.

The diammonium salt loses ammonia when the solution is evaporated, leaving the monammonium salt. An aqueous solution of the latter or of the acid, when added to a solution of silver nitrate, gives the monosilver salt as a colloidal precipitate, insoluble in cold, and very sparingly soluble in boiling water. The salt when air-dried is anhydrous.

A silver determination on the precipitate gave 38.30 per cent. $C_6H_3O_3NClAg$ requires $Ag = 38.40$ per cent.

The barium salt may be prepared in a similar way. When recrystallised from boiling water, it is deposited in needles which contain 9 molecules of water of recrystallisation.

0.2172 lost 0.0542 water at 120° ; the residue gave 0.0782 $BaSO_4$. $H_2O = 24.95$; $Ba = 21.7$ per cent.

$(C_6H_3O_3NCl)_2Ba9H_2O$ requires $Ba = 21.27$. $H_2O = 25.15$ per cent.

The copper salt, also prepared in the same way, crystallises in beautiful greenish-blue needles easily soluble in water.

The disilver salt, obtained by adding silver nitrate to a solution of the dipotassic salt, closely resembles the monosilver salt. It is unstable, and blackens considerably on drying even at ordinary temperatures. It is very sparingly soluble in water.

0.8003 gram acid was exactly neutralised with potash and a measured excess of N/10 silver nitrate added, the precipitate filtered off and

washed, and the excess of silver nitrate in the filtrate determined by a standard solution of sodium chloride. Used 97 c.c. N/10AgNO₃. Calculated 92.3 c.c.

Dichlorisonicotinic Acid.—This acid has been described by Behrmann and Hofmann (*loc. cit.*). In addition to the work already published, the following further facts have been observed. When purified by means of the lead salt or ethylic salt, this substance is colourless, and volatilises readily without charring, even when quickly heated.

Conversion of Dichlorisonicotinic Acid into Chlorhydroxyisonicotinic Acid.—When evaporated on the water bath with excess of aqueous soda, one of the chlorine atoms is replaced by a hydroxyl group, as represented by the equation :

If the ethylic salt, recrystallised from alcohol, be used instead of the acid, and the heating on the water bath continued for 5 or 6 hours, afterwards redissolving in water and precipitating with dilute sulphuric acid, a very pure and colourless product is obtained. A chlorine determination made on a specimen of chlorhydroxyisonicotinic acid prepared in this way gave the following numbers :

0.3055 gave 0.2540 grams AgCl. Cl = 20.58 per cent.

C₆H₄O₃NCl requires Cl = 20.38 per cent.

Conversion of aa'-Dichlorisonicotinic Acid into Citrazinic Acid.—Although from the relation of dichlorisonicotinic acid to citrazinic acid it seemed probable that the former could be reconverted into the latter by fusion with caustic alkali, it was regarded of sufficient interest to make the experiment. Accordingly, 2 grams of the dichloro-acid were mixed with 12 grams of caustic soda, slightly moistened with water, and heated to a temperature of about 170° in a nickel crucible for 15 minutes. On cooling, the melt was treated with water, and precipitated with dilute sulphuric acid. The substance recrystallised from water was found to contain no chlorine, and was recognised as citrazinic acid by (1) the fluorescence of its alkaline salts, (2) its reaction with alkaline nitrite, and (3) a nitrogen determination.

0.4040 gave 29.7 c.c. nitrogen at 764 mm. and 7.5°. N = 9.04 per cent.

C₅H₂(OH)₂N·COOH requires N = 9.03 per cent.

Action of Ammonia on Dichlorisonicotinic Acid.—When dichlorisonicotinic acid was treated with aqueous ammonia in the cold, only the ammonium salt was formed, but when heated to 200° in sealed tubes with ammonia solution, one of the chlorine atoms was found to have been replaced by amidogen according to the equation :

The clear solution, on neutralising with hydrochloric acid, gave a copious precipitate, soluble in excess of acid, thus separating the compound from any unchanged dichlorisonicotinic acid, which is insoluble in excess of this reagent. After filtering, the amidochlorisonicotinic acid may be reprecipitated by neutralising with ammonia and recrystallised from water.

This compound was also obtained by the action of an aqueous solution of potassium cyanide on the potassium salt of the acid when heated in sealed tubes for some hours at 200—210°. Ammonia being formed by the decomposition of the cyanide in presence of water, the reaction proceeds as above.

- I. 0.1135 gave 15.9 c.c. of nitrogen at 18° and 763 mm. $N = 16.5\%$.
 II. 0.2425 „ 0.2035 AgCl. $Cl = 20.76$ per cent.
 III. 0.0983 „ 0.1500 CO_2 and 0.0263 H_2O . $C = 41.61$; $H = 2.93\%$.
 $C_5H_2Cl(NH_2)N \cdot COOH$ requires $C = 41.76$; $H = 2.93$; $Cl = 20.58$;
 $N = 16.23$ per cent.

Specimens I and II were obtained by the direct action of ammonia on dichlorisonicotinic acid; III by the action of aqueous potassium cyanide.

This substance crystallises from hot water in yellowish needles, which are sparingly soluble in alcohol, water, and acetone. The solutions have a blue fluorescence which is destroyed by acids. It is soluble in all alkalis, alkaline carbonates, and mineral acids, and is reprecipitated on neutralisation. It is practically insoluble in ether.

The *silver* salt is thrown down as a curdy, nearly white precipitate when a solution of silver nitrate is added to a solution of the ammonium salt. It is soluble in boiling water, from which it separates on cooling in short, colourless needles. The *mercuric* salt is a white, amorphous precipitate. The *ferrous* salt separates as a nearly white precipitate, soluble on heating, and recrystallising on cooling in indistinct crystals. The *barium* and *copper* salts are soluble. The *calcium* salt is sparingly soluble, and separates in rosettes of needles.

The Acid Chloride of Dichlorisonicotinic Acid.—This was obtained as mentioned above by distilling the contents of the sealed tubes under reduced pressure. A pure specimen, obtained by the action of phosphorus pentachloride on recrystallised dichlorisonicotinic acid, boiled at 156—157° under a pressure of 25 mm. of mercury. It is a colourless, mobile liquid, which reacts energetically with water, forming the acid; with alcohol, forming the ethylic salt, and with ammonia solution forming the amide.

Dichlorisonicotinamide.—This substance was formed with considerable rise of temperature when the acid chloride of dichlorisonicotinic acid was gradually poured into strong ammonia solution. It crystal-

lises from boiling water in beautiful, colourless needles an inch or more in length, which melt at 200° (uncorr.).

0.1450 gave 17.8 c.c. nitrogen at 17° and 775 mm. $N = 14.7$ per cent.

$C_5H_2Cl_2N \cdot CONH_2$ requires $N = 14.7$ per cent.

This substance volatilises readily without charring. It is easily soluble in alcohol and acetone, sparingly soluble in boiling water and in ether, and practically insoluble in cold water and in chloroform. It is hydrolysed by boiling 80 per cent. sulphuric acid, but not readily by boiling hydrochloric acid. Caustic alkalis cannot be used on account of the readiness with which one of the chlorine atoms is attacked.

Ethyllic Dichlorisonicotinate.—The ethylic salt is formed with considerable development of heat when the acid chloride is poured into absolute alcohol. It is also readily obtained by saturating an alcoholic solution of the acid with hydrochloric acid gas in the usual way. It crystallises from water and alcohol in long, colourless needles melting at $65-66^{\circ}$ (uncorr.), and is volatile in steam.

I. 0.1463 gave 0.2360 CO_2 and 0.0425 H_2O . $C = 44.00$; $H = 3.15$ %.

II. 0.3580 „ 0.5070 $AgCl$. $Cl = 32.3$ per cent.

III. 0.1203 „ 6.4 c.c. nitrogen at 21.5° and 762 mm. $N = 6.21$ %.

$C_5H_2Cl_2N \cdot COOC_2H_5$ requires $C = 43.63$; $H = 3.18$; $Cl = 32.27$;

$N = 6.37$ per cent.

This salt is easily soluble in ether, acetone, and hot alcohol, slightly soluble in cold alcohol, and practically insoluble in cold water. The acid cannot be recovered by saponification with caustic alkalis for the reason mentioned above in connection with the amide. Boiling with sulphuric acid of 50 to 80 per cent., however, is effective. Strong hydrochloric acid in open vessels has no action.

The Acid Chloride of Tetrachlorisonicotinic Acid.—Since it has been shown that the carboxyl group in citrazinic acid undoubtedly occupies the (γ) position, the structure of this compound must be represented by the formula

Purified by recrystallisation from ether, it is obtained in small, colourless needles melting sharply at $47-48^{\circ}$ (uncorr.), is freely soluble in benzene, chloroform, and carbon tetrachloride, and separates from the latter in large, well-formed crystals. Its vapour attacks the eyes.

- I. 0.0976 gave 0.2500 AgCl. Cl = 63.33 per cent.
 II. 0.1173 „ 0.3020 AgCl. Cl = 63.64 „
 III. 0.1315 „ 5.8 c.c. nitrogen at 21° and 763 mm. N = 5.16 %.
 Theory requires Cl = 63.42; N = 5.16 per cent.

The presence of a small quantity of the crude oily distillate in the ethereal solution appears to have a remarkably modifying influence on the size and shape of the crystals. Occasionally solutions which did not contain more than 6 grams of the acid chloride yielded single crystals weighing upwards of 3 grams.

This acid chloride is remarkably stable in the presence of water, contact with which in the cold for months produces no effect, whilst it is only slowly decomposed by boiling. Aqueous or alcoholic ammonia readily converts it into the amide. With alcohol, it reacts slowly in the cold, more readily on heating, to form the ethylic salt.

The following crystallographic constants have been kindly determined by Mr. Hutchinson, Demonstrator in Mineralogy :—

“Crystalline system :—Asymmetric (Holoedral).

$$a : b : c = 0.8916 : 1 : 0.9567.$$

$$\alpha = 80^\circ 40'. \quad \beta = 89^\circ 56'. \quad \gamma = 61^\circ 24'.$$

Forms observed :— $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $q\{101\}$, $x\{\bar{1}01\}$, $s\{121\}$.

Table of Angles.

Angle.	Observed.	Calculated.
ac 100:001	*84° 56'	—
$a'b$ 100:010	*61 0	—
bc 010:001	100 21	100° 37'
aq 100:101	*37 35	—
am 100:110	54 35	54 35
bm 010:110	*64 25	—
$b'q$ 010:101	*61 55	—
bs 010:121	45 36	45 37
cx 001: $\bar{1}$ 01	53 21	53 21
mq 110:101	67 45	67 45
bx 010: $\bar{1}$ 01	74 15	74 29

“Large, simple crystals can be easily grown from solution in carbon tetrachloride, the faces a , m and q are usually well-developed, while b , a , d , c are small.

“From ether, small crystals were obtained twinned about the normal to the face b , on these crystals the planes a and m were always prominent and elongated in the direction of the z axis, whilst the crystals were terminated by q , c and x .

“There is a good cleavage parallel to the plane b ,”

Tetrachlorisonicotinamide.—If the acid chloride be gently warmed with methylated spirit diluted with its own volume of aqueous ammonia until a clear solution is formed, on cooling a copious precipitate of the amide is obtained, the reaction proceeding according to the equation

This substance is very soluble in alcohol, ether, and acetone; moderately soluble in boiling, and sparingly so in cold water, and fairly soluble in benzene. It is most readily recrystallised from hot dilute alcohol, in which it is abundantly soluble, separating on cooling in beautiful, colourless, rhombic plates, which melt at $235-236^\circ$ (uncorr.).

It is not acted on by boiling hydrochloric acid, but may be hydrolysed by the nitrite method above-mentioned or by heating with a 70 per cent. solution of sulphuric acid.

- I. 0.1282 gave 0.2830 AgCl. Cl = 54.56 per cent.
 II. 0.1180 „ 0.2600 AgCl. Cl = 54.50 „
 III. 0.1275 „ 11.8 c.c. nitrogen at 20.5° and 760 mm. N = 10.98%.
 $\text{C}_5\text{Cl}_4\text{N} \cdot \text{CO} \cdot \text{NH}_2$ requires Cl = 54.51; N = 10.79 per cent.

Tetrachlorisonicotinic Acid.—This acid, which, as is indicated above, must be represented by the formula

is obtained by hydrolysis of the amide, or by the prolonged action of boiling water on the acid chloride. It separates from a hot, saturated, aqueous or alcoholic solution in minute, colourless crystals which appear to be cubes, or a modification of cubes, frequently resembling maltese crosses. These crystals melt at $224-225^\circ$ (uncorr.), and gave the following numbers on analysis:

- I. 0.1425 gave 0.1420 CO_2 and 0.0045 H_2O . C = 27.27; H = 0.38%.
 II. 0.1368 „ 0.3007 AgCl. Cl = 54.30 per cent.
 $\text{C}_5\text{Cl}_4\text{N} \cdot \text{COOH}$ requires C = 27.65; H = 0.38; Cl = 54.30 per cent.

This acid is moderately soluble in hot and but sparingly soluble in cold water, readily soluble in alcohol, ether, and hot nitrobenzene. From the latter, it separates, on cooling, in star-like crystals.

In benzene and toluene, it is moderately soluble. Carbon disulphide, carbon tetrachloride, and chloroform dissolve it to a slight extent, and from the latter it crystallises in rhombs. It is insoluble in ligroin. Readily soluble in all alkalis, it is reprecipitated by dilute acids. It forms well-defined metallic salts which exhibit the same general solubility in water as those of dichlorisonicotinic acid, with the exception that the silver salt is much more soluble. This circumstance can be made use of in the separation of the two acids.

If to a solution of the ammonium salt, copper sulphate solution be added in the cold, on standing beautiful blue rhombic plates of the copper salt separate out which contain 8 molecules of water of crystallisation, as the following figures show.

I. 0.3885 gave 0.0450 CuO. Cu = 9.19 per cent.

II. 0.3230 „, when heated at 120°, 0.0640 H₂O. H₂O = 19.81 %.
(C₅Cl₄NCOO)₂Cu + 8H₂O requires H₂O = 19.97 ; Cu = 8.70 per cent.

If, however, the solutions be mixed at a temperature above 60°, or if the cold, saturated solution be boiled, a nearly white precipitate is thrown down which is only slowly redissolved by much water. This precipitate, collected by the aid of the filter pump, lost, at 120°, an amount which approximately corresponds to 2 molecules of water in the salt.

Ethyllic Tetrachlorisonicotinate.—The ethyllic salt of tetrachlorisonicotinic acid is readily obtained by the action of the acid chloride on alcohol. The reaction requires several days for completion in the cold, but on warming proceeds rapidly, long, colourless needles separating out when the solution is again cooled. A chlorine determination on these crystals, which melt at 66°—67° (uncorr.), gave the following numbers:

0.1130 gave 0.2245 AgCl. Cl = 49.11 per cent.

C₅Cl₄N·COOC₂H₅ requires Cl = 49.03 per cent.

This salt is readily soluble in ether and hot alcohol, less soluble in cold alcohol, sparingly soluble in boiling, and practically insoluble in cold water. It cannot readily be hydrolysed by hydrochloric acid, but the ethyl group is eliminated with ease by boiling with 50 per cent. sulphuric acid.

Pentachloro-γ-picoline.—This substance separated from the acid chloride of tetrachlorisonicotinic acid in the manner described above, and recrystallised from dilute alcohol, was obtained in colourless crystals resembling urea, which melt sharply at 58° (uncorr.).

- I. 0.3462 gave 0.9340 AgCl. Cl = 66.71 per cent.
 II. 0.3817 „ 1.0327 AgCl. Cl = 66.90 „
 III. 0.4570 „ 0.4555 CO₂ and 0.0322 H₂O. C = 27.18; H = 0.78%.
 IV. 0.2340 „ 0.2325 CO₂ and 0.0165 H₂O. C = 27.10; H = 0.77%.
 V. 0.2755 „ 12.6 c.c. nitrogen at 19° and 765 mm. N = 5.21%.
 VI. 0.3750 „ 17.3 c.c. nitrogen at 18° and 765 mm. N = 5.35%.
 C₆Cl₅H₂N requires C = 27.16; H = 0.76; Cl = 66.75; N = 5.29 per cent.

This substance is readily soluble in ether and alcohol, moderately soluble in hot dilute alcohol, and insoluble in water. It is not acted on by alcoholic ammonia in open vessels. Its constitution is shown by the fact that when heated with 80 per cent. sulphuric acid, hydrochloric acid is given off and dichlorisonicotinic acid is formed, the reaction proceeding according to the equation

IV.—*Conversion of Chlorisonicotinic Acids into Chloropyridines and Amidochloropyridines.*

When tetrachlorisonicotinic acid is heated with water in sealed tubes to a temperature of about 180°, carbon dioxide is given off and $\alpha\beta\alpha'\beta'$ -tetrachloropyridine is formed. The same result is obtained by distilling the acid with glycerol. If ammonia solution be used instead of water in the sealed tubes, the chlorine atoms are also attacked, and amidotrichloropyridine and diamidodichloropyridine are formed, according to the temperature reached. If tetrachloropyridine be further subjected to the action of phosphorus pentachloride at 300°, pentachloropyridine is formed. Dichlorisonicotinic acid treated in the same manner yields pentachloropyridine and pentachloropicoline, whilst citrazinic acid under the same conditions gives a similar result.

$\alpha\beta\alpha'\beta'$ -Tetrachloropyridine.—When tetrachlorisonicotinic acid was heated with water in sealed tubes to 180–200° for several hours, and the product distilled in steam, an oil came over which mostly solidified in the condenser to a white, crystalline substance. This dissolved readily in hot dilute alcohol, from which it separated on cooling in small, colourless crystals melting at 90–91° (uncorr.).

- I. 0.1163 gave 0.1180 CO₂ and 0.0070 H₂O. C = 27.66; H = 0.66%.
 II. 0.1317 „ 0.3473 AgCl. Cl = 65.22 per cent.
 III. 0.1105 „ 6 c.c. nitrogen at 17° and 770 mm. N = 6.50 per cent.
 C₅Cl₄HN requires C = 27.66; H = 0.46; Cl = 65.44; N = 6.48 „

That the formation of tetrachloropyridine from tetrachlorisonicotinic acid proceeds according to the equation

is shown by the following experiment.

One gram of tetrachlorisonicotinic acid was heated at 200° in a sealed tube with water for 6 hours. The gas given off by warming the tube to about 80° was collected and measured, when 72 c.c. was obtained, and was shown to be carbon dioxide by passing it into lime water. The contents of the tube were then distilled in steam, when 0.7 gram of solid passed over. The liquid remaining in the flask, on evaporation to dryness, gave 0.1 gram of residue. The solid volatile in steam, recrystallised from dilute alcohol, melted sharply at 90° . The volume of carbon dioxide required by theory for 0.7 gram of tetrachloropyridine = 72 c.c.

A similar result is obtained when tetrachlorisonicotinic acid is distilled from glycerol, and this constitutes the readiest method for the preparation of this substance.

It is readily soluble in ether, alcohol, benzene, and hot dilute alcohol, sparingly soluble in cold, and insoluble in water, dilute alkalis, and dilute acids. It does not form a platinum salt, and, indeed, shows no basic properties. Its boiling point, taken by Siwoloboff's method, was found to be $250\text{--}251^{\circ}$ (uncorr.).

Pentachloropyridine.—This substance was first obtained in the present work by the action of excess of phosphorus pentachloride on dichlorisonicotinic acid in a sealed tube at 300° . The heating was continued for 12 hours, the tube being allowed to cool and opened from time to time to allow of the escape of hydrogen chloride. Finally, the contents of the tube were poured into cold water and distilled with steam, when the pentachloropyridine came over and solidified in the condenser. It was recrystallised from dilute alcohol until the melting point was constant at 124° (uncorr.).

- I. 0.2370 gave 0.2067 CO_2 and 0.003 H_2O . $\text{C} = 23.79$; $\text{H} = 0.14\%$.
 - II. 0.3133 „ 0.8925 AgCl . $\text{Cl} = 70.50$ per cent.
 - III. 0.1296 „ 0.3700 AgCl . $\text{Cl} = 70.66$ „
 - IV. 0.2525 „ 12 c.c. nitrogen at 754 mm. and 16° . $\text{N} = 5.50$ per cent.
- $\text{C}_5\text{Cl}_5\text{N}$ requires $\text{C} = 23.90$; $\text{Cl} = 70.51$; $\text{N} = 5.58$ per cent.

The same product was also obtained by the further action of phosphorus pentachloride on tetrachloropyridine prepared as above.

In view of these results, it was of interest to try the chlorinating effect of phosphorus pentachloride on pyridine and other bases directly. Details of this work will more properly find a place in a subsequent communication which is in preparation, but in the meantime it may be here mentioned that, among other interesting results, a pentachloropyridine identical with the above was isolated.

Pentachloropyridine prepared by any of these methods is a colourless, crystalline substance. It is fairly soluble in hot alcohol, from which it crystallises, on cooling, in small, rectangular plates which run

together to form short, thick needles if deposited slowly. It is very little soluble in cold alcohol and ether, and practically insoluble in water. It is readily volatile in steam. As might be expected, it shows no basic properties.

Conversion of Tetrachlorisonicotinic Acid into Trichloramidopyridine and Dichlorodiamidopyridine.—If tetrachlorisonicotinic acid be heated with excess of ammonia solution in sealed tubes to a temperature of 150—160° for 1 to 2 hours, carbon dioxide is given off, and one chlorine atom is replaced by the amido-group thus :

If ammonia sp. gr. 0.880 be used, and the temperature raised to 200°, a second chlorine atom is replaced by the amido-group,

Trichloramidopyridine.—The crystals which separated out on cooling the tubes, after heating at 150—160°, were filtered by means of a filter-pump, and recrystallised once from alcohol, they then melted at 158—160°.

I. 0.1336 gave 0.1500 CO_2 and 0.0190 H_2O . C = 30.61 ; H = 1.60 %.

II. 0.0904 ,, 0.1990 AgCl. Cl = 54.27 per cent.

III. 0.1023 ,, 0.2250 AgCl. Cl = 54.40 ,,

$\text{C}_5\text{Cl}_3(\text{NH}_2)\text{HN}$ requires C = 30.47 ; H = 1.53 ; Cl = 54.00 per cent.

This substance is readily soluble in hot alcohol, moderately soluble in cold, fairly soluble in acetone and hot glacial acetic acid, very little soluble in water and dilute acids, and insoluble in dilute alkalis. It is moderately soluble in ether, from which it crystallises on evaporation in colourless needles an inch or more in length. It does not form a platinum salt, and, indeed, shows no basic properties. The position occupied by the amido-group has not been determined.

Dichlorodiamidopyridine.—This compound is the principal product of the reaction after heating at 200° for some hours with concentrated ammonia, but there is always a small quantity of trichloramidopyridine present unless the heating has been long continued. The latter may be removed by several recrystallisations from alcohol or moderately dilute acetone. A specimen of the recrystallised substance melting at 200° was analysed.

I. 0.0975 gave 0.1200 CO_2 and 0.0237 H_2O . C = 33.57 ; H = 2.70 %.

II. 0.1370 ,, 0.2200 AgCl. Cl = 39.70 per cent.

III. 0.0852 ,, 17 c.c. of nitrogen at 21° and 760 mm. N = 23.30 per cent.
 $\text{C}_5\text{Cl}_2(\text{NH}_2)_2\text{HN}$ requires C = 33.76 ; H = 2.81 ; Cl = 39.80 ; N = 23.63 %.

This compound is somewhat less soluble in alcohol than the preceding one, readily soluble in acetone, slightly in ether, and sparingly

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soluble in hot water, from which it crystallises on cooling in fine, colourless needles. It is insoluble in alkalis and only very little soluble in dilute acids. If to its solution in alcohol platinum chloride be added, the double platinum salt separates out in orange-coloured plates which, when air-dried, contain no water of crystallisation.

0.1366 gave on ignition 0.0340 Pt. Pt = 25.02 per cent.

0.0708 " " 0.0179 Pt. Pt = 25.28 "

$(C_5H_5Cl_2N_3)_2H_2PtCl_6$ requires Pt = 25.45 per cent.

So far, the trichlorinated acid has not been isolated. If formed at all, it must bear but a small proportion to the quantity of tetrachloris-nicotinic acid produced, and must be sought for in the residues yet to be examined. The whole subject is still under investigation, the results of which will be offered to the Society in due course.

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