

**312.** *Researches on the Polypyridyls.*

By FRANCIS H. BURSTALL.

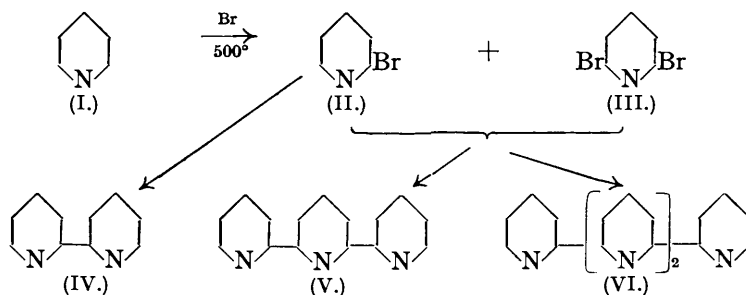
It was already known that bromination of pyridine in the vapour phase at 500° led to 2-bromo- and 2:6-dibromo-pyridine, and it is now found that application of this process to 2:2'-dipyridyl gives mainly 6-bromo- and 6:6'-dibromo-2:2'-dipyridyl. Moreover, bromination of 2:6-di-2'-pyridylpyridine (2:2':2''-tripyridyl) also furnished mono- and di-brominated compounds in which the bromine atoms occupy positions adjacent to the two terminal nitrogen atoms of the triamine. These brominated bases react either singly or two together with copper powder in a diphenyl medium, producing polypyridyls of known constitution and containing two, three, four, five or six pyridine rings. For example, a mixture of 2-bromo- and 2:6-dibromo-pyridine and copper powder in boiling diphenyl furnishes 2:2'-dipyridyl, 2:6-di-2'-pyridylpyridine (2:2':2''-tripyridyl) and 6:6'-di-2''-pyridyl-2:2'-dipyridyl (2:2':2'':2'''-tetrapyridyl). The brominated 2:2'-dipyridyls and 2:2':2''-tripyridyls react in a similar way. Moreover, the halogen atoms in these brominated

polypyridyls can be readily replaced by amino-, cyano-, or carboxyl groups. Following on earlier work by Wibaut on the dehydrogenation of benzene and pyridine with iodine, it has been found that 2 : 2'-dipyridyl and iodine at 310° furnish a good yield of 6 : 6'-di-2''-pyridyl-2 : 2'-dipyridyl, together with a smaller proportion of an isomeric *tetrapyridyl* of unknown constitution. These two tetramines are also formed when 2 : 2'-dipyridyl is heated with anhydrous ferric chloride or ruthenium trichloride, but in these instances the yields are low. Both 4 : 4'-dipyridyl and 3 : 4'-dipyridyl furnish *tetrapyridyls* with iodine, and there is some evidence that the union of the two dipyridyl radicals is adjacent to the nitrogen atoms. 2 : 6-Di-2'-pyridylpyridine and iodine above 300° yield 6 : 6'-di-6''-(2'' : 2'''-dipyridyl)-2 : 2'-dipyridyl (2 : 2' : 2'' : 2''' : 2'''' : 2'''''-hexapyridyl), the constitution of which has been determined by synthesis.

POLYPYRIDYLS are bases in which two or more pyridine rings are linked (but not fused) together. Several derivatives of pyridine which have proved of considerable importance in the synthesis of higher members of the polypyridyl series are now mentioned. Bromination of pyridine in the vapour phase at 500° leads to good yields of 2-bromopyridine (II) and 2 : 6-dibromopyridine (III) (Den Hertog and Wibaut, *Rec. Trav. chim.*, 1932, **51**, 381) which are free from isomeric mono- and di-bromopyridine. The bromine in 2-bromopyridine, and to a less extent 2 : 6-dibromopyridine, is readily replaced by other groups such as amino, hydroxy, ethoxy, piperidyl, cyano, etc. (*idem, ibid.*, 1935, **55**, 122) when these brominated pyridines are heated with suitable reagents.

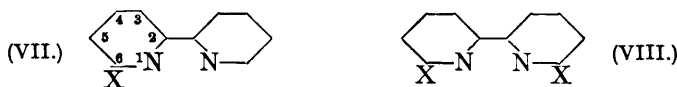
*Dipyridyls*.—Of the six isomeric dipyridyls, the present communication is concerned chiefly with 2 : 2'-dipyridyl (IV), which possesses noteworthy properties as a co-ordinating group with metallic salts. The following processes have been devised for its production : (1) pyrolysis of cupric picolinate (Blau, *Monatsh.*, 1888, **21**, 1077), (2) pyrolysis of pyridine at red heat (Meyer and Hofmann-Meyer, *J. pr. Chem.*, 1921, **102**, 287), (3) as a by-product in the reaction between sodium and pyridine (Smith, *J. Amer. Chem. Soc.*, 1924, **46**, 414), (4) dehydrogenation of pyridine by anhydrous ferric chloride or other metallic chlorides (Hein and Retter, *Ber.*, 1928, **61**, 1790; Morgan and Burstall, *J.*, 1932, 20; *J. Indian Chem. Soc.*, 1933, Ray Commemoration Vol., p. 1; Hein and Schwedler, *Ber.*, 1935, **68**, 681), (5) catalytic dehydrogenation of pyridine at 320° with a nickel catalyst (Wibaut and Willink, *Rec. Trav. chim.*, 1931, **50**, 287), (6) heating pyridine with iodine at 320° (Willink and Wibaut, *ibid.*, 1935, **54**, 275), (7) action of copper powder on 2-bromopyridine dissolved in cymene (Wibaut and Overhoff, *ibid.*, 1928, **47**, 761).

It has now been found that diphenyl is a particularly efficacious solvent for carrying out the debromination of halogenated pyridines or polypyridyls (*v. infra*) substituted



in the 2-position to the nitrogen atom. Copper powder gives with 2-bromopyridine in diphenyl a good yield of 2 : 2'-dipyridyl, whereas a mixture of 2-bromopyridine and 2 : 6-dibromopyridine with copper powder at the boiling point of diphenyl furnishes 2 : 2'-dipyridyl as the chief product and 2 : 6-di-2'-pyridylpyridine (2 : 2' : 2''-tripyridyl) (V) and 6 : 6'-di-2''-pyridyl-2 : 2'-dipyridyl (2 : 2' : 2'' : 2'''-tetrapyridyl) (VI) (*v. infra*) in small quantities. The synthesis of (V) and (VI) by this method is important, since their constitutions are thus referred directly to substituted pyridine derivatives of known orientation.

*Substituted 2:2'-dipyridyls.* Although 2:2'-dipyridyl manifests considerable resistance to substitution, bromination in the vapour phase can be accomplished at 500°, leading chiefly to 6-bromo-2:2'-dipyridyl (VII) and 6:6'-dibromo-2:2'-dipyridyl (VIII) (X = Br). By suitable reactions the bromine in these compounds has been replaced by other groups. With aqueous ammonia at 200—210°, the mono- and the di-substituted



bromo-2:2'-dipyridyl furnish water-soluble 6-amino-2:2'-dipyridyl and 6:6'-diamino-2:2'-dipyridyl (X = NH<sub>2</sub>) respectively. The latter diamine is identical with the product obtained from the amination of 2:2'-dipyridyl with sodamide (Willink and Wibaut, *Rec. Trav. chim.*, 1935, 54, 281). In diphenyl medium the compounds (VII) and (VIII) (X = Br) react with cuprous cyanide above 200°, giving deep red complex cuprous compounds from which 6-cyano-2:2'-dipyridyl (VII, X = CN) and 6:6'-dicyano-2:2'-dipyridyl (VIII, X = CN) are isolated after removal of copper salts with aqueous potassium cyanide. These cyano-compounds are readily hydrolysed by heating with concentrated hydrochloric acid with the formation of 2:2'-dipyridyl-6-carboxylic acid (VII, X = CO<sub>2</sub>H) and 2:2'-dipyridyl-6:6'-dicarboxylic acid (VIII, X = CO<sub>2</sub>H) respectively. The latter acid has also been obtained by oxidation of 6:6'-dimethyl-2:2'-dipyridyl (VIII, X = CH<sub>3</sub>) with selenium dioxide in pyridine. This dimethyl derivative is produced in small yield during the dehydrogenation of 2-methylpyridine with ferric chloride. A more convenient process consists in heating 2-methylpyridine with a nickel catalyst at 325°. The compound has been synthesised by heating 6-bromo-2-methylpyridine with copper powder (Willink and Wibaut, *loc. cit.*). The carboxylic acids corresponding to (VII) and (VIII) (X = CO<sub>2</sub>H) yield 2:2'-dipyridyl on heating and form characteristic products with copper acetate.

All the foregoing substituted 2:2'-dipyridyls show a very marked decline in co-ordinating power in comparison with the parent diamine, the mono-substituted derivatives giving only a feeble colour with ferrous salt solutions, and the disubstituted compounds, with the exception of the dicarboxylic acid, no colour at all. This fact is attributed to the screening effect of a relatively large group adjacent to the nitrogen atom.

That these 2:2'-dipyridyl derivatives are substituted in 2-positions to the nitrogen atoms depends in the main on a knowledge of the orientation of the bromo-2:2'-dipyridyls (VII) and (VIII) (X = Br) and the clue to the position of these substituents has been obtained from a study of their interaction with copper powder in diphenyl medium. The compound (VII, X = Br) yields the tetrapyrindyl (VI), and a mixture of (VIII, X = Br) with 2-bromopyridine also gives the tetramine (VI), the orientation of which is known by its synthesis from 2-bromopyridine and 2:6-dibromopyridine (*v. supra*). These reactions will be considered in more detail under "Tetrapyrindyls" (*v. infra*).

Den Hertog and Wibaut (*loc. cit.*) showed that bromination of pyridine at 300° gave a mixture of 3-bromopyridine and 3:5-dibromopyridine in contrast to 2-bromo- and 2:6-dibromo-pyridines obtained at 500°. Bromination of 2:2'-dipyridyl at lower temperature gives only traces of brominated products, but passage of bromine vapour over 2:2'-dipyridyl dihydrobromide at 250° produces two brominated 2:2'-dipyridyls, which, by analogy with pyridine, are accorded the provisional structures 5-bromo-2:2'-dipyridyl and 5:5'-dibromo-2:2'-dipyridyl. The monobromo-derivative gives an intense red colour with ferrous salts and reacts with copper powder in diphenyl medium. The dibromo-compound yields no colour with ferrous salts and is unaffected by copper in diphenyl whether alone or in a mixture with other brominated compounds.

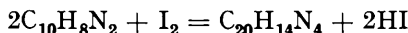
*Tripyridyls.*—2:6-Di-2'-pyridylpyridine (2:2':2''-tripyrindyl) (V), first obtained as a by-product in the dehydrogenation of pyridine with ferric chloride, forms a remarkable series of co-ordination compounds with metallic salts in which the base acts as a tridentate group (Morgan and Burstall, *loc. cit.*; J., 1934, 1498; 1937, 1649). Its synthesis from 2-bromopyridine and 2:6-dibromopyridine is not a satisfactory one for its preparation

in quantity. It has also been synthesised by the action of copper powder on a mixture of 6-bromo-2:2'-dipyridyl (VII) and 2-bromopyridine in diphenyl and in this method, too, the triamine is accompanied by 2:2'-dipyridyl and 2:2':2'':2'''-tetrapyridyl (VI). The reaction serves to confirm the orientation of the bromo-2:2'-dipyridyl (VII). It has now been found that heating iodine in an equimolecular mixture of 2:2'-dipyridyl and pyridine at 310° furnishes notable quantities of the base; ferric chloride can replace the iodine, but the yield is then poor. Both processes require an adequate supply of 2:2'-dipyridyl, much of which is lost owing to carbonisation and tar formation, so the original method from pyridine and ferric chloride is still the best process for the production of the triamine.

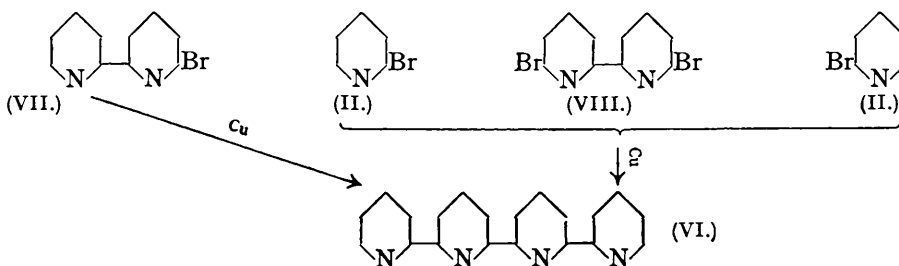


*Substituted tripyridyls.* Bromination of 2:6-di-2'-pyridylpyridine at 500° under conditions similar to those used for pyridine and 2:2'-dipyridyl leads chiefly to 6'-bromo-2:6-di-2'-pyridylpyridine (IX) and 6':6''-dibromo-2:6-di-2'-pyridylpyridine (X), the latter being the main product. The bromo-compound (IX) gives only a feeble magenta coloration with ferrous salts, but dissolves in dilute acids, whereas (X) yields no colour with ferrous salts and is insoluble in dilute halogen acids. The labile character of the bromine atoms in these compounds and their orientation in the molecule are shown by their reaction with copper powder in diphenyl medium: (IX) gives only the hexapyridyl (XVI), and a mixture of (X) and 2-bromopyridine furnishes the pentapyridyl (XV) (*v. infra*). Lack of material prevented any more than a qualitative examination of the reaction of these bromo-compounds with ammonia and cuprous cyanide, but both these reagents react with the brominated tripyridyls, thus supporting the view that reactivity is associated with substituents in positions adjacent to nitrogen atoms.

*Tetrapyridyls.*—Willink and Wibaut (*loc. cit.*) showed that pyridine could be dehydrogenated by iodine, 2:2'-dipyridyl then being formed. This reaction has been extended to produce tetrapyridyls from dipyridyls by heating 2:2'-dipyridyl and iodine at 310° in an autoclave, a good yield of 6:6'-di-2''-pyridyl-2:2'-dipyridyl (2:2':2'':2'''-tetrapyridyl) (VI) is obtained, accompanied by a small quantity of an isomeric tetramine of lower melting point:



The tetrapyridyl (VI) is also formed by heating 2:2'-dipyridyl with ferric chloride (FeCl<sub>3</sub>) or ruthenium chloride (RuCl<sub>3</sub>),  $8C_{10}H_8N_2 + 2FeCl_3$  (RuCl<sub>3</sub>) =  $2[Fe(Ru)3C_{10}H_8N_2]Cl_2 + C_{20}H_{14}N_4 + 2HCl$  (compare Burstall, J., 1936, 173), the base being mixed in both cases with small quantities of the isomeric tetramine. These preparations, however, are much less satisfactory than the iodine dehydrogenation process. None of these methods gives any indication of the orientation of these tetrapyridyls, but the base prepared in largest yield is identical with the tetrapyridyl (VI) formed by the action of copper on a mixture of 2-bromopyridine and 2:6-dibromopyridine in diphenyl (*v. supra*) and must therefore be 6:6'-di-2''-dipyridyl-2:2'-dipyridyl (VI).

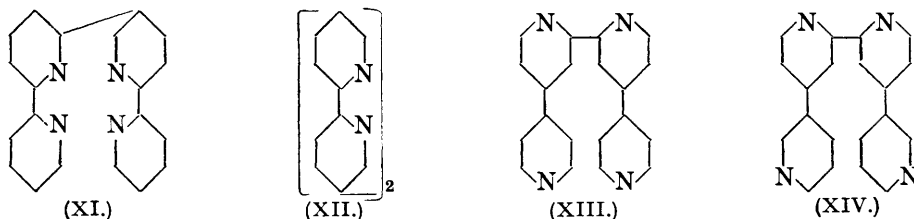


The additional synthetic processes outlined in the diagram serve to fix the orientation of the bromo-2:2'-dipyridyls (VII) and (VIII). The compound (VII) gives an excellent

yield of (VI), and a mixture of (VIII) with 2-bromopyridine (II) (2 mols.) provides a mixture of 2 : 2'-dipyridyl and 2 : 2' : 2'' : 2'''-tetrapyridyl (VI), which are readily separated.

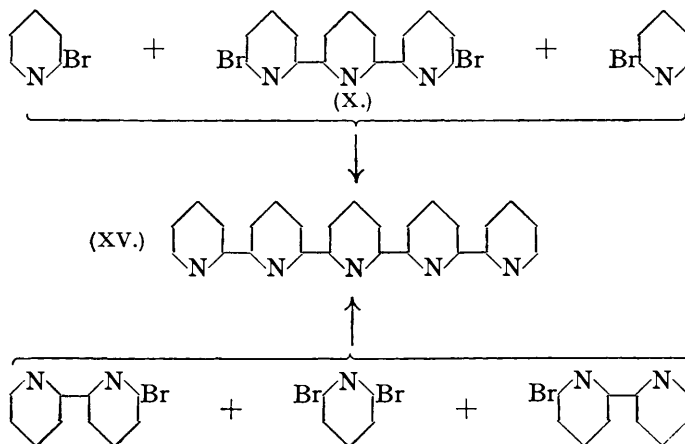
The tetrapyridyl (VI) furnishes a *trihydrated dihydrochloride*, a *dipicrate*, and a notable series of complex compounds with metallic salts (following paper).

In addition to the foregoing tetramine (VI) there are several other tetrapyridyls, the constitutions of which are not known with certainty, but, since they all give a characteristic red coloration with ferrous salts, the presence of 2 : 2'-dipyridyl residues is indicated. The by-product in the dehydrogenation of 2 : 2'-dipyridyl in view of its low melting point probably has an unsymmetrical constitution such as (XI). The *tetrapyridyl* arising from the interaction of 5(?)-bromo-2 : 2'-dipyridyl (*v. supra*) and copper powder in diphenyl is given the structure (XII) in preference to a compound with the point of attachment at position 3. The chief product of the dehydrogenation of 4 : 4'-dipyridyl with iodine at 310° is a crystalline *tetrapyridyl* to which the structure (XIII) is given. The orientation



of the tetrapyridyl derived from 3 : 4'-dipyridyl by the action of iodine is less certain, but the arrangement (XIV) is regarded as the most likely one.

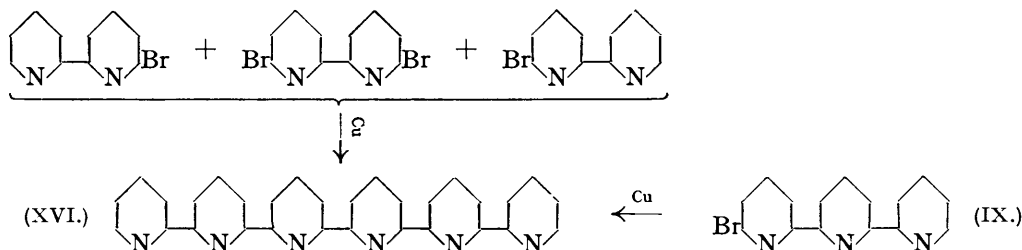
*Pentapyridyl*.—The only representative of the group containing five pyridine residues so far obtained is 2 : 6-di-6''-(2' : 2''-dipyridyl)pyridine (2 : 2' : 2'' : 2''' : 2''''-pentapyridyl) (XV), which is best obtained by heating a mixture of 2-bromopyridine and 6' : 6''-dibromo-2 : 6-di-2'-pyridylpyridine (X) in diphenyl with copper powder; some 2 : 2'-dipyridyl is also formed, but is readily separated. Another method for the production of this pentamine consists in heating a mixture of 6-bromo-2 : 2'-dipyridyl and 2 : 6-dibromopyridine in



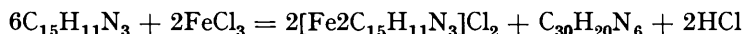
diphenyl with copper, but this method leads to a mixture which also contains the tetrapyridyl (VI) and hexapyridyl (XVI); these are not easily separated. Sufficient pentapyridyl, however, was obtained in a state of purity to confirm the identity of this base with that obtained from the first synthesis. It furnishes a *hydrated trihydrochloride* and gives a deep red colour with ferrous salts. Lack of material has prevented a more detailed study of the pentapyridyl. Polypyridyls containing an odd number of rings are more difficult to obtain than those containing an even number.

*Hexapyridyl*.—The reaction between iodine and 2 : 6-di-2'-pyridylpyridine (V) at 320° furnishes a small yield of colourless crystalline 6 : 6'-di-6''-(2'' : 2'''-dipyridyl)-2 : 2'-di-

pyridyl (2 : 2' : 2'' : 2''' : 2'''' : 2'''''-hexapyridyl) (XVI), the orientation of which has been determined by the following synthetic processes. A mixture of 6-bromo-2 : 2'-dipyridyl and 6 : 6'-dibromo-2 : 2'-dipyridyl (*v. supra*) in diphenyl with copper powder yielded the hexapyridyl together with the tetrapyridyl (VI), which was separated by means of its



greater solubility in organic solvents. The second synthesis comprises the action of copper powder on 6'-bromo-2 : 6-di-2'-pyridylpyridine (IX), a good yield of the hexapyridyl alone being produced. Small quantities of the hexamine are also formed from the action of ferric chloride on 2 : 2' : 2''-tripyridyl :



The hexamine forms a *tetrahydrochloride*, readily hydrolysed by water, and a series of complex derivatives with salts of the transition metals in which one molecule of the base is united with one atomic proportion of metal ion. The stereochemistry of such derivatives is particularly interesting inasmuch as they contain a sexadentate group and should possess a planar distribution of the six nitrogen atoms round a central atom. Both characteristics have not been previously recorded. These salts will be the subject of a separate communication.

#### EXPERIMENTAL.

2-Bromopyridine and 2 : 6-dibromopyridine were prepared by the vapour phase method of Hertog and Wibaut (*loc. cit.*). The vapours of pyridine and bromine were heated to 500° before mixing. The apparatus was a modification of that used by the foregoing authors and consisted of a horizontal furnace, tilted to about 30° from the normal, which served to heat a hard-glass tube ( $\frac{3}{4}$ " bore) containing two narrow-bore tubes down half its length, into which pyridine and bromine were separately dropped. The viscid reddish-brown brominated products were collected at the lower end of the hard-glass tube and worked up and purified by the method of the original authors. 2-Bromopyridine was a colourless liquid, b. p. 193°/762 mm., which slowly darkened on keeping; it had a not unpleasant odour (Found : Br, 49.8. Calc. : Br, 50.6%). 2 : 6-Dibromopyridine formed white crystals, m. p. 118—119°, b. p. 249°/762 mm., having a pleasant terpinaceous odour (Found : Br, 67.2. Calc. : Br, 67.5%). In a typical experiment, pyridine (50 g.) and bromine (102 g.) gave 2-bromopyridine (20 g.) and 2 : 6-dibromopyridine (33 g.).

*The Action of Copper Powder on 2-Bromopyridine in Diphenyl.*—2-Bromopyridine (10 g.) in diphenyl (30 g.) was heated to incipient boiling, and copper bronze (15 g.) added all at once. The temperature was raised slowly until at 230° a vigorous reaction began which was marked by a sharp rise in temperature and the conversion of the copper into a viscid, dark brown product. The mixture was boiled for 1 hour, and a further quantity of copper powder (5 g.) then added. After further heating (2 hours) at the b. p., the mixture was cooled and extracted with light petroleum (b. p. 40—60°) to remove solvent. A solution of the residue in dilute nitric acid was filtered, basified with excess of aqueous ammonia, and treated with aqueous potassium cyanide. The yellow mixture was extracted several times with benzene, the solvent evaporated, and the residue of bases distilled. A little pyridine passed over first, but the main product consisted of slightly impure 2 : 2'-dipyridyl (3.5 g.), which was crystallised from light petroleum (b. p. 40—60°); m. p. 70°, b. p. 272°/760 mm. (compare Wibaut and Overhoff, *loc. cit.*).

*The Action of Copper Powder on a Mixture of 2-Bromopyridine and 2 : 6-Dibromopyridine in Diphenyl.*—2-Bromopyridine (25 g.) and 2 : 6-dibromopyridine (18 g.) in diphenyl (80 g.) were treated with copper powder (30 g. + 10 g.), and the product worked up, as described in

the foregoing experiment. The solvent benzene was removed, and the residual mixture of bases distilled, whereby 2 : 2'-dipyridyl (7.0 g.) was removed. When the residual bases were warmed with light petroleum (b. p. 40—60°), 2 : 6-di-2'-pyridylpyridine and any remaining 2 : 2'-dipyridyl were dissolved. The residue of brown 2 : 2' : 2'' : 2'''-tetrapyridyl was sublimed under reduced pressure at 220°, triturated with acetone, and crystallised from benzene-petroleum; it then melted at 219—220°. Yield, 0.13 g. This tetramine was identical in m. p. and mixed m. p. with other preparations of this base (see p. 1670). The petroleum solution containing the tripyridyl and a little 2 : 2'-dipyridyl was evaporated, and the bases dissolved in alcohol and treated with excess of picric acid. The more sparingly soluble fraction of the crystallised picrates was decomposed with 2N-caustic soda, and the base extracted with benzene and crystallised several times from petroleum, oily impurities being removed by draining on unglazed porcelain. 2 : 6-Di-2'-pyridylpyridine (0.1 g.), m. p. 88—89°, gave a characteristic deep magenta tint with ferrous salts and was identical with preparations from other sources (see p. 1670).

#### *Dipyridyls.*

2 : 2'-Dipyridyl was prepared by dehydrogenation of pyridine with ferric chloride (Morgan and Burstall, *loc. cit.*) and purified by crystallisation from petroleum and distillation; m. p. 70°, b. p. 272°/758 mm. 3 : 4'-Dipyridyl, obtained as a by-product, was crystallised and distilled before use; m. p. 63°, b. p. 295°/759 mm. 4 : 4'-Dipyridyl was prepared by Smith's method (*loc. cit.*) by the action of sodium on pyridine. The anhydrous base was distilled immediately before use; m. p. 114°, b. p. 305°/760 mm.

*Bromination of 2 : 2'-Dipyridyl.*—(1) *At 500°.* This bromination was carried out in exactly the same way as that of pyridine. The apparatus was modified by heating the burette and accessory parts outside the furnace electrically in order to maintain the base in a liquid condition. 2 : 2'-Dipyridyl (95 g.) and bromine (100 g.) were passed through the tube heated to 500°. The hard green product was boiled with water, and the grey residue (A) separated. The acid filtrate was basified with caustic soda and extracted with benzene, which removed unchanged 2 : 2'-dipyridyl and monobromo-2 : 2'-dipyridyl. The former base was removed by shaking the benzene solution with successive quantities of ferrous sulphate solution until the aqueous layer retained only a pale pink tint. The benzene extract was dried, the solvent removed, and the residue crystallised from light petroleum (b. p. 40—60°); 6-bromo-2 : 2'-dipyridyl then separated in white crystals, m. p. 74° (Found : C, 52.0; H, 3.2; N, 11.7; Br, 34.3. C<sub>10</sub>H<sub>7</sub>N<sub>4</sub>Br requires C, 51.1; H, 3.0; N, 11.9; Br, 34.0%). Although readily soluble in organic solvents and in dilute mineral acids, it was only sparingly soluble in water. Its picrate crystallised from alcohol-acetone in yellow needles, m. p. 181—182°.

The grey residue (A) was digested with 2N-caustic soda, washed with water, dried, and triturated with acetone to remove oily impurities. The insoluble portion was sublimed at 220°/20 mm., and the sublimate crystallised from hot benzene; 6 : 6'-dibromo-2 : 2'-dipyridyl separated in small white needles, m. p. 218°, insoluble in water and dilute acids and sparingly soluble in most organic solvents (Found : C, 39.1; H, 2.2; N, 9.5; Br, 50.8. C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>Br<sub>2</sub> requires C, 38.2; H, 1.8; N, 8.9; Br, 50.9%). It gave neither a picrate nor a coloration with ferrous salt solutions.

(2) *At 300°.* 2 : 2'-Dipyridyl (56 g.) and bromine (60 g.) were passed through a tube at 300°. The viscid red-brown product, which contained a large proportion of bromine in the form of 2 : 2'-dipyridyl perbromide, was boiled with water, and the solution treated with sodium bisulphite to remove bromine, filtered from a black carbonaceous residue, and basified. Extraction with benzene and distillation gave practically pure 2 : 2'-dipyridyl. The black residue also was substantially free from brominated 2 : 2'-dipyridyls.

(3) *Bromination of 2 : 2'-dipyridyl hydrobromide at 250°.* A solution of 2 : 2'-dipyridyl (30 g.) in excess of constant-boiling hydrobromic acid was evaporated to dryness in a stream of carbon dioxide, the temperature being gradually raised to 250°. Bromine (30 g.) was passed over the solid hydrobromide in a stream of carbon dioxide. The reddish product was treated with aqueous sodium bisulphite to remove bromine, and the solution filtered, basified, and extracted with benzene. After removal of solvent, unchanged 2 : 2'-dipyridyl was distilled, and the residue of crude bromo-2 : 2'-dipyridyl converted into picrate with excess of picric acid in alcohol. The pure picrate, m. p. 182—183°, was decomposed with caustic soda, and the base crystallised from petroleum; 5(?)-bromo-2 : 2'-dipyridyl separated in white plates, m. p. 79°, which gave an intense red colour with ferrous salts (Found : Br, 34.3. C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>Br requires Br, 34.0%). The residue insoluble in acid was dried and crystallised from hot benzene, 5 : 5'(?)-

*dibromo-2:2'-dipyridyl*, m. p. 212—213°, separating in lustrous white plates (Found: Br, 51.6.  $C_{10}H_8N_2Br_2$  requires Br, 50.9%).

**6-Amino-2:2'-dipyridyl.**—6-Bromo-2:2'-dipyridyl (1.0 g.) was heated with aqueous ammonia (10 c.c., *d* 0.880 + 5 c.c. of water) in a sealed tube at 210—220° for 6 hours. The brown product was boiled, cooled, filtered from unchanged bromo-compound (0.3 g.), and strongly basified with solid caustic soda. The oily amine was extracted with benzene and crystallised from light petroleum (b. p. 60—80°), *6-amino-2:2'-dipyridyl* separating in white, water-soluble crystals, m. p. 89° (Found: C, 70.6; H, 5.2; N, 24.0.  $C_{10}H_8N_3$  requires C, 70.2; H, 5.3; N, 24.6%). It gave a yellow coloration with ferrous salts.

**6:6'-Diamino-2:2'-dipyridyl.**—6:6'-Dibromo-2:2'-dipyridyl (3.0 g.) was heated with aqueous ammonia (20 c.c.) in a sealed tube at 220° for 14 hours. The brown solution was diluted, boiled, cooled, filtered, and evaporated to dryness. The dry residue was mixed with sodium carbonate and heated at 240°/20 mm. The sublimate crystallised from water in long thin needles, m. p. 185° (picrate, m. p. 256°) (Found: C, 64.1; H, 4.9; N, 30.1. Calc. for  $C_{10}H_{10}N_4$ : C, 64.5; H, 5.4; N, 30.1%).

**6-Cyano-2:2'-dipyridyl.**—6-Bromo-2:2'-dipyridyl (1.5 g.) in diphenyl (10 g.) was heated and stirred with dry cuprous cyanide (2.0 g.) until a viscid, dark red product separated. After a further addition of cuprous cyanide (1.0 g.) the mixture was boiled for 15 minutes, diphenyl decanted, and the residue washed with benzene, powdered, and digested with concentrated potassium cyanide solution at 90°. The copper-free yellow residue was separated, dried, and sublimed at 210°/20 mm. The white sublimate (0.4 g.) of *6-cyano-2:2'-dipyridyl* was crystallised from light petroleum (b. p. 60—80°); m. p. 151° (Found: N, 23.2.  $C_{11}H_7N_3$  requires N, 23.2%). The nitrile was soluble in warm water and gave a red coloration with ferrous salts.

**6:6'-Dicyano-2:2'-dipyridyl**, prepared in exactly the same way as for the monocyanoderivative, crystallised from benzene in white needles, m. p. 255° (Found: C, 70.2; H, 3.1; N, 27.0.  $C_{12}H_6N_4$  requires C, 69.9; H, 2.9; N, 27.2%).

**2:2'-Dipyridyl-6-carboxylic Acid.**—6-Cyano-2:2'-dipyridyl (0.2 g.) was evaporated three times with concentrated hydrochloric acid (10 c.c.). The solid was dissolved in water and treated successively with sodium acetate and copper acetate solutions. After 12 hours the crystalline copper salt was collected and decomposed in aqueous suspension with hydrogen sulphide. Filtration and evaporation gave the *acid* in small white needles, which decomposed at 210—220° after previous sintering at 155°, forming 2:2'-dipyridyl and carbon dioxide (Found: N, 14.3.  $C_{11}H_8O_2N_2$  requires N, 14.0%).

**2:2'-Dipyridyl-6:6'-dicarboxylic Acid.**—(1) 6:6'-Dicyano-2:2'-dipyridyl was boiled and evaporated three times with concentrated hydrochloric acid. The residue was dissolved in 2*N*-caustic soda, from which the moderately soluble sodium salt crystallised. After purification this salt was treated with dilute acid. The sparingly soluble *carboxylic acid* crystallised from much hot water in small white needles, which decomposed at 286° into 2:2'-dipyridyl and carbon dioxide (Found: C, 58.7; H, 3.1; N, 12.2.  $C_{12}H_8O_4N_2$  requires C, 59.0; H, 3.3; N, 11.5%). It gave an amorphous greenish-yellow compound with cupric acetate solution and both this and the foregoing monocarboxylic acid furnished red tints with ferrous salts. (2) 6:6'-Dimethyl-2:2'-dipyridyl (*vide infra*) (1.0 g.) in pure pyridine (10 c.c.) was boiled with selenium dioxide (3.0 g.) for 5 hours. Solvent was removed from the dark brown mixture, water added, and excess of selenium dioxide removed with sulphur dioxide. The acid was dissolved in caustic soda solution, the sodium salt recovered by crystallisation, and the dicarboxylic acid regenerated as in method (1).

**6:6'-Dimethyl-2:2'-dipyridyl.**—(1) 2-Methylpyridine (224 g.) and ferric chloride (166 g.) were heated at 350° for 4 hours in an autoclave fitted with a stirrer. The cooled, almost black product was powdered, basified with excess of caustic soda, and distilled in steam. The distillate after evaporation with hydrochloric acid was basified, extracted, dried, and distilled. Cooled below 0°, the fraction (3.0 g., b. p. 250—310°) gave white crystals (0.5 g.), which after crystallisation from petroleum melted at 89—90° (picrate, m. p. 170°). (2) 2-Methylpyridine (300 g.) and a nickel catalyst were heated at 325° for 6 hours according to the method of Willink and Wibaut (*loc. cit.*). The yield of dimethyl derivative was 0.2 g. The foregoing authors give m. p. 89.5—90.5° (picrate, m. p. 170—171°). It was confirmed that this diamine gave no colour with ferrous salts.

#### *Tripyridyls.*

*Action of Copper Powder on a Mixture of 6-Bromo-2:2'-dipyridyl and 2-Bromopyridine in Diphenyl.*—6-Bromo-2:2'-dipyridyl (3.0 g.) and 2-bromopyridine (3 g.) in diphenyl (20.0 g.)



were heated with copper powder (10 g.), and the process continued as in experiment 3 (p. 1667). The product yielded 2:6-di-2'-pyridylpyridine (0.2 g.), 6:6'-di-2'-pyridyl-2:2'-dipyridyl (0.2 g.), and 2:2'-dipyridyl (not estimated).

*Action of Iodine on a Mixture of 2:2'-Dipyridyl and Pyridine.*—Iodine (94 g.) was dissolved in 2:2'-dipyridyl (312 g.) and pyridine (158 g.), and the mixture heated in a glass container in an autoclave at 310° for 4 hours. The dark brown product was distilled in steam from a strongly alkaline solution to remove pyridine, and the residue extracted repeatedly with boiling light petroleum (b. p. 60—80°). Solvent was removed from these extracts, and unchanged 2:2'-dipyridyl distilled (97 g.). 2:2':2''-Tripyridyl was extracted from the residual bases with light petroleum (b. p. 40—60°) and distilled under reduced pressure (yield, 15 g.). The petroleum-insoluble fraction consisted of crude 2:2':2'':2'''-tetrapyridyl (11 g.).

*Action of Ferric Chloride on Mixtures of 2:2'-Dipyridyl and Pyridine.*—Ferric chloride (100 g.), 2:2'-dipyridyl (312 g.), and pyridine (156 g.) were heated in a steel autoclave with stirring at 330° for 6 hours. The product was worked up according to the method already described (J., 1932, 20). The yield of purified 2:6-di-2'-pyridylpyridine was 10 g.

*Bromination of 2:6-Di-2'-pyridylpyridine at 500°.*—The triamine (10 g.) and bromine (10 g.) were passed through the apparatus used for the bromination of 2:2'-dipyridyl at 500°. The hard greenish-black product was boiled with water, and the residue separated. The filtrate was basified and extracted with benzene; the hydrocarbon solution was then shaken with small quantities of aqueous ferrous sulphate until the aqueous layer retained only a faint persistent red colour. The benzene solution was evaporated, and the residue crystallised from light petroleum (b. p. 60—80°), 6'-bromo-2:6-di-2'-pyridylpyridine separating in white needles (1.5 g.), m. p. 153° (Found: Br, 25.1. C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>Br requires Br, 25.6%).

The acid-insoluble residue (8.0 g.) was digested with 2*N*-sodium hydroxide, washed with water, dried, and sublimed at 250°/20 mm., the white sticky sublimate triturated with acetone, and the insoluble portion crystallised from boiling toluene; 6'':6''-dibromo-2:6-di-2'-pyridylpyridine separated in white needles, m. p. 248°, which were insoluble in acids and gave no coloration with ferrous salts (Found: Br, 40.7. C<sub>15</sub>H<sub>9</sub>N<sub>3</sub>Br<sub>2</sub> requires Br, 40.9%). This bromo-derivative gave a red complex compound with cuprous cyanide, and aqueous ammonia at 220° furnished white needles of an amine, m. p. 183—184°.

#### Tetrapyridyls.

*Action of Iodine on 2:2'-Dipyridyl at 310°.*—A well-mixed solution of iodine (100 g.) in 2:2'-dipyridyl (500 g.) was heated in a glass container in an autoclave at 310° for 4 hours. The cooled product was boiled with 100 g. of sodium hydroxide in 1 l. of water and then repeatedly extracted with hot benzene. The extract was separated from a black carbonaceous residue (20 g.), the solvent removed, and unchanged 2:2'-dipyridyl distilled under reduced pressure (403 g.). The residual tetrapyridyls were washed with light petroleum (b. p. 40—60°) to remove any 2:2'-dipyridyl and other soluble products, and the residue sublimed at 220—230°/20 mm.; crystallisation of the sublimate from hot benzene gave 6:6'-di-2'-pyridyl-2:2'-dipyridyl as the more sparingly soluble fraction, m. p. 219—220° [Found: C, 77.1; H, 4.75; N, 18.6; *M* (Rast), 303. C<sub>20</sub>H<sub>14</sub>N<sub>4</sub> requires C, 77.4; H, 4.5; N, 18.1%; *M*, 310]. The tetramine was practically insoluble in water, but gave a sparingly soluble, crystalline trihydrated dihydrochloride with dilute hydrochloric acid (Found: Cl, 16.7; H<sub>2</sub>O, 11.7. C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>·2HCl·3H<sub>2</sub>O requires Cl, 16.2; H<sub>2</sub>O, 12.4%) and formed a very sparingly soluble, yellow, microcrystalline dipicrate, m. p. 312° (decomp.) (Found: N, 18.4. C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>·2C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires N, 18.2%. 0.5865 G. of the picrate gave 0.2294 g. of the base). Ferrous salts yielded a reddish-yellow colour with the base.

The more soluble benzene fractions were evaporated and treated with excess of hydrochloric acid, and the mixture taken to dryness. The hydrochlorides were triturated with a little cold water, the insoluble portion separated, the filtrate made alkaline, and the base crystallised from hot alcohol; white leaflets of an isomeric tetrapyridyl (m. p. 141°), to which the formula 6:6'-di-2'-pyridyl-2:3'-dipyridyl (XI) was ascribed, then separated. This base gave an intense red coloration with ferrous salts and furnished an insoluble greenish-blue deposit with cupric chloride in hydrochloric acid [Found: C, 77.4, 77.1; H, 4.4, 4.3; N, 18.3%; *M* (Rast), 306].

*Action of Copper Powder on 6-Bromo-2:2'-dipyridyl.*—6-Bromo-2:2'-dipyridyl (1.0 g.) in diphenyl and copper powder (2.0 g.) were heated to boiling for 2 hours. The cooled mixture was treated successively with light petroleum, nitric acid, aqueous ammonia, and potassium

cyanide solution, and the insoluble base filtered off, dried, and sublimed. After crystallisation and resublimation 6 : 6'-di-2''-pyridyl-2 : 2'-dipyridyl was obtained pure (0.2 g.), m. p. 219—220°.

*Action of Copper Powder on a Mixture of 6 : 6'-Dibromo-2 : 2'-dipyridyl and 2-Bromopyridine in Diphenyl.*—A solution of 6 : 6'-dibromo-2 : 2'-dipyridyl (2.0 g.) and 2-bromopyridine (3.0 g.) in diphenyl (10 g.) was heated to boiling, and copper powder (10 g.) added. The product was treated as in the foregoing experiment except that the 2 : 2'-dipyridyl (*ca.* 1.0 g.) formed was extracted with light petroleum (b. p. 40—60°) before purification of the 6 : 6'-di-2''-pyridyl-2 : 2'-dipyridyl (0.05 g.), m. p. 219—220°, which was then carried out as already described.

*Action of Ferric Chloride on 2 : 2'-Dipyridyl.*—Ferric chloride (22 g.) and 2 : 2'-dipyridyl (120 g.) were heated in a sealed tube at 310° for 4 hours. The product was extracted with benzene, and the residue mixed with sodium carbonate and heated in a stream of carbon dioxide. The volatilised bases were added to the benzene extract, the solvent removed, and 2 : 2'-dipyridyl (107 g.) distilled. The residue was extracted with light petroleum (b. p. 40—60°), and the insoluble portion sublimed. The sublimate was triturated with acetone, crystallised from benzene, and resublimed; the tetrapyridyl (10 g.) then melted at 219—220°. The isomeric tetrapyridyl, m. p. 141°, was obtained in traces from the more soluble portions of the mixture.

*Action of Ruthenium Trichloride on 2 : 2'-Dipyridyl.*—Ruthenium trichloride (15 g.) and 2 : 2'-dipyridyl (100 g.) were heated with stirring; at 260° a vigorous reaction began and the temperature rose to 270°. After 3 hours at the b. p. the reaction mixture was treated as in the foregoing experiment with ferric chloride. Yield of tetrapyridyl (m. p. 219—220°) 1.5 g. and of isomeric tetramine (m. p. 141°) *ca.* 0.01 g.

*Action of Iodine on 4 : 4'-Dipyridyl.*—Anhydrous 4 : 4'-dipyridyl (50 g.) and iodine (10 g.) were heated with stirring to the b. p. of the base (305°) for 3 hours. The cooled product was extracted with benzene, and the residue mixed with sodium carbonate and heated to dull redness in a stream of carbon dioxide. The volatilised bases were added to the benzene extract, the solvent removed, and 4 : 4'-dipyridyl distilled. The residue was triturated with alcohol, and the insoluble portion sublimed at 240°/20 mm. The sublimate after crystallisation from hot dimethylaniline and resublimation consisted of pure 4 : 4'-di-4''-pyridyl-2 : 2'-dipyridyl (XIII), m. p. 232—233°; yield, 1.5 g. [Found: C, 77.3; H, 4.7; N, 18.15%; *M* (Rast), 301]. This tetrapyridyl gave an intense red coloration with ferrous salts.

*Action of Iodine on 3 : 4'-Dipyridyl.*—A well-stirred mixture of 3 : 4'-dipyridyl (50 g.) and iodine (10 g.) was heated to boiling (296°) for 3 hours. The cooled, dark brown product was treated as in the foregoing experiment with 4 : 4'-dipyridyl; 4 : 4'-di-3''-pyridyl-2 : 2'-dipyridyl, m. p. 222°, then formed white needles giving an intense coloration with ferrous salts [Found: C, 77.2; H, 4.0; N, 18.4%; *M* (Rast), 302].

*Action of Copper Powder on 5(?) -Bromo-2 : 2'-dipyridyl.*—The bromo-2 : 2'-dipyridyl (1.0 g.) in diphenyl (5.0 g.) was heated with copper powder for 2 hours. The cooled brownish-green product was treated successively with benzene, nitric acid, aqueous ammonia, and potassium cyanide solution, and the insoluble base was separated and purified by crystallisation from alcohol and sublimation. 6 : 6'-Di-2''-pyridyl-3 : 3'-dipyridyl, m. p. 233°, formed white crystals readily soluble in dilute acids [Found: C, 77.3, 77.5; H, 4.5, 4.6; N, 18.2, 18.4%; *M* (Rast), 306].

#### *Pentapyridyl.*

*Action of Copper Powder on a Mixture of 6' : 6''-Dibromo-2 : 6-di-2'-pyridylpyridine and 2-Bromopyridine.*—6' : 6''-Dibromo-2 : 6-di-2'-pyridylpyridine (2.0 g.) and 2-bromopyridine (5.0 g.) in diphenyl (15.0 g.) were heated to boiling with copper powder (10 g.). After 1 hour a further quantity of copper (5.0 g.) was added, and heating continued for 2 hours. The cooled mixture was heated with benzene, the residue digested with dilute nitric acid, and the solution filtered from insoluble products, basified with ammonia, and treated with excess of aqueous potassium cyanide. The crude bases were washed, dried, triturated with acetone to remove 2 : 2'-dipyridyl, and sublimed at 320°/20 mm. After crystallisation from dimethylaniline and resublimation, 2 : 6-di-6''-(2' : 2''-dipyridyl)pyridine (XV), m. p. 265°, formed white crystals (0.1 g.), which gave a deep red coloration with ferrous salts [Found: C, 77.25; H, 4.3; N, 17.95; *M* (Rast), 382. C<sub>25</sub>H<sub>17</sub>N<sub>5</sub> requires C, 77.5; H, 4.4; N, 18.1%; *M*, 387]. A solution of this pentamine in excess of hydrochloric acid was evaporated to dryness; a dihydrated trihydrochloride, which decomposed on heating and was hydrolysed by water, was obtained (Found: Cl, 20.3. C<sub>25</sub>H<sub>17</sub>N<sub>5</sub>, 3HCl, 2H<sub>2</sub>O requires Cl, 20.0%).

*Action of Copper Powder on a Mixture of 6-Bromo-2 : 2'-dipyridyl and 2 : 6-Dibromopyridine.*—

6-Bromo-2 : 2'-dipyridyl (12 g.) and 2 : 6-dibromopyridine (6.0 g.) in diphenyl (50 g.) were heated with copper powder (15 g.) for 1 hour, more metal (5 g.) added, and heating continued for 2 hours. The product was treated as in the foregoing experiment, a white sublimate (3.0 g.) being obtained. Warm benzene removed tetrapyridyl (2.5 g.) and the residue was sublimed at 260—270°/20 mm., crystallised from dimethylaniline, and resublimed. These processes were repeated until pure 2 : 2' : 2'' : 2''' : 2''''-pentapyridyl, m. p. 265°, was isolated. The yield was about 0.1 g. The residues contained mixtures of pentapyridyl and hexapyridyl (0.4 g.).

*Hexapyridyl.*

*Action of Iodine on 2 : 6-Di-2'-pyridylpyridine.*—2 : 6-Di-2'-pyridylpyridine (66 g.) and iodine (13.2 g.) were heated with stirring at 310—320° for 3 hours. The cooled product was dissolved in hydrochloric acid, filtered from a carbonaceous residue (2.0 g.), basified, and treated with benzene to remove unchanged triamine; the dry grey residue was sublimed (350°/20 mm.). The sublimate was washed with acetone, crystallised from dimethylaniline, and resublimed. A repetition of these crystallisations and sublimations gave white crystals of 6 : 6'-di-6''-(2'' : 2'''-dipyridyl)-2 : 2'-dipyridyl (XVI), m. p. 350°; yield, 1.5 g. (Found: C, 77.5; H, 4.4; N, 18.4; *M*, ebullioscopic in diphenyl, 471.  $C_{30}H_{20}N_6$  requires C, 77.5; H, 4.3; N, 18.1%; *M*, 464). This sparingly soluble hexamine, by evaporation to dryness with excess of hydrochloric acid gave a crystalline *tetrahydrochloride*, which decomposed without melting and was extensively hydrolysed by water (Found: Cl, 23.6.  $C_{30}H_{20}N_6 \cdot 4HCl$  requires Cl, 23.2%).

*Action of Ferric Chloride on 2 : 6-Di-2'-pyridylpyridine.*—Ferric chloride (4.0 g.) and the triamine (25 g.) were heated at 330° for 3 hours. The cold brownish-black product was powdered and extracted with benzene, and the residue mixed with sodium carbonate and heated in a stream of carbon dioxide. The volatile bases were added to the benzene extract, the solvent removed, and the triamine distilled. The residue after trituration with acetone was sublimed and crystallised from dimethylaniline; the hexapyridyl, m. p. 350°, was then obtained. Yield, 0.1 g.

*Action of Copper Powder on a Mixture of 6-Bromo-2 : 2'-dipyridyl and 6 : 6'-Dibromo-2 : 2'-dipyridyl.*—The two substances (1.8 g. and 1.2 g. respectively) in diphenyl (10 g.) were heated with copper powder (5 g.) for 1 hour and then for a further hour after addition of more copper (2.0 g.). The cold product was treated successively with petroleum, nitric acid, aqueous ammonia, and potassium cyanide solution and the insoluble bases were separated, dried, and sublimed. The sublimate (0.6 g.) was washed with benzene to remove tetrapyridyl (0.5 g.) and the hexapyridyl, m. p. 350°, was purified as already described.

*Action of Copper Powder on 6'-Bromo-2 : 6-di-2'-pyridylpyridine.*—6'-Bromo-2 : 6-di-2'-pyridylpyridine (0.5 g.) in diphenyl (5.0 g.) was heated with copper powder (5.0 g.), added in two portions. The product, treated as in the foregoing experiment except that washing with benzene was omitted, gave 0.15 g. of pure hexapyridyl, m. p. 350°.

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