## 104. *Experiments on the Preparation of Certain Derivatives of 2- and 4-Benzylpyridine.*

By A. J. Nunn and K. Schofield.

Satisfactory conditions for the preparation of certain nitro- and amino-derivatives of 2- and 4-benzyl- and -benzoyl-pyridine are described. The use of copper sulphate as a catalyst in deaminations utilising hypophosphorous acid is recommended.

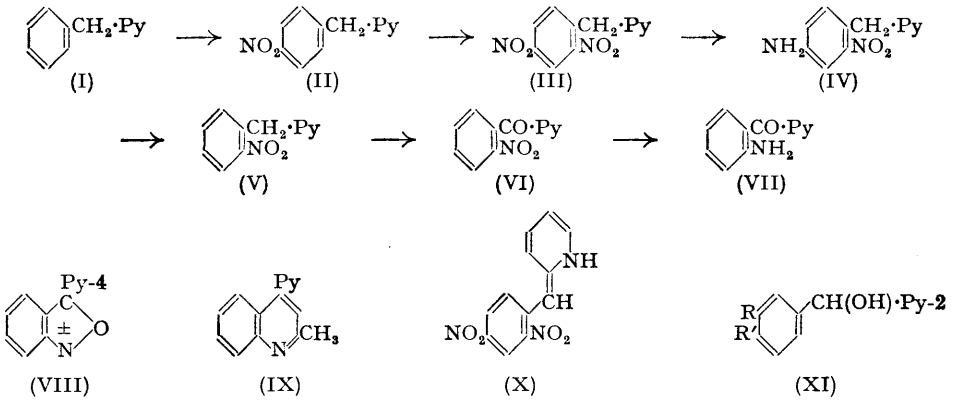
Amino-ketones of the types (VII) are required in these laboratories for a variety of experiments. Whilst we are examining other and, it is hoped, more flexible routes to such compounds, we have found it convenient so far to obtain (VII*a*) and (VII*b*) by the methods described below.

Conditions for effecting the series of reactions (I*a* ⟶ VII*a*), starting from 2-benzylpyridine, have recently been given by one of us (Schofield, *J.*, 1949, 2408). The present paper describes certain improvements in some of them, and the results obtained have served as models in extending the work to the analogous compounds (I*b* ⟶ VII*b*), originating in the relatively scarcer 4-benzylpyridine.

Tschitschibabin, Kuindshi, and Benewolenskaja (*Ber.*, 1925, **58**, 1580) nitrated 2-benzylpyridine in sulphuric acid, but Koenigs, Mensching, and Kirsch (*ibid.*, 1926, **59**, 1717), working with a mixture of 2- and 4-benzylpyridine, used fuming nitric acid. In a quantitative study, Bryans and Pyman (*J.*, 1929, 549) added 2-benzylpyridinium nitrate to sulphuric acid and isolated 58·8% of (II*a*). We have been able to isolate (II*a*) by the last method in 40% yield under preparative conditions, and so the adaptation by Schofield (*loc. cit.*) of Tschitschibabin's procedure is preferred.

The dinitro-compound (III*a*) was prepared by Tschitschibabin and his associates (*loc. cit.*) both by direct dinitration of 2-benzylpyridine and by further nitration of (II*a*), but these workers failed to record the essential experimental details. Clearly, successful direct dinitration would be attractive from the preparative point of view and we have

devised conditions which in small-scale experiments gave 41·4% of (III*a*) directly from 2-benzylpyridine, a yield slightly better than that (39%) previously obtained in two stages (Schofield, *loc. cit.*). However, this success could not be repeated on a large scale, and the two-stage process is still preferred.




"*a*" series: Py = 2-$C_5H_4N$. "*b*" series: Py = 4-$C_5H_4N$.

Wilson's original method (*J.*, 1931, 1936) for selectively reducing 2-(2 : 4-dinitrobenzyl)-pyridine to 2-(4-amino-2-nitrobenzyl)pyridine (IV*a*) was adapted by Schofield (*loc. cit.*) to give 75—80% yields in small-scale work, and rather less than this when large quantities were used. Slight modifications have now enabled us to prepare (IV*a*) quantitatively from (III*a*) on any desired scale.

The deamination of (IV*a*) to give 2-*o*-nitrobenzylpyridine (V*a*) was described by Wilson (*loc. cit.*) and later improved (Schofield, *loc. cit.*), to yield 48% of (V*a*). Both Wilson and Schofield used hypophosphorous acid prepared *in situ* from sodium hypophosphite and hydrochloric acid, the former purifying the product by vacuum-distillation. We have compared this with the direct use of commercial 30% hypophosphorous acid: the latter appears to be slightly preferable, but whilst increase in the amount used, from 15 to 30 equivalents, did give some improvement in yield, this was not sufficient to justify such a large expenditure of reagent. Kornblum, Cooper, and Taylor (*J. Amer. Chem. Soc.*, 1950, **72**, 3013), in recent experiments on the mechanism of hypophosphorous acid deaminations, found the rate of reaction to be increased by the addition to the reaction mixture of certain inorganic salts as catalysts, notably copper sulphate. It seemed to us possible that in the preparation of 2-*o*-nitrobenzylpyridine this might accelerate the deamination reaction compared with undesirable alternative decompositions of the diazonium compound; on the medium scale this device did in fact raise the yield of (V*a*) from 48% to 61·7%, but on the large-scale only 55·6% was obtained. In the light of this experience we would recommend the use of such catalysis in preparative deaminations utilising hypophosphorous acid, particularly when amines difficult of access are involved.

The yield obtained in the oxidation (V*a* ⟶ VI*a*) was unfortunately not accurately reported in the earlier paper (Schofield, *loc. cit.*), the 71% there claimed actually being the recovery of crude material. Of pure material there was obtained from this crude product only 55%. We now record a standardised oxidation procedure which consistently provides 57% of pure 2-*o*-nitrobenzoylpyridine.

Pure 4-*p*-nitrobenzylpyridine would appear to have been prepared only twice previously, Tschitschibabin and his co-workers (*loc. cit.*) obtaining it by means similar to those used in the 2-benzylpyridine series whereas Koenigs *et al.* (*loc. cit.*) obtained the compound only as an oil. In their quantitative studies Bryans and Pyman (*loc. cit.*) obtained 67·3% of (II*b*) from 4-benzylpyridine. The nitration method used by Schofield in preparing (II*a*) was not satisfactory in this case, but an adaptation of the procedure of Bryans and Pyman provided 53% of the desired product. The purity of the 4-benzylpyridinium nitrate, of which we describe the preparation, appeared to have little effect upon the reaction.

As in the 2-benzylpyridine series, Tschitschibabin *et al.* (*loc. cit.*) prepared the dinitro-compound (III*b*) both by direct dinitration of 4-benzylpyridine and by further nitration of (II*b*), but again details are lacking. Nitration of (II*b*) has now given 78·5% of the dinitro-compound (an overall yield of 41·6% from 4-benzylpyridine), whilst fuming nitric acid in sulphuric acid, used successfully by Huntress and Shaw (*J. Org. Chem.*, 1948, **13**, 674) in the case of 4-benzyl-2 : 6-dimethylpyridine, gave only 30·3% of the dinitro-compound.

4-(4-Amino-2-nitrobenzyl)pyridine, like its isomer, was isolated in almost quantitative yield through the agency of hydrogen sulphide and ammonia. In this series also, deamination of (IV*b*) was effected by means of hypophosphorous acid and copper sulphate, and the resulting 4-*o*-nitrobenzylpyridine (V*b*) was satisfactorily oxidised to 4-*o*-nitrobenzoylpyridine (VI*b*).

Unexpectedly, in view of the behaviour of the α-isomer, 4-*o*-nitrobenzoylpyridine was converted by an equivalent of stannous chloride into a mixture of the corresponding amine

FIG. 1. (I) 2-*Benzylpyridine ;* (II) 2-p-*Nitrobenzylpyridine ;* (III) 2-(2 : 4-*Dinitrobenzyl)pyridine ;* (IV) 2-(4-*Amino*-2-*nitrobenzyl)pyridine.* (*In absolute alcohol.*)

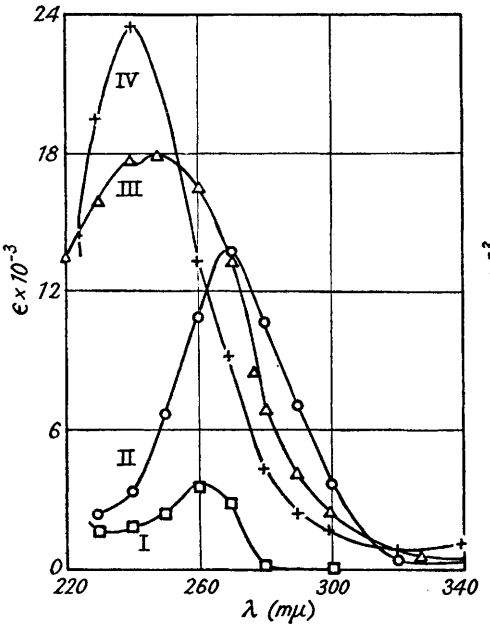
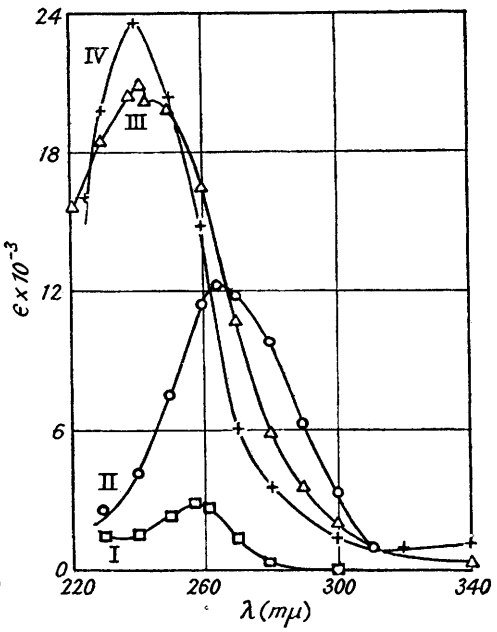



FIG. 2. (I) 4-*Benzylpyridine ;* (II) 4-p-*Nitrobenzylpyridine ;* (III) 4-(2 : 4-*Dinitrobenzyl)pyridine ;* (IV) 4-(4-*Amino*-2-*nitrobenzyl)pyridine.* (*In absolute alcohol.*)




(VII*b*) and the pyridylanthranil (VIII). Excess of the reducing agent gave solely the amine, and the anthranil could also be further reduced to this compound.

The orientation of the amino-ketone (VII*b*), and therefore of 4-*o*-nitrobenzoyl-, 4-*o*-nitrobenzyl-, and 4-(4-amino-2-nitrobenzyl)-pyridine, was proved by the preparation from it of 4-4′-pyridylquinaldine (IX*b*). 2-*o*-Aminobenzoylpyridine also reacted with acetone to give 4-2′-pyridylquinaldine. These derivatives of quinaldine have recently been described by Hey and Williams (*J.*, 1950, 1678).

Crystals of 2-(2 : 4-dinitrobenzyl)pyridine have the interesting property of changing to an intense violet colour when exposed to light, and of returning to yellow when kept in the dark. Neither the 4-isomer, nor any other member of the 2- and 4-series here described, exhibits this property. Tschitschibabin attributed the change to the conversion of (III*a*) by light into the structure (X), a conversion which is presumably rendered difficult in the 4-benzylpyridine derivative by the remoteness of the nitrogen atom in the pyridine ring. Both 2- and 4-(2 : 4-dinitrobenzyl)pyridine give yellow solutions in organic solvents, the colours of which are not obviously affected by light. We now record the ultra-violet absorption spectra of these and related compounds (Figs. 1 and 2), and it seems that in

solution they possess similar structures. It would be of interest to compare these spectra with those obtained by compounding the curves of suitable benzene and pyridine derivatives in order to detect any conjugation which may exist between the phenyl and pyridyl nuclei of benzylpyridine derivatives (cf. Braude, *J.*, 1949, 1902). We are collecting data for this purpose.

At the beginning of this work we envisaged the possibility of utilising Emmert and Asendorf's reaction (*Ber.*, 1939, **72**, 1188) to prepare carbinols of the type (XI) which it might have been feasible to oxidise and nitrate to give derivatives of (VI). This reaction has recently been exploited by Tilford, Shelton, and Van Campen (*J. Amer. Chem. Soc.*, 1948, **70**, 4001) for preparing a number of these carbinols. In the case of (XI; R = R′ = H) the American workers obtained a yield of 39%, whereas we could obtain no more than 22% of pure material. Again, with [XI; RR′ = $CH_2O_2$] Tilford *et al.* isolated an oil in 37% yield. However, Sperber, Papa, Schwenk, and Sherlock (*J. Amer. Chem. Soc.*, 1949, **71**, 887), who prepared the same compound by a different method, described it as a crystalline solid. In repeating the experiment of Tilford and his co-workers we were able to isolate 29% of product as an oil, but only 6% of the pure crystalline compound. These results, and others mentioned below, led us to abandon this route to the ketones (VI). (XI; RR′ = $CH_2O_2$) was oxidised to 2-(3 : 4-methylenedioxybenzoyl)-pyridine by means of aluminium *iso*propoxide and acetone.

## Experimental

M. p.s are uncorrected. Ethereal extracts were dried with anhydrous sodium sulphate.

2- *and* 4-*Benzylpyridine.*—These compounds were readily prepared by Crook's method (*J. Amer. Chem. Soc.*, 1948, **70**, 416), modified in minor details, which we found to be superior in both convenience and efficiency to any other previously reported. The violent initial reaction between pyridine and benzyl chloride met with by previous workers and also in our own experiments using earlier methods does not occur under Crook's conditions. We found the same ratio of 2- and 4-benzylpyridine in the reaction mixture as is reported by this author.

2234 C.c. of benzyl chloride (used in 19 batches) thus provided 2315 g. of mixed benzylpyridines. Ether proved to be a more convenient solvent in extracting these compounds from the reaction mixture than the benzene–ligroin mixture used by Crook, which produced troublesome emulsions. The isomers were separated by fractional distillation under reduced pressure rather than at the near-atmospheric pressure used by Crook, and in this way the mixture provided 1632 g. of 2-benzylpyridine (b. p. 152—154°/20 mm.) and 503 g. of 4-benzylpyridine (b. p. 162—164°/20 mm.).

### *Derivatives of 2-benzylpyridine*

2-*Benzylpyridinium Nitrate.*—Both of the following methods were used: (i) 2-Benzylpyridine (10 g.) and nitric acid (40 c.c.; 2N) saturated with sodium nitrate were shaken together at room temperature for ½ hour, and the resulting white suspension was kept at 0° for 3 hours. The nitrate (14·6 g.), m. p. 109—116°, was collected and dried *in vacuo*.

(ii) (Cf. Huntress and Walter, *J. Amer. Chem. Soc.*, 1948, **70**, 3702.) A solution of 2-benzylpyridine (20 g.) in concentrated nitric acid (8·4 c.c.) and water (59 c.c.) was cooled in an ice–salt bath for 5 hours. The solid white mass was allowed to thaw at room temperature and the product was then collected and dried *in vacuo*. It (23·1 g.; m. p. 111—112°) was recrystallised from hot water (24 c.c.), giving small white crystals (19·9 g.), m. p. 107—110°. Basification of the combined aqueous filtrates, followed by ether-extraction, permitted the recovery of some 2-benzylpyridine (2·8 g.).

2-p-*Nitrobenzylpyridine.*—2-Benzylpyridinium nitrate (19·9 g.) was added during ½ hour to concentrated sulphuric acid (40 c.c.) cooled in ice. The mixture was warmed to 50° for 5 minutes and then poured on ice. Careful basification of the solution with ammonia, whilst cooling in a freezing mixture, gave a yellow solid which was dried on a porous plate *in vacuo*. 2-*p*-Nitrobenzylpyridine was thus obtained as a pale yellow solid (8·72 g.), m. p. 77—78° (40% based on the amount of 2-benzylpyridine used in preparing the nitrate).

2-(2 : 4-*Dinitrobenzyl*)*pyridine.*—Nitric acid (3 c.c.; *d* 1·5) was added dropwise, with shaking, to 2-benzylpyridine (5 g.) in concentrated sulphuric acid (22 c.c.) at −5° to 0°. The mixture was set aside for 2 hours at room temperature and then poured on ice, neutralised with aqueous ammonia, and extracted with ether (400 c.c.). Removal of the solvent gave tarry crystals

which after being twice crystallised from ethanol (charcoal) gave 2-(2 : 4-dinitrobenzyl)pyridine (3·2 g., 41·4%), m. p. 91—93°. On the 40-g. scale the yield fell to 25%.

2-(4-*Amino*-2-*nitrobenzyl*)*pyridine*.—A suspension of the above dinitro-compound (40 g.) in alcohol (200 c.c.) and aqueous ammonia (24 c.c.; *d* 0·88) was treated with hydrogen sulphide for 4 hours at 0° and for 2 hours whilst boiling under reflux. The resulting mixture was evaporated to dryness and the residue was extracted with dilute hydrochloric acid (700 c.c.). Gradual basification of the acid extract with aqueous ammonia, whilst cooling it in a freezing mixture, gave a light brown oil which quickly solidified. The resulting brown solid (34·6 g.), m. p. 106—112°, was satisfactory for use in the next stage. Omission of the initial saturation at 0° with hydrogen sulphide caused the reaction to fail.

2-o-*Nitrobenzylpyridine*.—(*a*) The amino-nitro-compound (10 g.) in hydrochloric acid (30 c.c.; 6N) was diazotised at 0° with aqueous sodium nitrite (10%), and the solution was treated with an ice-cold mixture of hypophosphorous acid (150 c.c. of 30%; 15 equivs.) and concentrated hydrochloric acid (50 c.c.). The solution was set aside at 0° for 24 hours and then basified with sodium hydroxide (5N) and extracted with ether. Concentration of the extract and distillation of the residue gave a yellow oil (4·5 g., 48%), b. p. 160—170°/0·4 mm.

The use of 30 equivs. of hypophosphorous acid raised the yield very slightly to 49·2%.

(*b*) To a solution of the diazonium salt prepared from the amine (10 g.) as above, were added at 0° hypophosphorous acid (150 c.c. of 30%), concentrated hydrochloric acid (50 c.c.), and powdered copper sulphate (0·5 g.). A vigorous evolution of nitrogen occurred for about 10 minutes. The solution was kept at 0° for 24 hours and then worked up as in (*a*), giving a yellow oil (5·8 g., 61·7%), b. p. 160—170°/0·5 mm. With 30 g. of the amine the yield fell to 55·6%.

2-o-*Nitrobenzoylpyridine*.—2-*o*-Nitrobenzylpyridine (4·1 g. of distilled material) and aqueous potassium permanganate (8 g. in 700 c.c. of water) were boiled under reflux, further amounts of permanganate (8 g. and 2 g.) being added 1½ hours and 2 hours from the time of starting. After refluxing for a total of 3 hours the mixture was decolorised with a few drops of alcohol, left to cool, and then filtered. The filter cake was digested with alcohol (300 c.c. in all), and the extract concentrated (charcoal), giving 2·5 g. of product, m. p. 117—118°. The use of undistilled 2-nitrobenzylpyridine gave much inferior yields, as did the conditions used by Huntress and Walter (*loc. cit.*) for oxidising 2-benzylpyridine, and also oxidation in aqueous acetone.

4-2′-*Pyridylquinaldine*.—2-*o*-Aminobenzoylpyridine (0·1 g.; Schofield, *loc. cit.*), alcohol (2 c.c.), acetone (2 c.c.), and 50% aqueous sodium hydroxide (1 c.c.) were refluxed together for 7 hours. After the resulting mixture had been diluted and the alcohol removed, the aqueous residue was acidified and extracted with ether. Basification of the aqueous layer and extraction with ether, followed by removal of the solvent, gave a yellow oil (0·12 g.) which provided colourless glistening prisms, m. p. 84—85° (Found: C, 81·7; H, 5·5. Calc. for $C_{15}H_{12}N_2$: C, 81·8; H, 5·5%), on crystallisation from ether–light petroleum (b. p. 40—60°). Hey and Williams (*loc. cit.*) give m. p. 84°.

### *Derivatives of 4-benzylpyridine*

4-*Benzylpyridinium Nitrate*.—(i) A method similar to that described under (i) for the 2-isomer, except that the mixture was simply shaken at room temperature for 5 hours, gave 80—90% of a white crystalline product, m. p. 103—106° (the yield is estimated on the amount of 4-benzylpyridine recovered from the aqueous acid mixture).

(ii) A solution of 4-benzylpyridine (20 g.) in nitric acid (8·4 c.c.; *d* 1·42) and water (20 c.c.) was treated as in the preparation of the 2-isomer, and with allowance for recovered 4-benzylpyridine, gave an almost quantitative yield of the nitrate, m. p. 100—105°. 4-Benzylpyridinium nitrate is more soluble than its 2-isomer.

4-p-*Nitrobenzylpyridine*.—4-Benzylpyridinium nitrate (20 g.) was treated according to method (ii) for the preparation of 2-*p*-nitrobenzylpyridine. After dilution and basification of the reaction mixture the product was extracted with ether, and the extract concentrated to *ca.* 40 c.c. This solution was allowed to evaporate spontaneously to 15 c.c. and the product was collected (7·8 g.; m. p. 72—73°). Removal of the remaining ether from the filtrate gave an oil which slowly deposited more crystals of the required compound (*ca.* 2 g.; m. p. 72—73°). The total yield was 9·8 g. (53%). The method described by Schofield for the 2-isomer gave only about 15% of this compound.

4-(2 : 4-*Dinitrobenzyl*)*pyridine*.—(i) 4-*p*-Nitrobenzylpyridine (20 g.) was nitrated according to the method used by Schofield (*loc. cit.*) for its isomer. Basification with aqueous ammonia of the dilute reaction mixture, accompanied by ice-cooling, precipitated a grey oil which soon

solidified. It was extracted with ether (2·5 l.), and concentration of the extract provided yellow prisms (19·3 g.), m. p. 79—80°. Further concentration gave a minor crop (1·8 g.), m. p. 72—80°. A specimen of the compound recrystallised from ether formed large yellow prisms, m. p. 80—81° [Tschitschibabin *et al.* (*loc. cit.*) give m. p. 80—81°] (Found : C, 54·2; H, 3·6. Calc. for $C_{12}H_9O_4N_3$ : C, 55·6; H, 3·5%). The picrate formed small yellow prisms, m. p. 152—153° (lit., 150—151°) (Found : C, 44·9; H, 2·4. Calc. for $C_{12}H_9O_4N_3,C_6H_3O_7N_3$ : C, 44·3; H, 2·5%), after crystallisation from ethanol–ethyl acetate.

(ii) Fuming nitric acid (3 c.c.; *d* 1·5) was added dropwise to a solution of 4-benzylpyridine (5 g.) in concentrated sulphuric acid (34 c.c.) shaken at 0°. After remaining for 4 hours at room temperature the solution was poured on ice and neutralised with aqueous ammonia. The precipitated oil was extracted with ether (1 l.), and the extract concentrated. On seeding of the resultant brown oil and evaporation of the remaining ether, yellow prisms (2·3 g.) of the impure dinitro-compound, m. p. 74—76°, were obtained.

4-(4-*Amino*-2-*nitrobenzyl*)*pyridine*.—Reduction of the dinitro-compound (40 g.) as described above for its isomer gave a product (34·3 g.), m. p. 108—109°, suitable for use in the next stage. Pure 4-(4-*amino*-2-*nitrobenzyl*)*pyridine* separated from aqueous ethanol as mustard-yellow needles, m. p. 130—131° (Found : C, 63·1; H, 4·6. $C_{12}H_{11}O_2N_3$ requires C, 62·9; H, 4·8%).

4-o-*Nitrobenzylpyridine*.—The nitro-amine (10 g.) in hydrochloric acid (30 c.c.; 6N) was diazotised at 0° with aqueous sodium nitrite (10%). Ice-cold hypophosphorous acid (150 c.c. of 30%), concentrated hydrochloric acid (50 c.c.), and powdered copper sulphate (0·5 g.) were added, and the mixture was kept for 24 hours at 0°. Basification with sodium hydroxide solution and ether-extraction in the usual way provided a brown oil (6 g.) which on distillation gave 4-*o*-*nitrobenzylpyridine* (4·9 g.) as a pale yellow oil, b. p. 160—170°/0·4—0·6 mm. The *picrate*, prepared in alcohol, formed yellow plates (from methanol), m. p. 156—157° (Found : C, 49·1; H, 3·0. $C_{12}H_{10}O_2N_2,C_6H_3O_7N_3$ requires C, 48·8; H, 3·0%).

4-o-*Nitrobenzoylpyridine*.—Obtained in 40% yield by the procedure described above for its isomer, 4-o-*nitrobenzoylpyridine* crystallised from hot water as long thin white needles, m. p. 77—78° (Found : C, 62·2; H, 3·6. $C_{12}H_8O_3N_2$ requires C, 63·1; H, 3·5%).

*Reduction of* 4-o-*Nitrobenzoylpyridine*.—(i) The nitro-compound (5 g.) in concentrated hydrochloric acid (5 c.c.) was treated with stannous chloride (15 g.) in the same solvent (20 c.c.) and after being heated for 1 hour at 95° the mixture was set aside for 5 hours at room temperature. Basification and ether-extraction, followed by removal of the solvent, gave a yellow solid (3·3 g.), m. p. (80) 92—95°. This crude product was diazotisable, as shown by the usual tests, but several crystallisations from aqueous methanol gave a compound which was not an amine. Pure 3-4′-*pyridylanthranil* formed fawn-coloured needles, m. p. 124—125° (Found : C, 73·1; H, 4·2; N, 14·3. $C_{12}H_8ON_2$ requires C, 73·45; H, 4·1; N, 14·3%), from dilute methanol. Reduction of this compound by excess of stannous chloride gave the amine described in (ii).

(ii) 4-*o*-Nitrobenzoylpyridine (1·5 g.) in concentrated hydrochloric acid (7·5 c.c.) was treated with stannous chloride (18 g.) in the same solvent (23 c.c.), and the mixture was heated at 95° for 1 hour and then kept for 5 hours at room temperature. After working up in the usual way, 4-o-*aminobenzoylpyridine* (1·3 g.) was obtained. It crystallised from aqueous methanol as yellow leaflets, m. p. 160—161° (Found : C, 72·7; H, 4·8; N, 14·2. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·1; N, 14·1%).

4-4′-*Pyridylquinaldine*.—Prepared in the manner described above for the 2′-isomer this compound crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 103—104°, alone or mixed with a specimen (m. p. 103—104°) prepared by the method of Hey and Williams (*loc. cit.*) (Found : C, 81·6; H, 5·6%).

*Emmert–Asendorf Reactions*.—Methods " A " and " B " of Tilford, Shelton, and Van Campen (*loc. cit.*) were employed. Ether was used instead of toluene for all extractions. Phenyl-2-pyridylcarbinol was obtained in 22% yield by method " A ". Experiments with *m*-chlorobenzaldehyde using both methods gave no homogeneous product. 3 : 4-Methylenedioxyphenyl-2-pyridylcarbinol was prepared by method " B " in 29% yield. This oil crystallised to give feathery needles of the pure carbinol (6%), m. p. 142—143°. Sperber *et al.* (*loc. cit.*) give m. p. 142—142·5°. The *picrate* separated from ethanol as yellow needles, m. p. 178—180° (Found : C, 49·9; H, 3·0. $C_{13}H_{11}O_3N,C_6H_3O_7N_3$ requires C, 49·8; H, 3·0%).

2-(3 : 4-*Methylenedioxybenzoyl*)*pyridine*.—The above carbinol (2 g.) was refluxed for 16 hours with aluminium *iso*propoxide (5·6 g.), dry benzene (35 c.c.), and dry acetone (70 c.c.). After removal of most of the solvents the residue was extracted with dilute sulphuric acid, and the acid solution was then basified and extracted with ether. On removal of the ether and dissolution of the residue in alcohol (10 c.c.), 0·27 g. of starting material was recovered. Treatment of the

alcohol solution with picric acid and recrystallisation of the product from ethanol gave yellow needles (1·08 g.) of the ketone *picrate*, m. p. 153—154° (Found: C, 49·5; H, 3·0. $C_{13}H_9O_3N,C_6H_3O_7N_3$ requires C, 50·0; H, 2·65%).

The authors express their indebtedness to the Chemical Society, to the University College of the South West, and to Imperial Chemical Industries Limited for financial assistance, and also to Professor D. H. Hey who kindly provided a specimen of 4-4′-pyridylquinaldine.

WASHINGTON SINGER LABORATORIES,
PRINCE OF WALES ROAD, EXETER. [*Received, October 3rd*, 1951.]