241. *Arylpyridines. Part IV. 3- and 4-Pyridyldiphenyls.*

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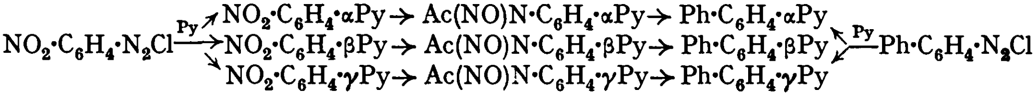
By the action of an aqueous solution of diazotised 3-aminodiphenyl on pyridine a mixture of 3-pyridyldiphenyls is obtained from which 3-α- and 3-*γ-pyridyldiphenyl* are isolated. In similar manner diazotised 4-aminodiphenyl and pyridine give 4-α- and 4-*γ-pyridyldiphenyl*. The same pyridyldiphenyls, together with the corresponding *β-pyridyldiphenyls*, are also obtained from the appropriate nitrophenylpyridine by successive reduction, acetylation, nitrosation, and reaction with benzene. The nitration of the three isomeric 4-pyridyldiphenyls is shown to give a mixture of the 4′- and *2′-nitro-4-pyridyldiphenyls*.

In Parts I, II, and III (this vol., pp. 349, 355, 358) it has been shown that a mixture of the α-, β-, and γ-arylpyridine is obtained when an aqueous solution of a diazotised arylamine is added to excess of pyridine, although it has not been possible to isolate all three isomerides in every case. Mixtures of the hitherto unknown 3- and 4-pyridyldiphenyls have now been obtained by the action of diazotised 3- and 4-aminodiphenyl respectively on pyridine and in each case two pure isomerides have been isolated from the product.

From the reaction between aqueous diazotised 3-aminodiphenyl and pyridine a mixture of 3-pyridyldiphenyls was obtained, from which 3-α- and 3-*γ-pyridyldiphenyl* were isolated by fractional crystallisation of the *picrates* from acetone. In a similar manner aqueous diazotised 4-aminodiphenyl and pyridine gave a mixture of 4-pyridyldiphenyls from which 4-α- and 4-γ-*pyridyldiphenyl* were isolated.

The same pyridyldiphenyls have also been prepared from the appropriate nitrophenylpyridine by reduction to the aminophenylpyridine, followed successively by acetylation, nitrosation, and reaction with benzene. Thus α-, β-, and γ-3-nitrophenylpyridine, isolated from the reaction between diazotised *m*-nitroaniline and pyridine (cf. Part I), have been separately reduced, acetylated, and nitrosated to yield the corresponding α-, β-, and γ-3-nitrosoacetamidophenylpyridine, which reacted in the normal manner with benzene with evolution of nitrogen and formation of the corresponding 3-α-, 3-β-, and 3-γ-*pyridyldiphenyl*. Similarly, α-, β-, and γ-4-nitrophenylpyridine, isolated from the reaction between diazotised *p*-nitroaniline and pyridine, have been converted through the appropriate nitroso-compounds into 4-α-, 4-β-, and 4-γ-*pyridyldiphenyl*. The identity of the 3-α- and 3-γ-pyridyldiphenyls as well as of the 4-α- and 4-γ-pyridyldiphenyls, isolated from the reaction between the appropriate diazotised aminodiphenyl and pyridine, with the corresponding compounds prepared from the nitrosoacetamidophenylpyridines, places the constitution of these compounds beyond doubt. The sequence of reactions described above is summarised diagrammatically below. The reactions were carried out with both the *m*- and the *p*-series.



$$\begin{tikzcd}
 & NO_2\cdot C_6H_4\cdot\alpha Py \arrow[r] & Ac(NO)N\cdot C_6H_4\cdot\alpha Py \arrow[r] & Ph\cdot C_6H_4\cdot\alpha Py & \\
NO_2\cdot C_6H_4\cdot N_2Cl \arrow[ur, "Py"] \arrow[r] \arrow[dr] & NO_2\cdot C_6H_4\cdot\beta Py \arrow[r] & Ac(NO)N\cdot C_6H_4\cdot\beta Py \arrow[r] & Ph\cdot C_6H_4\cdot\beta Py & Ph\cdot C_6H_4\cdot N_2Cl \arrow[ul] \arrow[l, "Py"] \arrow[dl] \\
 & NO_2\cdot C_6H_4\cdot\gamma Py \arrow[r] & Ac(NO)N\cdot C_6H_4\cdot\gamma Py \arrow[r] & Ph\cdot C_6H_4\cdot\gamma Py &
\end{tikzcd}$$

The formation of nitroso-compounds from the six acetamidophenylpyridines was to a certain extent unexpected, since it was known that α-acetamidopyridine could not be nitrosated by means of nitrous fumes or nitrosyl chloride (Haworth, Heilbron, and Hey, this vol., p. 372; France, Heilbron, and Hey, this vol., p. 369), but gave instead α-acetamidopyridinium nitrate. It is now evident that this inhibition to nitrosation does not persist when the acetamido-group is attached to the benzene nucleus in a phenylpyridine. In the preparation of the nitrosoacetamidophenylpyridines the nitrosyl chloride method described by France, Heilbron, and Hey (*loc. cit.*) was used. In the isolation of the nitroso-compounds it was frequently found that, owing to the presence of the basic pyridine ring, pouring into water alone did not precipitate the product unless sodium carbonate was added to neutralise some of the acetic acid present.

It may be noted that in the reaction between both γ-3- and γ-4-nitrosoacetamidophenylpyridine and benzene, in addition to the expected γ-pyridyldiphenyl, some γ-phenylpyridine was also isolated. In similar manner the reaction between α-4-nitrosoacetamidophenylpyridine and benzene gave both 4-α-pyridyldiphenyl and α-phenylpyridine. These are further examples of the dual character of the reaction of nitrosoacylarylamines with aromatic compounds, which may be represented thus:

$$Ar\cdot N(NO)\cdot CO\cdot CH_3 + Ar'H \longrightarrow Ar\cdot Ar' + N_2 + CH_3\cdot CO_2H \text{ (main reaction)}$$
$$Ar\cdot N(NO)\cdot CO\cdot CH_3 + Ar'H \longrightarrow Ar\cdot H + N_2 + [CH_3\cdot CO_2Ar'] \text{ (side reaction)}$$

This same feature was revealed in the preparation of *p*-terphenyl from the reaction between dinitrosodiacetyl-1 : 4-phenylenediamine and benzene, which gave in addition some diphenyl (cf. Haworth and Hey, this vol., p. 361). It is highly probable that phenylpyridines are also formed in small quantities in the corresponding reactions with α-3-, β-3-, and β-4-nitrosoacetamidophenylpyridines, but, owing to insufficiency of material and the fact that in these cases the phenylpyridines are liquid, they escaped detection.

Nitration of 4-α-pyridyldiphenyl gave mainly 4'-*nitro*-4-α-*pyridyldiphenyl* together with a smaller quantity of an isomeride regarded as 2'-*nitro*-4-α-*pyridyldiphenyl*. Both nitro-compounds were reduced to the corresponding *amines*. In similar manner nitration of 4-β-pyridyldiphenyl and of 4-γ-pyridyldiphenyl gave 4'- and 2'-*nitro*-4-β-*pyridyldiphenyl*, and 4'- and 2'-*nitro*-4-γ-*pyridyldiphenyl* respectively. In all three cases the 4'-nitro-compounds were oxidised to *p*-nitrobenzoic acid, the identification of which served to establish the position occupied by the nitro-group.

EXPERIMENTAL.

3-*Pyridyldiphenyls.*

Action of Diazotised 3-Aminodiphenyl on Pyridine.—An aqueous solution of the diazonium chloride prepared in the usual manner from 3-aminodiphenyl (15 g.) was added slowly with stirring during 2 hours to pyridine (250 c.c.) at 20°. After warming to complete the reaction, the pyridine was removed by distillation in steam, and the tarry residue extracted with benzene. After removal of the benzene, distillation at 145—205°/< 1 mm. gave a mixture of 3-pyridyldiphenyls as a viscous liquid (8·0 g.). By the fractional crystallisation of the picrates from acetone two pure compounds were obtained. The less soluble 3-*γ-pyridyldiphenyl picrate* separated in small needles, m. p. 231° (Found: N, 12·2. $C_{17}H_{13}N,C_6H_3O_7N_3$ requires N, 12·2%), whereas the more soluble 3-*α-pyridyldiphenyl picrate* separated in large prisms, m. p. 169° (Found: N, 12·2%). Their identity with the corresponding compounds prepared as described below was shown by means of mixed melting points.

3-*Nitrophenylpyridines.*—By the method described in Part I (*loc. cit.*), technical *m*-nitroaniline (140 g.) gave a mixture of 3-nitrophenylpyridines (85 g.), b. p. 204—214°/14 mm., from which α-3-nitrophenylpyridine (24 g.), m. p. 72—73°, β-3-nitrophenylpyridine (6·5 g.), m. p. 100—101°, and γ-3-nitrophenylpyridine (6·0 g.), m. p. 108—109°, were obtained.

3-*α-Pyridyldiphenyl.*—A solution of α-3-nitrophenylpyridine (14 g.) in hot alcohol (140 c.c.) was added to a solution of stannous chloride (75 g.) in concentrated hydrochloric acid (75 c.c.). When the initial reaction had subsided, the reduction was completed by boiling under reflux for 2 hours. After removal of most of the alcohol by distillation, a large excess of 50% caustic soda solution was added. The base, which separated as an oil, was extracted with ether. After removal of the ether, distillation at 213°/20 mm. gave α-3-aminophenylpyridine (10 g.) as an almost colourless, viscous liquid, which, on warming on the steam-bath with excess of acetic anhydride and pouring into aqueous ammonia, gave *α-3-acetamidophenylpyridine*; this crystallised from benzene–light petroleum (b. p. 40—60°) in colourless needles, m. p. 141—142° (Found: C, 73·5; H, 5·9. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7%). Nitrosation was carried out by adding a solution of nitrosyl chloride (6·0 g.) in an equal volume of acetic anhydride slowly to a stirred solution of α-3-acetamidophenylpyridine (10·0 g.) in a mixture of glacial acetic acid (60 c.c.) and acetic anhydride (30 c.c.) containing freshly fused potassium acetate (10 g.) and phosphoric oxide (0·1 g.) (cf. France, Heilbron, and Hey, *loc. cit.*). The nitroso-compound, which separated as an oily solid on pouring into ice-water, was immediately extracted with benzene. A further quantity of the nitroso-compound, which separated on the addition of sodium carbonate to the aqueous layer, was also extracted with benzene and the combined extracts (600 c.c.), after being washed twice with water to remove acetic acid as far as possible, were kept at room temperature over anhydrous sodium sulphate. Nitrogen was slowly evolved, and after 24 hours the excess of benzene was removed. Distillation of the residue at 75—85°/0·002 mm. gave 3-*α-pyridyldiphenyl* as a viscous liquid. The picrate (10 g.) separated from acetone in large prisms, m. p. 169° both alone and on admixture with the picrate of the same m. p. described above. Treatment of the picrate with 5% caustic soda solution liberated the free base as a colourless viscous liquid (Found: C, 88·5; H, 5·4. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6%).

In the following five examples the conversion of the nitrophenylpyridines into the pyridyldiphenyls (by successive reduction, acetylation, nitrosation, and reaction with benzene) was carried out exactly as described above for the conversion of α-3-nitrophenylpyridine into 3-α-pyridyldiphenyl, except where otherwise stated.

3-*β-Pyridyldiphenyl.*—Reduction of β-3-nitrophenylpyridine (6·0 g.) gave *β-3-aminophenylpyridine* (4·7 g.), which after extraction from the reaction mixture with benzene crystallised from chloroform–light petroleum (b. p. 40—60°) in needles, m. p. 77—78° (Found: C, 77·7; H, 6·1. $C_{11}H_{10}N_2$ requires C, 77·6; H, 5·9%). Acetylation gave *β-3-acetamidophenylpyridine*, which crystallised from benzene–light petroleum (b. p. 40—60°) in colourless needles, m. p. 135—136° (Found: C, 73·3; H, 5·8. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7%). Nitrosation of β-3-acetamidophenylpyridine (4·0 g.), followed by pouring into ice-water and neutralisation of most of the excess acid with sodium carbonate, gave the nitroso-derivative as a semi-solid oil, which was immediately extracted with benzene (300 c.c.). After removal of the benzene, distillation at 75—85°/0·002 mm. gave 3-*β-pyridyldiphenyl* as a viscous liquid, which was purified by passing its solution in benzene through a column of alumina (Found: C, 88·1; H, 5·8. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6%). The *picrate* (3·8 g.) crystallised from acetone in small needles, m. p. 178—179° (Found: N, 12·4. $C_{17}H_{13}N,C_6H_3O_7N_3$ requires N, 12·2%).

3-γ-Pyridyldiphenyl.—Reduction of γ-3-nitrophenylpyridine (5·5 g.) and extraction of the base with benzene gave *γ-3-aminophenylpyridine* (4·5 g.), which crystallised from benzene–light petroleum (b. p. 40—60°) in long needles, m. p. 165—166° (Found : C, 77·6; H, 6·1. $C_{11}H_{10}N_2$ requires C, 77·6; H, 5·9%). *γ-3-Acetamidophenylpyridine* crystallised from dilute alcohol in long colourless needles, m. p. 171—172° (Found : C, 73·5; H, 5·8. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7%). Nitrosation of the latter (4·0 g.), followed by pouring into water and neutralisation of most of the excess of acid with sodium carbonate, gave γ-3-nitrosoacetamidophenylpyridine (m. p. 85—86° decomp.) as a yellow solid, which was dried on a porous tile and added to benzene (250 c.c.). After removal of the benzene, distillation at 80—100°/0·002 mm. gave crude 3-γ-pyridyldiphenyl as a viscous yellow liquid, which solidified on cooling. Coloured impurities were removed by passing a solution in benzene through a column of alumina. After removal of the benzene, crystallisation of the residue from light petroleum (b. p. 40—60°) gave pure *3-γ-pyridyldiphenyl* in colourless plates (2·1 g.), m. p. 81—82° (Found : C, 88·3; H, 5·7. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6%). The picrate crystallised from acetone, in which it was sparingly soluble, in small needles, m. p. 231° both alone and on admixture with the picrate of the same m. p. obtained above from the product of the action of diazotised 3-aminodiphenyl on pyridine. A small quantity of a second colourless compound was collected at about 50° during the high-vacuum distillation of the reaction product. It melted at 73—74° and showed no depression in m. p. on admixture with γ-phenylpyridine.

4-Pyridyldiphenyls.

Action of Diazotised 4-Aminodiphenyl on Pyridine.—An aqueous solution of the diazonium chloride, prepared in the normal manner from 4-aminodiphenyl (27 g.), was dropped with stirring during 1½ hours into pyridine (250 c.c.) at 20°. After warming to complete the reaction, the solution was poured into water, and the brown precipitate filtered off and dried. Distillation at 215—255°/$<$ 1 mm. gave a mixture of 4-pyridyldiphenyls (13 g.) as a hard yellowish-brown solid. The picrates, prepared in glacial acetic acid solution, were fractionally crystallised from acetone. Two pure products were obtained, the less soluble *4-γ-pyridyldiphenyl picrate* separating in long needles, m. p. 215° (Found : N, 12·0. $C_{17}H_{13}N,C_6H_3O_7N_3$ requires N, 12·2%), and the more soluble *4-α-pyridyldiphenyl picrate* in small needles, m. p. 186—187° (Found : N, 11·9%). Their identity with the corresponding compounds prepared as described below was shown by means of mixed melting points.

4-Nitrophenylpyridines.—The α-, β-, and γ-4-nitrophenylpyridines were prepared from diazotised *p*-nitroaniline and pyridine as described in Part I (*loc. cit.*).

4-α-Pyridyldiphenyl.—α-4-Aminophenylpyridine was prepared by the reduction of α-4-nitrophenylpyridine as described above for the corresponding α-3-isomeride. This method was found to be more convenient than that described by Forsyth and Pyman (J., 1926, 2912). Acetylation gave *α-4-acetamidophenylpyridine*, which crystallised from benzene–light petroleum (b. p. 40—60°) in needles, m. p. 135—136° after drying at 100° (Found : C, 73·6; H, 5·6; N, 13·0. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7; N, 13·2%). On nitrosation the acetyl derivative (30 g.) gave *α-4-nitrosoacetamidophenylpyridine* in almost quantitative yield as a pale yellow solid, which was immediately filtered off, dried on a tile (m. p. 88—89° decomp.) (Found : N, 17·3. $C_{13}H_{11}O_2N_3$ requires N, 17·4%), and added to benzene (1000 c.c.). After removal of the benzene, distillation at 70—100°/0·0006 mm. gave first a pale yellow oil (1·5 g.), which was identified as α-phenylpyridine by the m. p. and mixed m. p. of its picrate : subsequently a yellowish-white solid collected, which was purified by passing its solution in benzene through a column of alumina. Crystallisation of the residue obtained on evaporation of the benzene from either alcohol or benzene–light petroleum (b. p. 40—60°) gave *4-α-pyridyldiphenyl* (16·2 g.) in colourless plates, m. p. 141—142° (Found : C, 88·5; H, 5·8. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6%). The picrate crystallised from acetone in small needles, m. p. 186—187° both alone and admixed with the picrate of the same m. p. described above.

4-β-Pyridyldiphenyl.—β-4-Aminophenylpyridine, prepared by the reduction of β-4-nitrophenylpyridine and extraction of the base with chloroform, gave *β-4-acetamidophenylpyridine*, which crystallised from dilute alcohol in needles, m. p. 181—182° (Found : C, 73·7; H, 5·9; N, 13·2. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7; N, 13·2%). Treatment of the acetyl derivative (10·0 g.) with nitrosyl chloride, pouring of the solution into ice-water, and partial neutralisation of the excess of acid with sodium carbonate, gave β-4-nitrosoacetamidophenylpyridine in almost theoretical yield, as a yellow solid (m. p. 70—71° decomp.), which was added to benzene (350 c c.). After removal of the benzene, distillation at 90—110°/0·001 mm. gave a yellowish-white solid, which was purified by passage over alumina as described above. Crystallisation from benzene–light petroleum (b. p. 40—60°) gave 4-β-*pyridyldiphenyl* (5·0 g.) in colourless plates, m. p. 151—152° (Found: C, 88·6; H, 5·7; N, 5·9. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6; N, 6·1%). The *picrate*, prepared in the normal manner, separated from acetone in long prismatic needles, m. p. 208—210° (Found: N, 12·0. $C_{17}H_{13}N,C_6H_3O_7N_3$ requires N, 12·2%).

4-γ-*Pyridyldiphenyl*.—γ-4-Aminophenylpyridine, prepared by the reduction of γ-4-nitrophenylpyridine and extraction of the base with chloroform, gave γ-4-*acetamidophenylpyridine*, which crystallised from dilute alcohol in needles, m. p. 210—211° (Found: C, 73·5; H, 5·8; N, 13·2. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7; N, 13·2%). Nitrosation of the acetyl derivative (4·0 g.) gave γ-4-nitrosoacetamidophenylpyridine in almost theoretical yield as a yellow solid (m. p. 81° decomp.), which was added to benzene (100 c.c.). After removal of the excess of benzene, distillation at 90—100°/0·001 mm. gave a yellowish-white solid, which was purified by passage in benzene solution over alumina. The 4-γ-*pyridyldiphenyl* (2·1 g.) thus obtained separated from benzene–light petroleum (b. p. 40—60°) in colourless plates, m. p. 209° (Found: C, 88·6; H, 5·7. $C_{17}H_{13}N$ requires C, 88·3; H, 5·6%). The picrate, prepared in the normal manner, crystallised from acetone in long needles, m. p. 215° both alone and admixed with the picrate of the same m. p. isolated above from the reaction between diazotised 4-aminodiphenyl and pyridine. As in the corresponding preparation of 3-γ-pyridyldiphenyl from γ-3-nitrosoacetamidophenylpyridine and benzene, a small quantity of a second compound was collected at about 50° in the high-vacuum distillation of the reaction product and was identified by m. p. and mixed m. p. as γ-phenylpyridine.

Nitration of 4-α-*Pyridyldiphenyl*.—A solution of fuming nitric acid (*d* 1·5, 70 c.c.) in glacial acetic acid (70 c.c.) was added to a solution of 4-α-pyridyldiphenyl (10 g.) in the minimum quantity of glacial acetic acid at 90°. After being heated on the steam-bath for ½ hour, the mixture was cooled and poured into water. The solid which separated was washed with dilute alkali and with water. Several crystallisations from alcohol gave 4'-*nitro*-4-α-*pyridyldiphenyl* (5·0 g.) in pale yellow plates, sparingly soluble in alcohol, m. p. 213° (Found: C, 73·6; H, 4·5; N, 9·9. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·3; N, 10·1%). From the alcoholic mother-liquors a second mononitro-derivative (2·0 g.), regarded as 2'-*nitro*-4-α-*pyridyldiphenyl*, was isolated, which separated from dilute acetic acid in pale yellow needles, m. p. 136—137° (Found: C, 73·8; H, 4·4%). The *nitrate* separated from alcohol in small yellow prisms, m. p. 188—190° (decomp.) (Found: C, 60·5; H, 4·0. $C_{17}H_{12}O_2N_2,HNO_3$ requires C, 60·2; H, 3·8%).

Oxidation of 4'-*Nitro*-4-α-*pyridyldiphenyl*.—To a solution of the nitro-compound (1·0 g.) in 50% sulphuric acid (50 c.c.) at 100° a solution of potassium permanganate (5·5 g. in 50 c.c. of warm water) was added dropwise with frequent shaking during 1½ hours; sulphur dioxide was then passed into the mixture until the precipitated manganese dioxide had dissolved. The solid which separated on cooling was filtered off and treated with dilute aqueous ammonia. Acidification of the filtered solution gave *p*-nitrobenzoic acid (0·2 g.) which separated from hot water in colourless leaflets, m. p. and mixed m. p. with an authentic specimen 232—234°.

4'-*Amino*-4-α-*pyridyldiphenyl*.—A solution of stannous chloride (9 g.) in concentrated hydrochloric acid (12 c.c.) was added to a solution of 4'-nitro-4-α-pyridyldiphenyl (2·5 g.) in hot glacial acetic acid (30 c.c.), and the whole heated on the steam-bath for 1 hour. After treatment with excess of alkali the base was extracted with ether. The ethereal solution exhibited a marked violet fluorescence. After removal of the ether, crystallisation of the residue from alcohol gave 4'-*amino*-4-α-*pyridyldiphenyl* (1·8 g.) in long, orange-yellow needles, m. p. 191—192° (Found: C, 83·0; H, 5·7. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%). Acetylation with acetic anhydride in the normal manner gave 4'-*acetamido*-4-α-*pyridyldiphenyl*, which separated from dilute alcohol in colourless leaflets, m. p. 236—237° (Found: C, 79·2; H, 5·7. $C_{19}H_{16}ON_2$ requires C, 79·2; H, 5·5%).

2'-*Amino*-4-α-*pyridyldiphenyl*.—A solution of stannous chloride (20 g.) in concentrated hydrochloric acid (25 c.c.) was added to a solution of 2'-nitro-4-α-pyridyldiphenyl (3·7 g.) in hot alcohol (50 c.c.), and the whole heated on the steam-bath for 1 hour. After removal of most of the alcohol by distillation, a large excess of 40% aqueous sodium hydroxide was added, and the base isolated with ether as above. Crystallisation from light petroleum (b. p. 60—80°) gave 2'-*amino*-4-α-*pyridyldiphenyl* (2·5 g.) in clusters of almost colourless needles, m. p. 98—99° (Found: C, 83·0; H, 5·8. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%). Acetylation gave 2'-*acetamido*-4-α-*pyridyldiphenyl*, which separated from benzene–light petroleum (b. p. 40—60°) in clusters of needles, m. p. 146—147° (Found: C, 79·4; H, 5·5. $C_{19}H_{16}ON_2$ requires C, 79·2; H, 5·5%).

Nitration of 4-β-*Pyridyldiphenyl*.—In similar manner nitration of 4-β-pyridyldiphenyl (1·7 g.) yielded a pale yellow solid, which after several crystallisations from alcohol gave

4'-nitro-4-β-pyridyldiphenyl (0·8 g.) in long, pale yellow needles, m. p. 192—193° (Found: C, 74·0; H, 4·6. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·3%). From the alcoholic mother-liquors a small quantity of a second mononitro-derivative, regarded as *2'-nitro-4-β-pyridyldiphenyl*, was obtained, which separated from methyl alcohol in pale yellow needle-prisms, m. p. 124—125° (Found: C, 74·0; H, 4·1. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·3%). Oxidation of 4'-nitro-4-β-pyridyldiphenyl, as described for the corresponding α-isomeride, gave *p*-nitrobenzoic acid, m. p. and mixed m. p. 232—234°.

Nitration of 4-γ-Pyridyldiphenyl.—4-γ-Pyridyldiphenyl (0·9 g.) was nitrated under similar conditions. Crystallisation of the product from alcohol gave *4'-nitro-4-γ-pyridyldiphenyl* (0·3 g.) in long, pale yellow needles, m. p. 196—197° (Found: C, 73·8; H, 4·4. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·3%). From the alcoholic mother-liquors a small quantity of a second mononitro-derivative, regarded as *2'-nitro-4-γ-pyridyldiphenyl*, was obtained, which crystallised from light petroleum (b. p. 60—80°) in small, pale yellow needles, m. p. 99—100° (Found: C, 74·1; H, 4·5. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·3%). Oxidation of 4'-nitro-4-γ-pyridyldiphenyl, as described for the corresponding α-isomeride, gave *p*-nitrobenzoic acid, m. p. and mixed m. p. 232—234°.

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