3. *Dehydrogenation of Pyridine by Anhydrous Ferric Chloride.*

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THE earliest preparation of 2 : 2′-dipyridyl, which involved a pyrolysis of cupric picolinate, was effected by Blau (*Ber.*, 1888, **21**, 1077; *Monatsh.*, 1889, **10**, 376), who stated that this process proceeded most satisfactorily in one-gram batches. Later he made the significant observation (*Monatsh.*, 1898, **19**, 647) that this *o*-diamine developed intense red colorations with ferrous salts and he prepared the complex bromide [Fe3dipy]Br_2,$6H_2O$, which was subsequently resolved by Werner into optically active enantiomerides (*Ber.*, 1912, **45**, 434).

More recently 2 : 2′-dipyridyl has been obtained by methods of direct dehydrogenation (Meyer and Hofmann-Meyer, *J. pr. Chem.*, 1921, **102**, 287; Hein and Retter, *Ber.*, 1928, **61**, 1790; Wibaut and Willink, *Rec. trav. chim.*, 1931, **50**, 287) and of these processes Hein and Retter's dehydrogenation of pyridine by anhydrous ferric chloride appeared the one most likely to furnish the diamine on a considerable scale :—

$$2C_5H_5N + 2FeCl_3 = C_{10}H_8N_2 + 2FeCl_2 + 2HCl.$$

These authors, who employed sealed tubes each containing 70 g. of dry pyridine and 13 g. of anhydrous ferric chloride, maintained these reagents at 300° for about 35 hours; a yield of 52% of 2 : 2′-dipyridyl was obtained calculated on the ferric chloride employed in the foregoing equation.

Being in need of considerable quantities of 2 : 2′-dipyridyl for the study of various co-ordination compounds, we have repeated Hein and Retter's dehydrogenation in steel autoclaves with amounts of pyridine ranging from 1 to 8 litres. By working with such quantities we have prepared 2 : 2′-dipyridyl as the main product, but have also isolated not less than 20 by-products. The reactions taking place are complex and some of the resulting ferrous chloride is reduced further to metallic iron. The temperature (340°) and pressure (50 atmos.) involved approximate closely to the critical temperature (344°) and critical pressure (60 atmos.) of pyridine as given by Landolt–Börnstein's tables and under such severe conditions it is probable that a certain amount of "cracking" occurs. Moreover the elements present in the steel autoclave (carbon, 0·3; silicon, 0·25; manganese, 0·6; sulphur and phosphorus, 0·022; nickel, 2·9; chromium, 0·6; and molybdenum, 0·65%) and in its "Staybrite" liner (carbon, 0·12; manganese, 0·30; silicon, 0·60;

chromium, 18·0; nickel, 8·5; tungsten, 0·7; sulphur and phosphorus, below 0·025%) may also have some catalytic effect on these far-reaching chemical changes. These analyses were supplied by Dr. W. H. Hatfield of the Brown-Firth Research Laboratories, Sheffield.

Under the conditions detailed in the experimental section we have obtained the following products:

(1) *Gases.* The gaseous product includes hydrogen, nitrogen, ammonia, saturated hydrocarbons (C_nH_{2n+2}, where n is about 1·5), and unsaturated hydrocarbons, chiefly ethylene. These gases, which arise from a complete rupture of the pyridine molecule, are identical with those (other than hydrogen) obtained by Thate (*Rec. trav. chim.*, 1931, **50**, 77) in the berginisation of pyridine at 500° under pressures of 50 to 100 atmospheres.

(2) *Neutral oil.* A small amount of non-basic oil having a considerable boiling range (90° to 310°) was isolated and found to be nitrogenous.

(3) *Monocyclic pyridines.* In view of the "cracking" revealed by the presence of gases it might be expected that alkylpyridines would be included in the basic fraction. 3-Ethylpyridine was isolated in largest amount and its isomerides 2- and 4-ethylpyridines were also identified. Of the lower homologues, 3- and 4-methylpyridines were present; there were also small amounts of 2 : 3- and 3 : 4-dimethylpyridines. 2-*iso*Propylpyridine was isolated and diethylpyridines were also indicated.

2-Aminopyridine, which was extracted in appreciable amount from the water-soluble portions of the oily product, probably arises from the direct interaction of ammonia and pyridine in presence of ferric chloride,

$$C_5H_5N + NH_3 + 2FeCl_3 = NH_2{\cdot}C_5H_4N + 2FeCl_2 + 2HCl$$

although Wibaut and van den Lande have shown (*Rec. trav. chim.*, 1929, **48**, 1005) that this base is produced to a small extent when ammonia and pyridine vapours are catalysed at 300—500°.

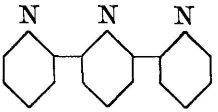
(4) *Dipyridyls and dipiperidyls.* From the dehydrogenation product boiling between 250° and 310° we have isolated five of the six possible dipyridyls. In all our experiments 2 : 2′-dipyridyl is the main product, 3 : 4′-dipyridyl follows next although in much smaller proportion; 2 : 3′- and 2 : 4′-dipyridyls were isolated as their picrates, whereas 3 : 3′-dipyridyl was identified only in one experiment. It is noteworthy that we have never isolated any 4 : 4′-dipyridyl, although this isomeride is the chief product of the action of sodium on pyridine (Anderson, *Annalen*, 1870, **154**, 274; C. R.

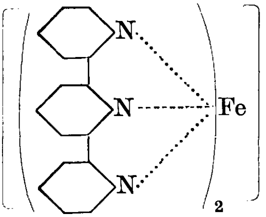
Smith, *J. Amer. Chem. Soc.*, 1924, **46**, 414). 4 : 4′-Dipyridyl was not noticed by Thate (*loc. cit.*) in his berginisation experiments, although small quantities of 2 : 2′- and 2 : 4′-dipyridyls were obtained by this process. Our experiments indicate the presence of alkylated dipyridyls, but so far no chemical entities have been characterised. These diamines are, however, derived to some extent from 2 : 2′-dipyridyl, which they resemble in giving red colorations with ferrous salts.

Small quantities of 2 : 2′-dipiperidyl and 3 : 4′-dipiperidyl were identified in our experiments and probably arose from the interaction of free hydrogen with the two most plentiful dipyridyls (compare C. R. Smith, *J. Amer. Chem. Soc.*, 1928, **50**, 1938).

(5) *Tripyridyls.* Two new triamines were isolated from the basic residues non-volatile in steam. The more abundant isomeride, 2 : 2′ : 2″-*tripyridyl* (*bis*-2′-*pyridyl*-2 : 6-*pyridine*), is a highly crystalline base giving rise to deep purple co-ordination compounds with ferrous salts in which it functions as a tridentate associating group as indicated in formula (II). The composition of this hydrated *bis*-2 : 2′ : 2″-*tripyridyl ferrous bromide* supports our suggested formulation for the triamine (I).

(I.)





$Br_2,1\frac{1}{2}H_2O$ (II.)

2 : 2′ : 2″-Tripyridyl is likely to be a useful associating triamine in the formation of complex metallic salts, for in addition to the iron derivatives similar co-ordination compounds have been obtained with other metals and notably with nickel and silver; these products will be described later. An isomeric 2 : 2′ : x″-tripyridyl has been identified which also furnishes coloured co-ordination complexes.

(6) *Resinamines.* The least volatile fraction of the basic oil has yielded only one crystalline base (m. p. 214°). The remainder of this product, which is still soluble in dilute hydrochloric acid, dissolves readily in organic media and separates on evaporation as an amorphous pitch.

(7) *Insoluble residue.* The portion insoluble in organic media contains 28% of combustible matter, while the remainder consists of iron compounds and some metallic iron.

The yields (grams) of the main fractions obtained from a series of dehydrogenations are given in the following table.

Pyridine used.	Ferric chloride.	Pyridine recovered.	Alkylated pyridines.	Di-pyridyls.	Tri-pyridyls.	Resin-amines.
1500	292	782	40	90	62	52
2000	381	1377	—	156	35	160
2000	381	1433	61	152	64	103
4000	762	2758	155	428	51	403
4000	762	2805	141	300	120	140
8000	1524	5630	245	794	225	512

Of the 8000 g. of pyridine used in the last experiment, 7406 g. are accounted for in the table. The combustible matter of the insoluble residue provides a further 490 g. and the neutral fraction gives 10 g., thus making up the total to 7906 g. The deficiency of 94 g. is traceable to the gases produced and to the unavoidable losses in working up the various dehydrogenation products.

EXPERIMENTAL.

The following description furnishes a typical example of experimental procedure. Pure dry pyridine (8000 g.) and anhydrous ferric chloride (1524 g.) were heated at 340—345° for 36 hours in a steel autoclave fitted with stirring gear. A pressure of 50—51 atmospheres developed and thereafter remained constant during the period of heating, and, when cold, the autoclave still showed a residual pressure of about 2 atmospheres.

I. *Gaseous Products.*—The air contained in the free space of the autoclave having been displaced by carbon dioxide at the commencement of the experiment, the gas was first passed through a vessel cooled in ether and solid carbon dioxide and, after being washed with a little dilute hydrochloric acid to remove any ammonia or pyridine vapour, was collected and the volume measured. Analysis of a sample showed that the gas consisted of hydrogen, nitrogen, saturated hydrocarbons (C_nH_{2n+2}, where $n = 1{\cdot}5$), and a small amount of ethylene. Some of the carbon dioxide present had been reduced to carbon monoxide.

There was no appreciable quantity of material in the vessel cooled by ether and solid carbon dioxide.

II. *Neutral Products.*—The dark red product from the autoclave was mixed with water (45·5 litres), acidified with hydrochloric acid, and extracted with petroleum (b. p. 40—60°), but the solution thus extracted only furnished 10 g. of a dark oil (boiling range 90—310°) in which no individual compound was identified.

Basic Products.—The acid liquor from the foregoing extraction was made alkaline with caustic soda and distilled in steam.

Distillate. The first runnings consisted mainly of unchanged pyridine mixed with alkylpyridines, and these were collected separately. The distillation in steam was then continued until a sample no longer gave any colour with ferrous salts. The aqueous distillate was evaporated with excess of hydrochloric acid to crystallising point, and the resulting hydrochlorides were mixed with the first runnings of pyridine. The mixture was then basified with caustic soda solution, solid alkali being added after neutralisation. The dark brown layer containing pyridine and pyridine derivatives was dried over solid caustic soda and fractionated under ordinary pressure; unchanged pyridine (5630 g.) was then recovered.

III. *Monocyclic pyridines.* These pyridine derivatives (245 g.) were present in the fraction boiling between 140° and 250°. Each fraction was first collected over a 10° range and subsequently refractionated through a Dufton column. There was no fraction corresponding with 2-methylpyridine.

Fraction 140—150°. The lower portion of this fraction, b. p. 140—146°, was treated with mercuric chloride in the presence of dilute hydrochloric acid, and the mercurichlorides fractionally crystallised. The less soluble mercurichloride, which proved to be that of 3-methylpyridine, melted at 145—146°. The free base recovered from this mercurichloride furnished 3-methylpyridine picrate, m. p. 149°. The more soluble double salts gave a small quantity of 4-methylpyridine mercurichloride in needles, m. p. 128—129°, and the recovered base yielded a picrate, m. p. 167°. The higher portion of this fraction, b. p. 146—152°, was converted into mercurichloride, and by fractional crystallisation from water and alcohol, 2-ethylpyridine mercurichloride, m. p. 103°, was obtained (Found : Hg, 58·2. Calc. for $C_7H_{10}NCl_5Hg_2$: Hg, 58·4%). The corresponding chloroaurate crystallised in yellow plates, m. p. 120—121° (compare Ladenburg, *Annalen*, 1888, **247**, 13; *Ber.*, 1899, **32**, 42).

Fraction 150—160°. The more volatile parts of this fraction contained mainly 2-ethylpyridine (b. p. 148·5°). The higher-boiling portion, b. p. 153—160°, was converted into a less soluble mercurichloride, m. p. 120°, which has not yet been identified with certainty but is probably the salt of 2-methyl-6-ethylpyridine; the more soluble crystals furnished 2-*iso*propylpyridine mercurichloride, m. p. 95—96° (Found : Hg, 57·3. Calc. for $C_8H_{12}NCl_5Hg_2$: Hg, 57·2%). The picrate obtained from the recovered base melted at 116—117° (compare Koenigs and Happe, *Ber.*, 1902, **35**, 1343; also Ladenburg, *loc. cit.*). A search was made at this stage for 2 : 4-dimethylpyridine, but no evidence was obtained of its presence.

Fraction 160—170°. The oil boiling over this range was the largest of the monocyclic pyridine fractions. It was converted into a mixture of mercurichlorides; 3-ethylpyridine mercurichloride, m. p. 131—132°, then crystallised in large white prisms (Found : N, 2·2; Hg, 58·2. Calc. for $C_7H_{10}NCl_5Hg_2$: N, 2·0; Hg, 58·4%).

The pure base recovered from its mercurichloride boiled at 165—166° and gave a picrate, m. p. 128°; it possessed a characteristic but not unpleasant odour (compare Stoehr, *J. pr. Chem.*, 1892, **45**, 20; 1891, **43**, 153; Williams, *Chem. News*, 1881, **44**, 307; Wyschnegradsky, *J. Russ. Phys. Chem. Soc.*, 1879, **11**, 184). The more soluble mercurichlorides after separation of 3-ethylpyridine crystallised slowly and individual compounds were most conveniently separated by hand and then recrystallised. 2 : 3-Dimethylpyridine mercurichloride, m. p. 120—121°, was obtained, but the quantity was insufficient for a more detailed examination (Found : Hg, 57·95. Calc. for $C_7H_{10}NCl_5Hg_2$: Hg, 58·4%). Previous workers on this substance are not in agreement (Garrett and Smythe, J., 1903, **83**, 764; Lipp and Widnmann, *Annalen*, 1915, **409**, 79).

3 : 4-Dimethylpyridine mercurichloride crystallised as fine needles, m. p. 164° (Found : Hg, 58·2. Calc. for $C_7H_{10}NCl_5Hg_2$: Hg, 58·4%). It also furnished a chloroplatinate, m. p. 207° (compare Ahrens, *Ber.*, 1896, **29**, 2996; Weidel and Pick, *Monatsh.*, 1884, **5**, 658).

4-Ethylpyridine mercurichloride, m. p. 150—151°, was isolated in slightly larger quantity than the double salts of the foregoing lutidines (Found : Hg, 58·0. Calc. for $C_7H_{10}NCl_5Hg_2$: Hg, 58·4%). The chloroplatinate melted at 207—208° (compare Ladenburg, *Annalen*, 1888, **247**, 18; *Ber.*, 1899, **32**, 45).

Fractions 170—180°, 180—190°. Individual compounds were not identified within these ranges, which appear to contain mixtures of methylethylpyridines with other basic substances.

Fraction 190—210°. This fraction was mixed with an equal volume of benzene and shaken several times with water. Solid alkali was added to the aqueous extract, and 2-aminopyridine then separated as an oil, which was dissolved in benzene, the solution dried, and the solvent removed. 2-Aminopyridine boiled at 205—207° and solidified to a mass of colourless crystals on cooling. This base (9·6 g.) crystallised in shining plates from hot petroleum (b. p. 40—60°), m. p. 56° (Found : N, 29·9. Calc. for $C_5H_6N_2$: N, 29·8%). It was easily soluble in water and gave a picrate, m. p. 216—217° (compare Marckwald, *Ber.*, 1893, **26**, 2189; 1894, **27**, 1320; Philips, *Annalen*, 1895, **288**, 263; Meyer, *Monatsh.*, 1894, **15**, 173; Tschitschibabin and Zeide, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 146 *et seq.*).

The residue remaining after the separation of 2-aminopyridine was freed from solvent and fractionally distilled. The portion boiling between 200—210° was converted into picrates, which were fractionally crystallised from alcohol. A well-defined *picrate*, m. p. 159—160°, crystallising in filamentous yellow needles, was obtained.

This picrate appeared to be a derivative of a base (probably a diethylpyridine) not previously recorded (Found: N, 15·6. $C_{15}H_{16}O_7N_4$ requires N, 15·4%).

Fractions 210—220°, 220—230°, 230—240°, 240—250°. These fractions amounted to 17 g. in all and no individual compound has been characterised from among them.

IV. *Dipyridyls and related substances.* That portion of the distillate boiling between 250° and 310° consisted of dipyridyls and related substances (794 g.). A small quantity of oil (40 g.) remained after removal of the dipyridyl fraction and was not further investigated.

2 : 2′-*Dipyridyl.* The fraction, b. p. 250—310°, was cooled to 0°, whereupon most of this dipyridyl (462 g.) crystallised. A further quantity was obtained from the remaining oil by fractional distillation. The fraction, b. p. 260—280°, was cooled and crystallised from petroleum, 2 : 2′-dipyridyl (62 g.) being obtained, giving a total yield of 524 g. of this base. 2 : 2′-Dipyridyl was readily crystallised from petroleum (b. p. 40—60°) and separated in large crisp white prisms, m. p. 69·5°, b. p. 272—273° (corr.) (Found : N, 17·9. Calc. for $C_{10}H_8N_2$: N, 17·95%). It gave an intense red coloration with ferrous salts, and equimolecular proportions of picric acid and the base gave a picrate, m. p. 155°, in yellow needles (compare Blau, *Monatsh.*, 1889, **10**, 376; Smith, *J. Amer. Chem. Soc.*, 1924, **46**, 414).

3 : 3′-*Dipyridyl.* A fraction of the oily filtrate (b. p. 280—310°) remaining after the separation of 2 : 2′-dipyridyl was shaken three times with small quantities of cold water (50 c.c.). The aqueous extracts, which contained 3 : 4′-dipyridyl mixed with the 3 : 3′-dipyridyl, was treated with solid caustic soda, and the oil which separated dissolved in benzene. The benzene solution was shaken with water to remove 3 : 3′-dipyridyl (compare Smith, *loc. cit.*) and the aqueous layer was evaporated and treated with alcohol and picric acid in excess. The resulting picrate melted at 230° after several recrystallisations; a sample of the base, recovered from the picrate, had m. p. 66—67° (compare Skraup and Vortmann, *Monatsh.*, 1883, **4**, 591; Smith, *loc. cit.*; Leone and Oliveri, *Gazzetta*, 1885, **15**, 276). 3 : 3′-Dipyridyl was only obtained on one occasion and in small yield (0·8 g.) from 381 g. of ferric chloride; it was characterised by comparing its picrate with the picrate of a specimen of 3 : 3′-dipyridyl synthesised from 3-bromopyridine.

3 : 4′-*Dipyridyl.* After separation of 3 : 3′-dipyridyl, the oils from the first water extractions and from the benzene solution were dissolved together in excess of hydrochloric acid and evaporated to dryness. The hydrochlorides were then triturated and shaken with

absolute alcohol (1500 c.c.), and the insoluble portion removed. A further quantity of insoluble hydrochloride was obtained by passing dry hydrogen chloride into the cooled filtrate until the alcoholic solution fumed slightly. The insoluble portion, consisting mainly of 3 : 4′-dipyridyl hydrochloride mixed with a little impurity, was dissolved in water and made alkaline with caustic soda, solid alkali being added after neutralisation. The oil which separated was dissolved in benzene and dried, and the solvent removed; the base then distilled at 295—297° under ordinary pressure and solidified on cooling (yield, 72 g.). 3 : 4′-Dipyridyl crystallised from petroleum (b. p. 40—60°) in shining white plates, m. p. 62° (Found : N, 18·2. Calc. for $C_{10}H_8N_2$: N, 17·95%). The sparingly soluble picrate, m. p. 215° after sintering at 210°, crystallised from water in needles. The foregoing base was liquefied by small quantities of water and dissolved easily in larger amounts of this solvent. Zinc dust and acetic acid gave a deep red tint with an aqueous solution of 3 : 4′-dipyridyl. Smith (*loc. cit.*) reports that 3 : 4′-dipyridyl gave a deep blue colour with zinc dust and acetic acid, but it is probable that his specimen contained a little 4 : 4′-dipyridyl as impurity, the blue coloration being a characteristic of the 4 : 4′-isomeride.

2 : 4′-*Dipyridyl and* 2 : 3′-*dipyridyl.* The bases present in the foregoing alcoholic filtrates which were recovered by evaporation of the solvent and treatment with caustic soda were mixed with the more volatile fractions (b. p. 250—280°) obtained as residues from the separation of 2 : 2′-dipyridyl. The collected oils (197 g.) were thoroughly shaken several times with cold water (aqueous extract, *v. infra*, p. 28), after having been mixed with benzene (400 c.c.). The benzene solution was shaken with a freshly prepared solution of ferrous sulphate until the extracts were no longer reddened; it was then washed with water and dried over solid caustic potash, and the solvent removed. The remaining oil (104 g.) was distilled and gave the following fractions : below 260°, 20 g.; 260—280°, 36 g.; 280—300°, 44 g.; residue, 4 g. The two middle portions were again fractionated and a sample of oil (49 g.), b. p. 275—295°, was collected and treated with picric acid. The mixture of picrates was repeatedly crystallised, first from hot water and finally from hot alcohol, until two individual substances were obtained. 2 : 4′-Dipyridyl picrate, m. p. 208°, crystallised in small lemon-yellow needles and was the more sparingly soluble of the two salts (compare Roth, *Ber.*, 1886, **19**, 360; Meyer and Hofmann-Meyer, *J. pr. Chem.*, 1921, **102**, 280). 2 : 3′-Dipyridyl picrate, m. p. 148—149°, separated in small needles and was more soluble than 2 : 4′-dipyridyl picrate (compare Skraup and Vortmann, *Monatsh.*, 1882, **3**, 599). The yields of these two

bases cannot be closely estimated owing to the great difficulty in separating their picrates, but 2 : 3′-dipyridyl is present in larger quantity than 2 : 4′-dipyridyl.

3 : 4′-*Dipiperidyl and* 2 : 2′-*dipiperidyl.* The bases present in the aqueous extract obtained during the separation of 2 : 4′-dipyridyl and 2 : 3′-dipyridyl were salted out by addition of solid caustic soda and dissolved in hot benzene. Crude 3 : 4′-dipiperidyl crystallised from the cooled solution and after further purification gave long white needles, m. p. 159—160°. The base gave a well-defined picrate, m. p. 212°, crystallising from water in shining yellow filamentous needles (compare Smith, *J. Amer. Chem. Soc.*, 1928, **50**, 1936).

The benzene solution from the foregoing dipiperidyl contained 2 : 2′-dipiperidyl in admixture with impurities. The oily base was purified through its picrate, m. p. 120°, and, moreover, gave a dinitroso-derivative, m. p. 159° (compare Blau, *Monatsh.*, 1892, **13**, 330; Smith, *loc. cit.*, 1928, **50**, 1936).

Alkylated 2 : 2′-*dipyridyls.* The ferrous sulphate washings obtained during the preparation of 2 : 4′-dipyridyl and 2 : 3′-dipyridyl were decomposed with caustic soda, and the oily bases extracted with benzene. This extract was dried and the solvent removed. The resulting oils distilled between 270° and 310° and gave intense red tints with ferrous salts. The mixture appeared to be very complex and no single substance has been separated (yield, 87 g.).

Residue. The residue remaining after the removal of substances volatile in steam consisted of a deep reddish-purple solution containing solid in suspension. This solid residue was washed with water.

V. 2 : 2′ : 2″-*Tripyridyl* (I). The foregoing purple aqueous filtrate was treated with a large excess of caustic soda; the colour then disappeared with concurrent formation of a thick black oil mixed with iron oxide. The oily layer was removed and extracted with hot benzene. The solvent was recovered, and the thick residual oil, containing mixed tripyridyls, distilled under reduced pressure; b. p. 190—280°/5 mm. (yield, 225 g.). The yellow, partly crystalline, viscid distillate was repeatedly extracted with petroleum (b. p. 40—60°); when the petroleum extracts were cooled, a yellow gum (20 g.) first separated and the more soluble portions gave well-defined white prisms contaminated with oily isomerides. These crystals were separated from oils by filtration, dried on porous tile, and crystallised several times from petroleum (b. p. 40—60°). Yield, 55 g. 2 : 2′ : 2″-*Tripyridyl* was obtained in hard white prisms, m. p. 88—89°, and distilled undecomposed at 370° under ordinary pressure (Found : C, 77·15; H, 4·9; N, 18·1; *M*, cryoscopic in benzene, 210, 239; ebullioscopic in benzene, 218, 234. $C_{15}H_{11}N_3$ requires C, 77·25; H, 4·7; N, 18·0%; *M*, 233). The picrate derived from this base by mixing equimolecular proportions of the reagents crystallised from alcohol in yellow needles, m. p. 210°. This tripyridyl, which furnished an intense purple colour with ferrous salts, was very sparingly soluble in cold but more soluble in hot water and dissolved in the common organic media; it was very resistant to oxidation by either acid or alkaline permanganate.

2 : 2′ : x″-*Tripyridyl.* The oily isomeric tripyridyls remaining after the separation of the 2 : 2′ : 2″-tripyridyl were distilled and the fraction, b. p. 210—230°/5 mm., was collected separately. When this yellow distillate was kept in a cool place for some time a cream-coloured caseous substance formed in the viscid liquid. This was separated by hand, pressed on porous tile, to remove oily impurities, and crystallised from warm petroleum (b. p. 40—60°). 2 : 2′ : x″-*Tripyridyl* formed tufted masses of an indefinitely crystalline nature; moreover, it frequently separated as a viscid oil which usually became solid after the removal of solvent (Found : N, 18·0. $C_{15}H_{11}N_3$ requires N, 18·0%). Yield, *ca.* 10 g. This tripyridyl melted at 84—85° and gave a picrate, m. p. 206°. It gave an intense purple coloration with ferrous salts and resembled the foregoing 2 : 2′ : 2″-tripyridyl in its solubility in water and organic solvents.

VI. *Resinamines.* These basic substances were insoluble in water and were contained in the solid residue remaining after the separation of the tripyridyl fraction. The solid was dried and then extracted in a Soxhlet apparatus with benzene. After the evaporation of the solvent a dark brown tar (512 g.) remained. This tar was insoluble in water and only slightly soluble in petroleum, but dissolved easily in other organic media and in dilute mineral acids. When an ethereal solution of this mixture of resinamines was kept at 0° for a prolonged period a small quantity of a *base* crystallised. Recrystallisation from hot benzene gave small white plates, m. p. 214° (Found : N, 16·95%; *M*, ebullioscopic in benzene, 613). The base was almost insoluble in water, but gave a feeble purple tint with ferrous salts. Yield, *ca.* 0·5 g.

VII. *Insoluble residue.* The black insoluble residue (1750 g.) which was not dissolved by benzene was a grey powder and contained 28% of its weight of combustible matter. This gave a total weight of 490 g. of carbonaceous material.

VIII. *Co-ordination Compound of 2 : 2′ : 2″-Tripyridyl and Ferrous Bromide.*—2 : 2′ : 2″-Tripyridyl was characterised by its very stable co-ordination compounds with ferrous salts.

Bis-2 : 2′ : 2″-tripyridyl ferrous bromide sesquihydrate (II). Ferrous sulphate (2·7 g.) and 2 : 2′ : 2″-tripyridyl (4·6 g.) were heated in aqueous medium under reflux for some hours. The cooled, deep purple solution was filtered, and excess of a concentrated solution of sodium bromide added; the *bromide* then crystallised in small, intensely purple prisms and was recrystallised from warm water and air-dried. When slowly crystallised, this complex bromide furnished almost black prisms (Found : Fe, 7·8; Br, 22·9, 22·8; N, 11·65; loss at 110°, 4·0. $C_{30}H_{22}N_6Br_2Fe,1\frac{1}{2}H_2O$ requires Fe, 7·9; Br, 22·55; N, 11·85; $1\frac{1}{2}H_2O$, 3·8%). This complex bromide was extremely stable and was not decomposed by cold dilute acids or warm *N*-alkalis; moreover, it was soluble in alcohol and slightly soluble in acetone.

Since the complex ferrous salts of di- and tri-pyridyls are highly coloured substances, samples were submitted to the Dyestuffs Group of Imperial Chemical Industries Limited for examination as to their dyeing properties. The Research Committee of the Dyestuffs Group report as follows :—" These compounds stain tannined cotton to some extent; they have some slight affinity for wool when dyed in the absence of acid. They dye silk, the dipyridyl salt in a brick red shade and the tripyridyl compound in a violet shade. These dyeings, however, have extremely poor fastness to washing; as regards light, the fastness is of the same order as that of direct cotton azo dyes of similar shade." From this report it is evident that in spite of their intense colours these co-ordination compounds have no particular interest as dyes.

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