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The partially opaque brown solution obtained by mixing *strong* solutions of nickel and cobalt might, I think, be used for making standards for the purposes of colorimetical analysis. For instance, the brown solution mixed with a few drops of potassic bichromate cannot be distinguished from Nesslerized ammonia. Probably the tests used to compare the solutions of steel in Eggertz's process for the estimation of carbon might be made in a similar manner. They would have the advantage of being permanent.

After the determination of the copper and nickel by the above methods, the zinc is obtained by difference. If lead is present in the alloy, it is separated by the evaporation with sulphuric acid.

III. *On Picoline and its Derivatives.* By WILLIAM RAMSAY, PH.D., *Tutorial Assistant of Chemistry in the Glasgow University.*

IN my last memoir (Phil. Mag. Oct. 1877, p. 251) I mentioned that on oxidizing lutidine with potassium permanganate an acid, or a mixture of acids, was obtained, the silver salt of which contained 45.82 per cent. of silver, corresponding to a molecular weight of 257, assuming the acid to be dibasic. Since that time I have ascertained that the silver salt of the acid giving the above percentage of silver is not a pure compound, but a mixture of an acid and a neutral salt of at least two acids of the same formula.

Oxidation of Lutidine.—About 100 grams of lutidine, C_7H_9N , boiling from 152° to 155° C., were oxidized with potassium permanganate in a tinned iron vessel in precisely the same manner as that described for picoline. After complete oxidation the manganese oxide was removed by filtration, and the filtrate was distilled to recover unoxidized lutidine; less had escaped oxidation than was the case with picoline, probably on account of its higher boiling-point, as well as of its being more easily oxidized than its lower homologue. The highly alkaline solution of the products of oxidation was then evaporated to dryness, and digested with absolute alcohol by means of an apparatus which permitted the hot alcohol continually to drop on the mixture of salts. After three or four days the insoluble residue consisted of nearly pure potassium carbonate, the organic salts having dissolved in the alcohol. The alcohol was then removed by evaporation. The residue had an extremely persistent bitter taste, almost comparable with that of strychnine. It was

* Communicated by the Author.

dissolved in water, neutralized, and precipitated while hot with lead nitrate, less being used than was necessary to combine with all the acid present. The precipitate was white and flocculent. When decomposed with sulphuretted hydrogen it yielded a liquid from which, on concentration, dicarbopyridenic acid separated out in its usual form of hair-like needles, and when purified by crystallization from water was obtained in its two other crystalline forms, viz. naphthalene-like plates and short thick crystals. Its purest form, the thick crystals were converted into the silver salt, after determination of the water of crystallization. It contained 10.94 per cent. of water; and the silver salt, on ignition, was found to contain 56.57 per cent. of silver. Dicarbopyridenic acid, in the same crystalline form, crystallizes with 9.83 per cent., or one molecule of water; and its silver salt contains 56.69 per cent. of silver. The silver salt was almost completely insoluble in boiling water, and was gelatinous and very bulky. The filtrate from a boiling solution deposited a few *amorphous* flocks on cooling.

The calcium salt, prepared by addition of calcium chloride to a hot solution of the ammonium salt, crystallized in thin plates, usually grouped together in masses. It contained 17.47 per cent. of water, which it lost at 150°, and the anhydrous salt 19.96 per cent. of calcium. $C_7H_3NO_4Ca \cdot 2\frac{1}{2}H_2O$ requires 18.00 per cent. of water, and the anhydrous salt 19.51 per cent. of calcium. I had not obtained the salt crystallized with water before; that described in my last memoir was anhydrous. On evaporation of the solution of the calcium salt, needles were precipitated which were anhydrous and on analysis yielded 19.01 per cent. of calcium. The formula of this acid is certainly $C_7H_3NO_4$; and from its crystalline forms it appears to be identical with the dicarbopyridenic acid discovered by Professor Dewar. The yield was somewhat more than ten grams. Whether it is derived from lutidine by oxidation, or from a possible impurity of picoline in the lutidine, I am unable to decide.

The mother liquor of the dicarbopyridenic acid contained a mixture from which an acid crystallizing in groups of acicular crystals radiating from a common centre was deposited, but not in sufficient quantity for complete examination. From consideration of its crystalline form it is probably identical with one shortly to be described.

The remainder of the solution of potassium salts, from which the dicarbopyridenic acid was precipitated in combination with lead, was treated with excess of lead nitrate. A copious flocky precipitate came down, from which the acids were

liberated as usual by treatment with sulphuretted hydrogen. The lead sulphide was well washed with boiling water; the filtrate and washings were evaporated; and on cooling, a white substance deposited mixed with spear-like crystals. After a long series of fractional crystallizations from water three distinct acids were obtained, of which I have investigated two; the third was unfortunately lost. As these two have the same percentage composition as Dewar's dicarbopyridenic acid, I propose to name that acid *α-dicarbopyridenic acid*.

The white substance, mentioned above, consisted chiefly of a sparingly soluble acid, which I shall call *β-dicarbopyridenic acid*.

The acid depositing from the mother liquor of the *β*-acid, in groups of spear-like crystals, shall be distinguished as *γ-dicarbopyridenic acid*.

β-Dicarbopyridenic acid, $C_7H_5NO_4$.—This acid, as has already been mentioned, separates out as a white crystalline powder when its aqueous solution is allowed to cool. It was purified by repeated crystallization from water. When viewed under the microscope it presents the appearance of truncated octahedra, grouped together in masses. The acid dried at 100° decomposes at $244\text{--}245^\circ$, frothing up, and giving off gas. It is very sparingly soluble in water; 0.2 gram, dissolved by boiling with about 200 cubic centimetres of water, crystallized out after standing for some hours. It is rather more soluble in alcohol, and dissolves sparingly in ether. When heated on platinum-foil it melts, effervesces, and gives off a smell resembling that of pyridine. It was analyzed, with the following results:—

I. Taken, 0.4012 gram of air-dried acid. Loss at 100° , 0.0532 gram; CO_2 obtained on combustion, 0.6611 gram; H_2O , 0.1045 gram.

II. Taken, 0.4233 gram of air-dried acid. Loss at 100° , 0.0560 gram; CO_2 , 0.6935 gram; H_2O , 0.1025 gram.

		Calculated for	
		$C_7H_5NO_4 \cdot 1\frac{1}{2}H_2O$.	
I.	II.	13.91 per cent.	
H_2O ...13.26 per cent.	13.20 per cent.		
		For $C_7H_5NO_4$.	
C51.81	51.49	50.30 per cent.	
H 3.33	3.10	3.00	

To ascertain if this acid, when heated, splits up into carbonic anhydride and pyridine, thus,

its vapour-density was taken at the boiling-point of sulphur ($446^\circ C.$) by means of the beautiful arrangement devised by

Victor Meyer, and described in the *Berichte der deutschen chemischen Gesellschaft*, ix. p. 1216.

Results. Taken, 0·0151 gram.

Weight of empty bulb.....	11·6 grams.
Weight of bulb full of alloy...	199·6 „
Weight of bulb after heating.	58·3 „
Height of barometer	750 millims.
Height of alloy in tube above level in bulb.....	60 „

The formula given by Meyer (*Berichte*, 1877, p. 2070),
S. 1543500

$$D = \left[P + \frac{2}{3}p \right] \left[\left(\frac{a}{9\cdot608} \right) 1\cdot01 - \frac{r}{9\cdot158} \right],$$

where D is the vapour-density compared with air;

S the weight of substance taken;

P the height of the barometer;

p the height of alloy in tube, above level in bulb;

a the amount of alloy used;

9·608 the spec. grav. of the alloy at 100°;

9·158 „ „ „ 446°;

r the weight of alloy remaining in the bulb after the operation is over.

Substituting the numbers found,

$$D = \frac{0\cdot0151 \times 1543500}{(750 + 40) \left\{ \left(\frac{188\cdot0}{9\cdot608} \right) 1\cdot01 - \left(\frac{46\cdot7}{9\cdot158} \right) \right\}} = 2\cdot06,$$

or, compared with hydrogen, 29·22. The molecular weight of C_5H_5N is 79, and of $2CO_2$ 88. Adding these together and dividing by 6 we get 27·8. It is therefore clear that the above equation is correct, and that β -dicarbopyridenic acid decomposes into pyridine and carbonic anhydride at the boiling-point of sulphur.

Reactions of β -Dicarbopyridenic acid.—A cold saturated solution gave no precipitate with the following salts:—Ca Cl₂, Ba Cl₂, Ba H₂ O₂, Mg SO₄, Zn SO₄, Cd Cl₂, Ni (NO₃)₂, Co (NO₃)₂, Hg Cl₂, alum, chrome-alum, Mn Cl₂, Sn Cl₄. With ferric chloride it gave a white flocculent precipitate soluble in hydrochloric acid; the precipitate, on addition of ammonia, turned reddish-brown in colour, and apparently changed to ferric hydrate. With mercurous nitrate it gives a bulky white precipitate; with copper sulphate a light blue precipitate, turning darker on drying; with lead nitrate a heavy white crystalline precipitate after some time; and with silver nitrate white crystalline flocks very sparingly soluble in water.

Ferrous sulphate gives a red coloration exactly resembling that produced by α -dicarbopyridenic acid.

Salts of β -Dicarbopyridenic acid.

Ammonium salt.—This salt was prepared by evaporating the acid to dryness with aqueous ammonia. It is moderately soluble, and crystallizes from a hot solution in needles.

Synthesis. Taken, 0.4025 gram of acid.

Gain, on evaporation with ammonia, 0.0925 gram,
= 18.68 per cent. NH_3 . Calculated, 16.91 per cent.

Calcium salt.—Prepared by adding calcium chloride to a hot solution of the ammonium salt. It forms very thin microscopic needles, sparingly soluble in water.

Analysis. Taken, 0.3190 gram.

Loss at 150° , 0.0483 gram, = 15.14 per cent. H_2O .

Ca CO_3 0.1320 gram, = 16.55 per cent. Ca.

Calculated for $\text{C}_7\text{H}_3\text{NO}_4\text{Ca} \cdot 2\text{H}_2\text{O}$ = 14.93 per cent. H_2O .
16.91 per cent. Ca.

Iron salt.—The white flocculent precipitate obtained by adding ferric chloride to the acid was analyzed, after being dried at 150° .

Taken, 0.1020 gram.

Fe_2O_3 , 0.0304 gram, = 0.0213 gram Fe, or 20.86 per cent.

Calculated for $(\text{C}_7\text{H}_3\text{NO}_4)_3\text{Fe}_2 \dots \text{Fe}$, or 18.45 per cent.

The salt is probably basic. On addition of ammonia to the moist salt it is converted into ferric hydrate.

Lead salt.—A white crystalline precipitate, very sparingly soluble in water, prepared from the ammonium salt with lead nitrate.

Taken 0.4165 gram.

Loss at 150° 0.0367 gram, = 8.81 per cent. H_2O .

Lead sulphate 0.3117 gram, = 51.14 per cent. Pb.

Calculated for $\text{C}_7\text{H}_3\text{NO}_4\text{Pb} \cdot 2\text{H}_2\text{O}$, 8.82 per cent. H_2O .
50.73 per cent. Pb.

Silver salt.—The silver salt of β -dicarbopyridenic acid, when precipitated by adding silver nitrate to a solution of the acid, contains 43.56 per cent. of silver, and is probably a mixture of neutral and acid salt. It was this which led me, in my last paper (Phil. Mag. Oct. 1877), to state that the molecular weight of the acids from lutidine was higher than that of the picoline acids. Two analyses of the silver salt prepared in this manner showed it to contain 43.56 per cent. and 44.05 per cent. of silver. When prepared by adding silver nitrate to the ammonium salt, it has the formula $\text{C}_7\text{H}_3\text{NO}_4\text{Ag}_2$, as the following analyses prove:—

I. Taken...0.3247 gram.

Silver...0.1825 gram, = 56.23 per cent.

II. Taken...0.3590 gram.

Silver...0.2031 gram, = 56.57 per cent.

$C_7H_5NO_4$ Ag_2 contains 56.69 per cent. of silver.

This silver salt is not nearly so bulky as that of α -dicarbopyridenic acid, but comes down in flocks. It is very sparingly soluble in hot water, and crystallizes out on cooling in tufts of microscopic needles. When heated it evolves the usual smell of pyridine. It does not blacken on exposure to light.

Methyl ether.—Prepared by cohobating the silver salt with methyl iodide. It is a very deliquescent white solid, crystallizing in needles, and soluble in water, alcohol, and ether.

Chloride.—One gram of β -dicarbopyridenic acid was distilled from a small retort along with 2.7 grams of phosphoric chloride. The mixture liquefied before heat was applied. The distillate was fractionated. After the oxychloride had distilled over at 110° the thermometer rose rapidly to 269 – 270° , and remained stationary while the chloride distilled. The distillate solidified to a mass of white needles, melting at 49° , and remaining liquid long after the ordinary temperature had been regained.

γ -Dicarbopyridenic acid, $C_7H_5NO_4$.— γ -Dicarbopyridenic acid is much more soluble than the β -acid, and crystallizes out from the mother liquor of the latter. After repeated recrystallization, to free it from the β -acid, and from a still more soluble bitter substance, it was obtained in a pure state. It forms tufts of spear-like crystals springing from a common nucleus. When its solution in hot water is allowed to cool, it crystallizes from nuclei which form on the surface of the liquid. After being dried by exposure to air it has a satin-like lustre. It is moderately soluble in water at 18° ; 100 cubic centimetres of its saturated solution left, on evaporation to dryness, 1.1580 gram of dry acid. It is easily soluble in alcohol and ether. Like its two isomerides, it decomposes when heated into pyridine and carbonic anhydride about 241 – 245° . To ascertain if it decomposed in the same manner as the β -acid, I determined the vapour-density of the mixture of pyridine and carbonic anhydride yielded by the acid at the boiling-point of sulphur. To save space I shall omit the details of the determination, and shall merely state that the number found was 28.4, compared with hydrogen. The number required by the equation

is 27·8. The equation is thus proved to represent what happens when γ -dicarbopyridenic acid is decomposed by heat.

γ -Dicarbopyridenic acid gave the following numbers on analysis:—

I. Taken 0·3075 gram.

Loss at 100°, 0·0475 gram, = 15·44 per cent. H_2O .

The remainder, 0·2600 gram, on combustion gave

CO_2 0·4929 gram, = 51·70 per cent. C.

H_2O 0·0740 gram, = 3·16 per cent. H.

II. Taken 0·3582 per cent. of dry acid.

CO_2 0·6697 gram, = 50·98 per cent. C.

H_2O 0·0974 gram, = 3·02 per cent. H.

III. When dried for one night over sulphuric acid, 0·3085 gram of the acid lost at 100° 0·0380 gram, = 12·31 per cent. of H_2O .

IV. After being dried for a long time in air, 0·2290 gram lost at 100° 0·0235 gram, = 10·26 per cent. H_2O .

$\text{C}_7\text{H}_5\text{NO}_4$ contains 50·30 per cent. C. and 3·00 per cent. H.
 $\text{C}_7\text{H}_5\text{NO}_4 \cdot \text{H}_2\text{O}$ contains 9·73 per cent. H_2O ; with $1\frac{1}{2}\text{H}_2\text{O}$, 13·91 per cent.; and with $2\text{H}_2\text{O}$, 17·78 per cent.

The acid, when dried in air, appears to contain less than two molecules of water, and when dried over sulphuric acid, more than one molecule.

Reactions of γ -Dicarbopyridenic acid.—A cold saturated solution of the acid gave no precipitate with the following salts:— CaCl_2 , even after addition of ammonia; BaCl_2 , MgSO_4 , ZnSO_4 , CdCl_2 , HgCl_2 , $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$. Ferric chloride causes a white flocculent precipitate, soluble in hydrochloric acid, and converted into ferric hydrate by ammonia; mercurous nitrate gives a bulky white precipitate; stannous chloride, a flocculent precipitate; copper sulphate, a whitish blue precipitate; lead nitrate, a white precipitate, which disappears at first, probably owing to formation of an acid salt, but on addition of more lead salt it becomes permanent; silver nitrate gives a white flocculent precipitate, slightly soluble in hot water. Ferrous sulphate gives a blood-red coloration.

Salts of γ -Dicarbopyridenic acid.

Ammonium salt.—White needles.

0·2708 gram of acid gained 0·0575 gram when evaporated with ammonia, = 17·37 per cent. NH_3 .

Calculated for $\text{C}_7\text{H}_3\text{NO}_4(\text{NH}_4)_2$, 16·91 per cent.

Calcium salt.—Prepared by adding calcium chloride to a

hot solution of the ammonium salt. On cooling, small plates crystallized out. After being dried over sulphuric acid it was analyzed.

Taken0.2530 gram.

Loss at 150°...0.0310 gram, = 12.25 per cent. H_2O .

The residue, after conversion into CaCO_3 , weighed 0.1116 gram, = 20.11 per cent. Ca in the dried acid. $\text{C}_7\text{H}_3\text{NO}_4\text{Ca} \cdot 2\text{H}_2\text{O}$ contains 14.93 per cent. H_2O ; and $\text{C}_7\text{H}_3\text{NO}_4\text{Ca}$, 19.51 per cent. Ca.

Silver salt.—The silver salt comes down on addition of silver nitrate to a solution of the acid as a flocculent precipitate, closely resembling that of the β -acid, but not nearly so gelatinous or bulky as that of the α -acid. It is very sparingly soluble in water.

I. Prepared by adding silver nitrate to the acid.

Taken... 0.4475 gram.

Ag 0.2465 gram, = 55.08 per cent.

II. and III. Prepared by adding silver nitrate to the ammonium salt.

Taken... 0.2967 gram.

Ag 0.1673 gram, = 56.38 per cent.

Taken... 0.2305 gram.

Ag 0.1305 gram, = 56.61 per cent.

$\text{C}_7\text{H}_3\text{NO}_4\text{Ag}_2$ contains 56.69 per cent. of silver.

γ -Dicarbopyridenyl chloride.—The chloride was prepared in the usual manner; it boiled at 265°. On exposure to air it turns bluish-violet, and liquefies. It solidifies with great reluctance at the ordinary temperature; and yet its melting-point is at 88–89°. It appears to be much more easily decomposed by water than the chlorides of the α - and β -acids, for it turns liquid at once on treatment with cold water.

Bitter substance.—The bitter substance already mentioned remained in the mother-liquor of the β - and γ -dicarbopyridenic acids. It was partially separated by adding lead or silver nitrates to a *neutral* solution; for both these salts are soluble in acid. The lead salt, when decomposed by sulphuretted hydrogen, gave a solution which was evaporated to a syrup. The bitter substance does not crystallize from water or alcohol; it is extremely soluble in both these solvents, but less easily soluble in ether. It is an acid; its barium salt is a syrup, which dries up to a vitreous mass over sulphuric acid. The acid, as well as its salts, give off the usual smell of pyridine when heated, and also give a red coloration with ferrous sulphate. It was unfortunately lost, after it had been separated in a nearly pure state.

Theoretical considerations.—If the formula proposed for pyridine by Alder Wright, be accepted as correct, six isomeric acids of the formula $C_5H_3N(CO.OH)_2$ are theoretically possible. They are as follows :—

Even if structural formulæ be discarded, it is evident from the analogy between pyridine and chinoline, and benzol and naphthalene, that a number of isomerides are to be expected when two external groups replace two atoms of hydrogen in pyridine. In the case of benzol, three isomerides are known under such conditions; and it is to be expected that pyridine, a more complicated substance than benzol, owing to its containing an atom of nitrogen, should yield more than three isomeric bodies.

Now, that α -, β -, and γ -dicarbopyridenic acids are isomeric, and not identical, is rendered highly probable by the following considerations :—the β -acid is much less soluble in water than the other two modifications; as a rule its salts are much less soluble; its crystalline form is different. Copper sulphate produces no precipitate with the α -acid, whereas the other two

give whitish blue precipitates. With ferric chloride, the β - and γ -acids give a white precipitate, which is changed to ferric hydrate on addition of ammonia; the α -acid gives no precipitate with ferric chloride, even after addition of excess of ammonia, showing that ferric hydrate is soluble in the ammonium salt of the acid. The methyl-ether of the α -acid forms thick isolated crystals; that of the β -acid consists of deliquescent needles. The chloride of the α -acid boils at 284° , that of the β -acid at 269 – 270° , and the chloride of the γ -acid at 265° . The melting-points of the chlorides are respectively:— α , 60.5 – 61° ; β , 49° ; γ , 88 – 89° .

I may anticipate that the acid obtained by oxidation of quinine, and since found to result from the four chief alkaloids of the cinchona-bark, and described by Mr. James Dobbie and myself in the 'Journal of the Chemical Society' for April of the current year, has the formula $C_7H_5NO_4$; but, from its crystalline form and properties, it appears to be distinct from any one of the acids described in this memoir. This subject, however, demands a more complete examination than we have as yet bestowed on it. It is my intention, should it prove different, to publish a table giving the characters of the isomeric acids.

It is also possible that the bitter substance, which, like these acids, gave off pyridine when heated, is also an isomeride; but of this I have no proof.

Dipyridine.—In purifying some oils, afterwards to be described, I obtained a considerable quantity of dipyridine, $C_{10}H_{10}N_2$, and purified it by crystallization from hot water. It presented the appearance of long hair-like white needles. As its vapour-density had only been once determined, it was deemed of sufficient interest to redetermine it, by means of Meyer's apparatus.

The amount taken was 0.0247 gram. The formula by which it was calculated is

$$D = \frac{0.0247 \times 1543500 \times 14.47}{\left\{ 743.5 + \left(36 \times \frac{2}{3} \right) \right\} \left\{ \left(\frac{213.7}{9.608} \right) 1.01 - \left(\frac{119.8}{9.158} \right) \right\}} = 76.63$$

Reference is made to the previous example for the meaning of the numbers. The theoretical density of dipyridine vapour compared with hydrogen is 79.

Isodipyridine.—Some test tubes full of oil, left by the late Professor Anderson, and labelled "Bases forced over from the residue on distillation of dipyridine," were submitted to examination. When heated at the ordinary atmospheric pressure, these bases boiled at a temperature above that at which

mercury boils; they were therefore fractionated in a vacuum produced by a Sprengel's air-pump. After numerous distillations, a fraction was separated, which boiled *in vacuo* at 145–155°, and in air at 295–305°. Two determinations of the vapour-density of this oil gave the following numbers:

I. 81.55; II. 82.80.

These numbers agree sufficiently well with the vapour-density of dipyridine, 79.

On analysis it gave the following results:—

I. Taken, 0.3935 gram.

CO₂ 1.1272 gram, = 78.10 per cent. C.

H₂O 0.2362 gram, = 6.67 per cent. H.

II. Taken, 0.3003 gram.

CO₂ 0.8750 gram, = 79.06 per cent. C.

H₂O 0.1778 gram, = 6.57 per cent. H.

III. Taken, 0.2830 gram.

CO₂ 0.8181 gram, = 78.84 per cent. C.

H₂O 0.1717 gram, = 6.74 per cent. H.

Dipyridine, C₁₀H₁₀N₂ contains 75.94 per cent. C.
6.38 per cent. H.

Both carbon and hydrogen in every case are too high; and I have been unable to conjecture any reason for the excess. I am inclined to believe, from the vapour-density, as well as from analyses of some compounds of the base, that it really has the formula of dipyridine.

Isodipyridine is a yellow viscid oil, of 1.08 specific gravity. It boils at 145–155° in a vacuum, and at 295–305° at the ordinary pressure. It does not solidify on exposure to the cold produced by a mixture of snow and salt, nor is crystallization induced by addition of crystals of dipyridine. It dissolves very sparingly in water, and communicates to it its characteristic heavy basic smell; it mixes in all proportions with alcohol and ether.

Isodipyridine hydrochloride.—When a solution of isodipyridine is evaporated to dryness with hydrochloric acid, redissolved in alcohol, and allowed to remain over sulphuric acid, small, hard, white crystals are deposited. With platinic chloride, the solution of this salt gives a yellow crystalline precipitate of the *platinichloride*. A determination of platinum was made with the following results:—

Taken, 0.3903 gram. Loss at 110°, 0.0085 gram, = 2.43 per cent.

Pt. 0.1298 gram, = 34.34 per cent.

$C_{10}H_{10}N_2 \cdot 2HCl \cdot PtCl_4$ contains 34.51 per cent. of platinum, and with one molecule of water, 3.07 per cent. H_2O .

Isodipyridine methyl-iodide.—When isodipyridine is mixed with excess of methyl iodide, the mixture grows warm, and a brown oil deposits in drops on the side of the tube. After the reaction is over, addition of anhydrous alcohol changes this brown oil into a brilliant red powder. The powder was analyzed.

Taken		0.2015 gram.	
Ag I		0.1985 gram	} = 58.14 per cent. of iodine.
Ag		0.0085 gram	

$C_{10}H_{10}N_2 \cdot 2CH_3I$ contains 57.99 per cent. of iodine.

This red powder is insoluble in absolute alcohol and ether. In aqueous alcohol it dissolves slightly with a yellow colour; and with water it forms a nearly colourless solution.

The *methyl-chloride* is a yellow syrup, which gives a yellow precipitate with platinic chloride, of the formula

It decomposes partially at 100° .

Taken		0.3426 gram.
Pt		0.1126 gram, = 32.86 per cent.

Calculated for $C_{10}H_{10}N_2 \cdot 2CH_3Cl \cdot PtCl_4$, 32.94 per cent. The small amount of isodipyridine at my disposal made it impossible to prepare more salts. In distilling this base at the atmospheric pressure, the last few drops fell on a red-hot surface; and on opening the bulb a strong smell of pyridine was perceived. This base therefore is apparently converted into pyridine by exposure to a high temperature.

The methyl-iodide of dipyridine, prepared from pure crystallized base, is also a red powder; I failed entirely to observe the white needles described by Dr. Anderson in his account of the base.

Dipicoline, $C_{12}H_{14}N_2$.—Dipicoline was prepared by Dr. Anderson by allowing picoline to remain in contact with metallic sodium. A bottle, set aside by him in 1874, contained a black, tarry mass; on exposure to moist air, it gradually became yellow, while the sodium unattacked by the picoline oxidized. After the whole had become yellow, water was added, and the oil, which sank to the bottom, was well washed to remove sodium hydrate. After an attempt to purify it by distillation with water-vapour (which did not succeed, owing to the slight volatility of the base), the oil was dried, and distilled alone. A large quantity of picoline came over at 134° ; the temperature then rose rapidly to 280° . A small fraction

distilled between 280° and 310° ; but by far the largest portion distilled between 310° and 320° . There was very little remaining; so that the fraction last mentioned constituted the bulk of the oil. After two more distillations, the portion boiling at 310 – 320° being collected separately, the base was considered sufficiently pure for investigation.

Its vapour-density was determined twice:

$$\text{I. } D = \frac{0.0420 \text{ gram} \times 1543500 \times 14.47}{760 + \left(42 \times \frac{2}{3}\right) \left\{ \left(\frac{221.3 \text{ grams}}{9.608}\right) 1.01 - \left(\frac{96.1 \text{ grams}}{9.158}\right) \right\}} = 95.30.$$

$$\text{II. } D = \frac{0.0411 \text{ gram} \times 1543500 \times 14.47}{752 + \left(45 \times \frac{2}{3}\right) \left\{ \left(\frac{253.9 \text{ grams}}{9.608}\right) 1.01 - \left(\frac{134.7 \text{ grams}}{9.158}\right) \right\}} = 97.99.$$

The theoretical vapour-density of dipicoline is 93.

Analysis of dipicoline dried over sodium and distilled:—

Taken		0.2932 gram.
CO ₂		0.8313 gram, = 77.32 per cent. C.
H ₂ O		0.1886 gram, = 7.14 per cent. H.

C₁₂H₁₄N₂ contains 77.41 per cent. of carbon, and 7.52 per cent. of hydrogen.

Dipicoline, C₁₂H₁₄N₂, is a yellow oil, closely resembling dipyridine in appearance. Its smell is similar, but slightly different. It mixes in all proportions with alcohol and ether, and is sparingly soluble in water, to which it communicates its taste and smell. Its specific gravity is 1.12, rather more than that of dipyridine. It boils at 310 – 320° at the ordinary pressure. It unites with acids to form salts which have little tendency to crystallize.

The *hydrochloride*, after standing in a syrupy condition over sulphuric acid for some days, showed a tendency to crystallize at the edge. The *platinichloride* has the formula

Analyses:—

I. Taken		0.5117 gram.
Pt		0.1692 gram, = 33.06 per cent.
II. Taken		0.5069 gram.
Pt		0.1684 gram, = 33.22 per cent.

The platinichloride contains 33.73 per cent. of platinum. Dipicoline unites with the iodides of the alcohol-radicals; of these compounds, the methyl-iodide was prepared.

Dipicoline methyl-iodide, $C_{12}H_{14}N_2 \cdot 2CH_3I$.—Obtained by the action of excess of methyl-iodide on dipicoline, at the ordinary temperature. It forms a reddish-brown oil, which solidifies after some time. On treatment with anhydrous alcohol, it changed to a bright yellow powder, almost insoluble in alcohol and in ether, but readily soluble in water, giving an almost colourless solution. It was dried and analyzed.

Taken		0.2764 gram	} = 54.29 per cent. I.
Ag I		0.2638 gram	
Ag		0.0085 gram	

$C_{12}H_{14}N_2 \cdot 2CH_3I$ contains 54.24 per cent. of iodine.

The *methyl-hydrate*, prepared by addition of silver oxide and water to the methyl-iodide formed a colourless liquid, which turned brown and evolved a peculiar smell on evaporation.

The *methyl-chloride*, obtained by addition of hydrochloric acid to the methyl-hydrate, is a white crystalline salt. The *platinichloride* is a buff-coloured precipitate, soluble in hot water, and crystallizing out in yellow crystals when the solution cools. It was analyzed.

Taken		0.1120 gram.
Pt		0.0345 gram, = 30.80 per cent.

$C_{12}H_{14}N_2 \cdot 2CH_3Cl \cdot PtCl_4$ contains 31.47 per cent. of platinum.

A strong solution of iodine in alcohol was added to a hot solution of the methyl-iodide in aqueous alcohol; brown scales with coppery lustre separated out on cooling. This compound was analyzed.

Taken		0.4125 gram,
Ag I		0.6245 gram, = 81.81 per cent. of I.

By titration with sodium thiosulphate, this compound was found to contain 61.25 per cent. of free iodine.

the *hexiodide of dipicoline methyl-iodide*, contains 82.46 per cent. of total iodine, and 61.85 per cent. of additive iodine. This compound is insoluble in water, but dissolves sparingly in alcohol with a deep yellow colour. It is insoluble in carbon disulphide.

An aqueous solution of dipicoline, on addition of bromine water, gave a very bulky buff-coloured precipitate. It was dried over sulphuric acid and analyzed.

Taken		0.4108 gram.
Ag Br		0.5161 gram, = 53.46 per cent. of Br.

$C_{12}H_{11}Br_3N_2$ contains 56.73 per cent. of bromine.

$C_{12}H_{13}BrN_2 \cdot 2HBr$ contains 55.70 per cent. of bromine. I am disposed to accept the latter formula as the correct one ; for one atom of bromine introduced into the molecule of dipicoline would probably not destroy its basic property.

Oxidation of Dipicoline.—Five grams of dipicoline were oxidized in the usual manner with potassium permanganate. The acids when separated from their lead salts, consisted :—(1) of an acid, almost totally insoluble in water, alcohol, and ether, and separating in amorphous flocks on evaporation of the solution containing other acids, in which it dissolves sparingly ; it gives off a smell of the polymerized bases when heated on platinum foil ; and (2) a mixture of acids (certainly containing no α -dicarbopyridenic acid), of which the quantity at my disposal was too small to admit of fractional crystallization. These acids also evolved a smell resembling that of dipyridine, when heated. The lead and silver salts of these acids are white insoluble precipitates. It is probable, from the fact of these acids evolving the smell of dipyridine when heated, that dipicoline, when oxidized, yields a polymeride of dicarbopyridenic acid.

General Conclusions.

1. Bases of the series $C_nH_{2n-5}N$ are tertiary bases ; they are not attacked by nitrous acid ; nor do they unite with more than one molecule of a halogen compound of an alcohol radical.

2. They are unsaturated compounds, but have no great tendency to form addition-compounds. The addition-compounds are divisible into three classes :—(a) compounds in which the base combines directly with an acid to form a salt ; (b) compounds in which the base unites with two atoms of a halogen, *e. g.* picoline chloriodide, $C_6H_7N.ClI$; and (c) those in which a salt combines with two atoms of a halogen, in the pyridine series, as, for example, the diiodide of picoline methyl-iodide, $C_6H_7N.CH_3I.I_2$, and with six atoms of a halogen, as in the case of the hexiodide of dipicoline methyl-iodide, $C_{12}H_{14}N.(CH_3I)_2I_6$.

3. Like the paraffins, they are not attacked by acid oxidizing agents in the cold. They differ from paraffins by withstanding such action even at a high temperature ; and this is probably owing to the increased stability given to the molecule by nitrogen, which renders them basic, and imparts to them the property of forming salts. The heat of formation of these bases is doubtless very high ; and when a still greater amount of heat is evolved by their combination with acids, the sum of

heat-units evolved by the union of the carbon, hydrogen, and nitrogen, plus that evolved by the formation of their salts, is probably greater than that evolved by their oxidation.

4. It is consequently only in alkaline solution that they can be oxidized. In this case, the amount of heat evolved by the acid formed by oxidation uniting with the alkali increases the sum of thermal units evolved by their oxidation to a number larger than that evolved during the formation of the base. The amount of heat evolved, moreover, is not increased by that arising from a union of the base with an acid.

5. At least three isomerides are formed by replacement of two atoms of hydrogen in pyridine by carboxyl, COOH . From analogy with benzol, and consideration of the greater complexity of the molecule of pyridine, it is highly probable that more than three exist. These acids are produced by oxidizing picoline and its higher homologues, and probably also by oxidizing pyridine. This behaviour is analogous to that of benzol; for benzol yields acids containing more than six atoms of carbon when oxidized. From picoline, $\text{C}_6\text{H}_7\text{N}$, it was to be expected that monocarbopyridenic acid, $\text{C}_5\text{H}_4\text{N} \cdot \text{COOH}$, should be produced; this acid has been obtained only by the oxidation of nicotine; α -dicarbopyridenic acid is the only one produced in large quantity by the oxidation of picoline. When lutidine, $\text{C}_7\text{H}_9\text{N}$, is oxidized, a mixture of at least three isomeric acids of the formula $\text{C}_5\text{H}_3\text{N}(\text{CO} \cdot \text{OH})_2$ is formed. This would imply the existence of as many different isomeric lutidines: and indeed it is highly probable that such isomerides exist; for great difficulty is experienced in separating isomeric liquids, especially (as in this case) when the presumption is that their boiling-points are almost identical.

6. These isomerides may be represented in graphic formulæ as on page 27. A closed chain appears best suited to express the behaviour of the bases and the isomeric compounds derived from them. I failed in several attempts to convert the dicarbopyridenic acid into its alcohol (from which I had hoped to obtain a base), owing to the instability of the acid at a high temperature and the small yield of aldehyde when the acid was distilled with calcium formate. I had hoped to achieve the formation of the base by the following stages:—

$\text{C}_5\text{H}_3\text{N}(\text{CO} \cdot \text{OH})$; $\text{C}_5\text{H}_3\text{N}(\text{CHO})_2$; $\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{OH})_2$;
 $\text{C}_5\text{H}_3\text{N} \cdot (\text{CH}_2\text{Cl})_2$; and $\text{C}_5\text{H}_3\text{N}(\text{CH}_3)_2$.

From similar reasons, an attempt to prepare lutidine, $\text{C}_7\text{H}_9\text{N}$, by distilling the methyl ether of the α -acid proved abortive; in every case, pyridine was formed. In spite of these failures, it appears to me probable that picoline is *methylpyridine*, lutidine *dimethylpyridine*, etc.,—the presence of

nitrogen, as conjectured in (3), giving stability to the molecule, and preventing the oxidation of the methyl-groups to carboxyl.

7. On treatment with sodium, these bases are polymerized, no hydrogen being evolved by the action of the sodium on the base. An addition-product is consequently formed, probably by two atoms of sodium being taken up by each molecule of base; on coming into contact with a fresh molecule of base, the sodium leaves the first molecule, which has thereby its affinities free for union with another similarly placed. I am very doubtful if any compound of picoline and sodium is formed. Certainly sodium does not combine with dipicoline; for that base can be freed from water by heating it to a high temperature with metallic sodium.

8. In conclusion, I would remark the analogy between the furfural and pyridine groups. That they are closely related appears very probable. An attempt to effect the conversion of furfural, $C_5H_4O_2$, into pyridine through the following series of reactions, failed owing to the instability of furfuryl chloride.

The furfural group, from its unstable nature, is probably analogous to the higher homologues of acetylene, and is best represented by an open chain; whereas the pyridine group, from its stability, and from the number of isomeric derivatives obtained from it, is, like benzol, best pictured by a closed chain.

In closing this research, I have to express my deep indebtedness to Professor Ferguson for placing at my disposal the material which belonged to the late Professor Anderson.

IV. On Salt Solutions and Attached Water.

By FREDERICK GUTHRIE*.

[Continued from vol. ii. p. 225.]

VI.

Further Examples of Cryohydrates and Cryogens.

§ 167. **H**YDRATE of Barium.—On cooling a saturated solution of this salt, the well-known recognizable crystals are continually deposited until the temperature reaches

* Communicated by the Physical Society.