XLV.—*The Chlorine Derivatives of Pyridine. Part I.*

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INTRODUCTION.

ALTHOUGH, according to our present views, there are nineteen possible
chlorine substitution derivatives of pyridine, comparatively few of
them have hitherto been prepared, and these have practically all been
obtained by indirect methods.   Moreover, when we come to consider
the compounds whose constitution is established, this small number is
still further restricted.

Briefly summarised, our knowledge of this class of compounds is
limited to the following.

1. a-Monochloropyridine, obtained from a-hydroxypyridine (Pech-
mann and Baltzar, *Ber.*, **24**, 3150).

2. β-Monochloropyridine, obtained from pyrroline (Ciamician and
Dennstedt, *Gazzetta*, **11**, 224, 300).

3. γ-Monochloropyridine, obtained from γ-oxypyridine (Haitinger
and Lieben, *Monats.*, **6**, 315).

4. A dichloropyridine, melting point $66-67°$, obtained from barium
pyridinesulphonate, the position of the chlorine atoms being un-
known (Königs and Geigy, *Ber.*, 1884, **17**, 1833).

5. A trichloropyridine, melting point $49-50°$, also obtained from
the barium salt of pyridinesulphonic acid.   One of the chlorine atoms
is said to occupy the a-position, the places of the others being unknown
(Königs and Geigy, *loc. cit.*).

6. A trichloropyridine (?) (the note of interrogation is Seyffürth's),
melting point $64-65°$.   This was obtained in too small a quantity to

be thoroughly examined. The orientation is unknown (Seyffürth, *J. pr. Chem.*, 1886, **2**, 261).

To these may be added.

7. A tetrachloropyridine, in which the chlorine atoms occupy the $a\beta a'\beta'$ positions, and

8. Pentachloropyridine, both obtained by the authors from citrazinic acid (Trans., 1897, **71**, 1068).*

Keiser (*Am. Chem. J.*, 1886, **8**, 308) has obtained a compound which he describes as a " hydrochlorate of di-chlor-pyridine " by the action of dry chlorine on dry pyridine, but, as will be shown later, this is not the hydrochloride of dichloropyridine, but a trichloropyridine.

In studying the action of phosphorus pentachloride on citrazinic acid, it was noticed that the hydrogen atoms of the nucleus were displaced by chlorine with the greatest ease by means of this reagent, even at atmospheric pressure. This suggested that an attempt should be made to chlorinate pyridine directly on similar lines. Königs and Geigy (*loc. cit.*) made some efforts to solve this problem, but their results do not appear to have been encouraging, and, so far as we are aware, nothing has been published.

The present communication deals exclusively with the interaction of phosphorus pentachloride and pyridine and some of the properties of the products thus obtained, the derivatives of these products being reserved for a future paper.

These products are :

1. Dichloropyridine melting at 87—88°
2. Trichloropyridine   ,,   49—50
3.   ,,   ,,   71—72
4.   ,,   ,,   67—68
5. Tetrachloropyridine   ,,   90—91
6.   ,,   ,,   21—22
7.   ,,   ,,   74—75
8. Pentachloropyridine   ,,   123—124
9. An oil, which forms a solid compound with mercuric chloride.
10. An oil which does not combine with mercuric chloride.

Thus the series above the trichlorinated derivatives is complete, and it is hoped that from (9) and (10) the remaining trichlorinated compounds, or some of them, may be isolated.

In these experiments, it was noticed that, although the higher chlorinated members of the series were abundant, the lower ones were

* On the authority of Anschütz, a verbal statement was made by Kekulé to the German Chemical Society that he had obtained the last two compounds. The memoir on the subject was never written, but a private communication to Anschütz finds place in his edition of Richter's " Organische Chemie," 1896. No description beyond the melting points is given, only one of which approximates to anything described by us.

obtained in very small quantity ; nor was it found possible to prevent
this, and all attempts to prepare the lower members, either by employ-
ing a lower temperature or a smaller proportion of phosphorus penta-
chloride, merely resulted in no action taking place at all in the
former case, and, in the latter, in a smaller yield of practically the
same products.

EXPERIMENTAL.

The first efforts in this chlorination were made by boiling pyridine
with a saturated solution of phosphorus pentachloride in phosphorus
oxychloride in a reflux apparatus, a method which had been so
efficacious in the case of citrazinic acid, but it was found that even
after boiling continuously for a fortnight, the original amount of penta-
chloride had diminished only very slightly, and on pouring the contents
of the flask into cold water and distilling in a current of steam the
yield of crude oil was very small.

After many attempts, the method finally adopted was to heat dry
pyridine with 10 times its weight (approximately 4 mols.) of phos-
phorus pentachloride in sealed tubes to a temperature of $210-220°$
for from 15 to 20 hours, the tubes being frequently opened to allow
the escape of hydrogen chloride. At this temperature, the pressure
of gas in the tubes soon becomes very great, and loss from bursting
tubes is almost unavoidable, whilst if a lower temperature is em-
ployed, the reaction is very slow and the operation tedious. The
contents of the tubes were poured into cold water and distilled in a
current of steam, when a brownish oil of a peculiar aromatic odour
came over ; this was separated from the watery part of the distillate
and allowed to stand overnight, when a small quantity of dense, hard
crystals of pentachloropyridine separated. When nothing further
came over with the steam, the contents of the flask were filtered from
a small quantity of tarry matter, excess of lime was added, and the
mixture again distilled in steam. The distillate was acidified with
strong hydrochloric acid, concentrated, and excess of soda added,
which caused the separation of a dark brown liquid ; this was removed,
dried over soda, and distilled. The amount of material thus obtained
was too small to investigate, but since it contained a fair proportion of
chlorine, it seems probable that some of the lower chloropyridines were
present.

The tarry residue, which is slightly soluble in alcohol and ether,
was slowly heated to $200°$ under diminished pressure, when it frothed
up violently, evidently decomposing, whilst practically nothing distilled
over. It was not further examined.

Isolation of the Products.

The crude oil, filtered from the crystals of pentachloropyridine, was dissolved in methylated spirit, and a solution of mercuric chloride in alcohol added. On cooling, a copious crop of crystals separated ; These were collected, using the pump, and more alcoholic mercuric chloride added, the operation being repeated until there was no further precipitate. The solution was then largely diluted with water, when that part of the oil which remained unacted on by the mercuric chloride was thrown down, together with a small quantity of the mercuric compound. This was drained by the aid of the filter pump, and the oil, separated from the dilute alcohol, was washed repeatedly with a saturated solution of sodium chloride to remove the last traces of mercuric chloride, and finally with distilled water. It was then dried in a vacuum over sulphuric acid, and distilled from an oil bath in a gentle stream of air at a pressure of 16—20 mm.

The mercuric compounds were recrystallised several times from alcohol, but, as a preliminary experiment had shown that it was hopeless to attempt a separation from such a complex mixture by recrystallisation alone, they were distilled in a current of steam from a saturated solution of sodium chloride, by which means the oil was liberated from the mercuric chloride. The same decomposition takes place on merely boiling with water, but is much hastened by the addition of sodium or potassium chloride. The last portions of the distillate, consisting of pentachloropyridine, solidified in the condenser. The pentachloropyridine, being very soluble in the crude oil, is thrown down in part on adding mercuric chloride, which removes a large portion of the principal solvent, and the pentachloropyridine cannot afterwards be easily separated from the mercuric compound by re-crystallisation from alcohol, but, being less volatile than the other products, is chiefly found in the last portions of the steam distillate. It is therefore expedient to collect these separately.

The oil thus collected was separated from the watery part of the distillate, dried in a vacuum over sulphuric acid, and distilled from an oil bath in a gentle stream of air at a pressure of 16 mm. of mercury, the receiver being changed at intervals of 5°. The first portions began to distil over below 100°, and the distillation was practically complete at 140°; the portions thus collected were again fractionated separately as before, but were, however, far from being pure. Each was placed in a freezing mixture of ice and salt, when all became solid or semi-solid, and were in turn drained at the pump, the temperature meanwhile being allowed to rise slowly. This operation was repeated with each fraction as long as any solid residue was left on the filter

plate after it had attained the temperature of the laboratory.   In this way, successive crops of crystals were obtained which were recrystallised from alcohol separately until the melting point of each was constant.   They were then examined with the following results.

The crystals obtained from the fraction boiling below 100° at 16 mm. pressure were found to be a mixture of the two trichloropyridines melting at 71—72° and 49—50° respectively, the former being small in amount.

The fraction boiling between 100° and 105° yielded a trichloropyridine melting at 49—50°

,,	,,	,,	105° ,, 110° the same, in smaller amount.
,,	,,	,,	110° ,, 115° the same, in very small amount.
,,	,,	,,	115° ,, 120° A tetrachloropyridine. melting at 21—22°.
,,	,,	,,	120° ,, 125° the same, together with some pentachloropryidine.

The fractions boiling above 125° all yielded pentachloropyridine ; in each case there was an oily residue, which is under further examination.

The oil which had been freed from everything which forms a solid compound with mercuric chloride was in turn fractionated.   This operation was repeated on each portion separately, and again on the fractions thus obtained, the receiver, as before, being changed in every case at intervals of 5°.   The liquid began to distil at about 100°, under a pressure of 16—20 mm., and the operation was practically complete at 140°.

These fractions, like the former, were not pure products, the first two portions and the last partially solidifying on standing, and all depositing crystals on being placed in a mixture of ice and salt.

Since the number of compounds contained in each of these oils is obviously considerable, whilst the range of their boiling points is comparatively small, it is not surprising that such imperfect separation should be effected by these means, and it was evident that much larger quantities of the oil than had been prepared would be necessary before satisfactory separation could be obtained by the method of fractional distillation alone.

The crystals from each fraction were recrystallised from alcohol with the results stated below.

The fraction distilling below 105°, between 105° and 110°, and between 110° and 115° each yielded a dichloropyridine melting at 87—88°.

The fraction distilling at 115—120°, and 120—125°, a trichloropyridine melting at 67—68°.

The fraction distilling at 125—130°, a tetrachloropyridine melting at 90—91°.

The fraction distilling at 130—135°, a tetrachloropyridine melting at 74—75°, together with a little pentachloropyridine.

The fraction distilling above 135° yielded pentachloropyridine.

As in the former case, from each portion there was a residual oil which remained liquid at temperatures above 0°. These are being further examined.

DESCRIPTIVE.

Dichloropyridine, melting at 87—88° *(uncorr.)*.—This was obtained in the manner described above from the first part of the distillate, which does not form an additive product with mercuric chloride. After several recrystallisations from 50 per cent. alcohol, it was obtained in rhomboidal plates of a glistening, satiny appearance, whose melting point was not changed by further recrystallisation. Analysis gave the following numbers.

I. 0·0888 gave 0·1308 CO_2 and 0·0154 H_2O. C = 40·18; H = 1·92.

II. 0·1032 ,, 0·1520 CO_2 ,, 0·0180 H_2O. C = 40·17; H = 1·93.

III. 0·0937 ,, 8·0 c.c. of nitrogen at 14° and 763 mm. N = 10·06.

IV. 0·1303 ,, 0·2550 AgCl. Cl = 48·44.

$C_5Cl_2H_3N$ requires C = 40·52 ; H = 2·02 ; Cl = 47·97 ; N = 9·46 per cent.

This dichloropyridine is very soluble in ether, benzene, light petroleum, chloroform, and hot alcohol ; moderately so in cold alcohol, and insoluble in water. Strong mineral acids dissolve it readily on warming, and from these it is reprecipitated by diluting or neutralising. It does not form a double salt with platinic chloride.

Trichloropyridine, melting at 49—50° *(uncorr.)*.—This was obtained from the crude compound with mercuric chloride described above, and was found in those parts of the distillate which came over between 100° and 120° (at 16 mm.). It crystallised from hot 50 per cent. alcohol in broad, flat needles, which melted constantly at 49—50°, and gave the following numbers on analysis.

I. 0·2787 gave 0·3333 CO_2 and 0·0271 H_2O. C = 32·62 ; H = 1·08.

II. 0·2468 required 40·5 c.c. $N/10AgNO_3$*. Cl = 58·09.

$C_5H_2Cl_3N$ requires C = 32·87. H = 1·09 ; Cl = 58·35 per cent.

* This chlorine determination, and some of the following ones, were made by fusing the substance with a mixture of equal weights of sodium and potassium carbonates, in the manner described by Schiff (*Ann.*, 1879, **195**, 293), subsequently dissolving in nitric acid, and estimating the soluble chlorides, with standard silver nitrate and ammonium thiocyanate (Volhard's method). If the fusion had been cautiously made, it was found that trustworthy results were obtained. The method has the advantage of being most expeditious, the whole operation requiring not more than half an hour.

This substance, which does not yield a compound with platinic chloride, is very soluble in ether, chloroform, acetone, benzene, and hot alcohol, moderately so in light petroleum and cold alcohol, and practically insoluble in water.   A comparison of the properties, so far as they have been described, showed that it was identical with the trichloropyridine obtained by Königs and Geigy (*loc cit.*) by the action of phosphorus pentachloride on the barium salt of pyridinesulphonic acid.

In the present work, the yield of this product was greater than that of any of the others, with the exception of pentachloropyridine.   It is plain, therefore, that the previous introduction of sulphonic groups into the pyridine nucleus is not necessary for its preparation.

Trichloropyridine, melting at 71—72° (*uncorr.*).—This was obtained from the compound with mercuric chloride, and was found in that part of the oily distillate which came over below 100° (at 16 mm.).   It was found that when this compound was especially sought, it was more expedient to separate it from the other products of the reaction by distilling the first crop of the recrystallised mercuric compound, obtained as described above, separately, from a saturated solution of sodium chloride, the receiver being changed as soon as the distillate no longer solidified on cooling.   Recrystallised from 50 per cent. alcohol, this compound was obtained in silky needles which became opaque on exposure to the air.   These needles melted constantly at 71—72°, and gave the following numbers on analysis.

I. 0·1243 gave 0·1515 CO_2 and 0·0120 H_2O. C = 33·24 ; H = 1·08.
II. 0·1123   ,,   0·2660 AgCl.   Cl = 58·61.
  $C_5Cl_3H_2N$ requires C = 32·93 ; H = 1·09 ; Cl = 58·35 per cent.

This trichloropyridine is very soluble in chloroform, ether, benzene, acetone, light petroleum, and hot alcohol, and more sparingly in cold alcohol ; it is dissolved to a slight extent by boiling water, from which it crystallises on cooling in long, silky needles.   Strong hydrochloric, nitric, and sulphuric acids dissolve it readily, and from these it is reprecipitated on diluting or neutralising.

If to its alcoholic solution an alcoholic solution of mercuric chloride be added, the double compound is obtained in long, fine needles, which are insoluble in water and only very sparingly soluble in cold alcohol, although hot alcohol and ether dissolve them readily.   These needles melt at 168—170° (uncorr.), and from the following mercury and chlorine determinations have the composition expressed by the formula $(C_5H_2Cl_3N)_2,HgCl_2$.

I. 0·4020 gave 0·1247 Hg and 0·7220 AgCl. Hg = 31·02 ; Cl = 44·46. Calculated for the above formula, Hg = 31·49 ; Cl = 44·46 per cent.

Treated with cadmium chloride in a similar way, a compound is ob-

tained which crystallises in rosettes of short, thick needles, which are insoluble in water and nearly so in cold alcohol.

If to the alcoholic solution of this trichloropyridine a solution of chloroplatinic acid be added, a crystalline, yellow precipitate is obtained on long standing in the cold, or immediately on boiling; this, when dried in the air, contains no water of crystallisation, and, from the results of a platinum determination, seems to have the composition represented by the formula $(C_5Cl_3H_2N)_2PtCl_4$, as the following numbers show.

I. 0·2340 gave 0·0658 Pt. Pt = 28·12.

Calculated for the above formula, Pt = 27·66 per cent., whilst the formula $(C_5Cl_3H_2N)_2,H_2PtCl_6$ requires Pt = 25·13 per cent.

This compound with platinic chloride is practically insoluble in water and alcohol. From it, the base is most conveniently re-obtained by subjecting it to a gentle heat in a stream of dry hydrogen. It was not found possible to recover it by the action of aqueous hydrogen sulphide.

Trichloropyridine melting at 67—68° *(uncorr.).*—This was obtained from that portion of the crude oil which did not form a compound with mercuric chloride, and was frozen out from the fractions boiling between 115° and 125° (at 16—20 mm.). It is very soluble in hot alcohol, from which it crystallises on cooling in long, somewhat flattened needles; it is fairly soluble in cold alcohol, and, indeed, shows the same general solubility in the ordinary organic solvents as the previously described trichloropyridines. Although readily soluble in hot, strong mineral acids, it crystallises out for the greater part, on cooling, and does not appear to be quite so basic as the others. It is readily distinguished and separated from them by its forming no additive products with either cadmium chloride, mercuric chloride, or platinic chloride.

I. 0·2535 gave 0·3037 CO_2 and 0·0260 H_2O. C = 32·67; H = 1·14
II. 0·1830 required 30·2 c.c. of $N10AgNO_3$. Cl = 58·41.
$C_5Cl_3H_2N$ requires C = 32·87; H = 1·09; Cl = 58·35 per cent.

Tetrachloropyridine, melting at 90—91° *(uncorr.).*—The fraction of the oily distillate boiling between 125° and 130° (at 16—20 mm.), obtained from that portion of the original oil which forms no compound with mercuric chloride, on being recrystallised several times from methylated spirit, had a constant melting point, 90°—91°, and gave the following numbers on analysis.

I. 0·1126 gave 0·0058 H_2O and 0·1144 CO_2. C = 27·70; H = 0·57.
II. 0·1000 required 18·45 c.c. $N/10AgNO_3$; Cl = 65·26.
C_5Cl_4HN, requires C = 27·66; H = 0·46; Cl = 65·44 per cent.

G G 2

Whilst closely resembling the trichloropyridines in general solubility, it is dissolved to a less extent by organic solvents, and is quite insoluble in water. In crystalline form and general properties, it agrees entirely with the tetrachloropyridine obtained by the authors from citrazinic acid (Trans., 1897, **71**, 1081), and is obviously identical with it. Hence its structure must be represented by the formula

<div align="center">
H
C
ClC   CCl
ClC   CCl
N
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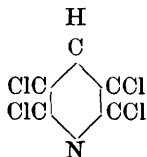
Tetrachloropyridine, melting at 21—22° (*uncorr.*).—This was obtained from the compound with mercuric chloride, and was found in that portion of the distillate boiling between 120° and 125° (at 16 mm.). It separates from this oily distillate, on standing in a cold place, in transparent, massive crystals, which readily melt at the temperature of the hand. From alcoholic solution, at temperatures below 20°, it crystallises in needles, which, if the alcohol be allowed to evaporate slowly, grow to a large size. It is very soluble in ether, chloroform, benzene, and the usual organic solvents, very sparingly so in strong hydrochloric acid, and insoluble in water. It does not yield a compound with cadmium chloride or chloroplatinic acid, although it very readily unites with mercuric chloride, forming an easily crystallisable and well-defined salt. The following numbers were obtained on analysis.

I. 0·1387 gave 0·1387 CO_2 and 0·0043 H_2O.   C = 27·27 ; H = 0.35.

II. 0·1799 required 33·2 c.c. $N/10 AgNO_3$; Cl = 65·28.

C_5Cl_4HN requires C = 27·66 ; H = 0·46 ; Cl = 65·44 per cent.

Tetrachloropyridine, melting at 74—75° (*uncorr.*).—This was contained in the second of the oils described above, and was frozen out from the fraction boiling between 130° and 135° (at 16—20 mm.). The yield was very small. On recrystallising from alcohol several times, the substance melted sharply at 74—75°, and this melting point was not changed by subsequent recrystallisation. After three such purifications, it gave the following numbers on analysis.

I. 0·1537 gave 0·1580 CO_2 and 0·0050 H_2O.   C = 28·04 ; H = 0·38.

II. 0·1070 required 19·7 c.c. $N/10 AgNO_3$.   Cl = 65·12.

C_5Cl_4HN requires C = 27·66 ; H = 0·46 ; Cl = 65·44 per cent.

It crystallises from 50 per cent. alcohol in thin, elongated, rectangular plates. It is very soluble in ether and the usual organic solvents, but insoluble in water and acids. It forms no additive compound with mercuric chloride, cadmium chloride, or chloroplatinic acid.

Of the three possible tetrachloropyridines, it has been shown above that the compound melting at 90—91° has the constitution represented by the formula I.

I. II. III.
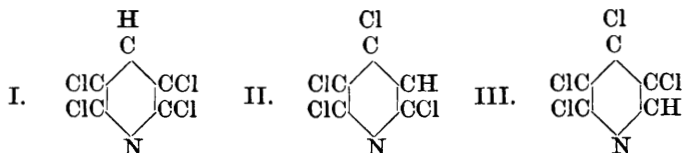
And the remaining two must, therefore, be represented by the formulæ II and III. As to which of the two tetrachloropyridines described above these formulæ respectively belong is an open question, but, so far as our present knowledge extends, it is probable that the compound melting at 74—75° has the constitution represented by formula II, whilst that melting at 21—22° is represented by formula III.

Pentachloropyridine, melting at 123—124°. This is
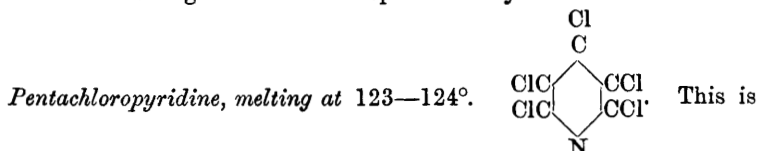
by far the most abundant and most easily isolated of the products of the action of phosphorus pentachloride on pyridine; a portion of it separates from the crude oil on standing, and the remainder is found in the last fractions of both distillates described above. Although volatile in steam, it is much less so than any of the other products of the reaction, and, consequently, in the distillations with steam, was always found chiefly in the last portions which came over.

From boiling alcohol, it crystallises in cubes, or modifications of cubes, frequently in skeleton forms resembling ammonium chloride. It is dissolved by the same organic solvents as are the tetrachloropyridines, but to a much smaller extent. The following numbers were obtained on analysis.

I. 0·1460 gave 0·1275 CO_2 and 0·0015 H_2O. C = 23·81 ; H = 0·10.
II. 0·2450 ,, 0·2100 CO_2 ,, 0·0005 H_2O. C = 23·42 ; H = 0·02.
III. 0·2307 ,, 10·7 c.c. moist nitrogen at 16·5° and 766 mm. N = 5·44.
IV. 0·1220 ,, 0·3470 AgCl. Cl = 70·40.
    C_5Cl_5N requires C = 23·90 ; Cl = 70·51 ; N = 5·58 per cent.

Pentachloropyridine thus prepared coincides in every way with that obtained by the authors from citrazinic acid (*loc. cit.*).

In conclusion, the authors desire to express their thanks to Mr. H. Jackson, B.A., B.Sc., for his assistance in the analyses.

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