CCLXIII.—2-o-*Aminobenzylpyridine.*

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SINCE tricyclic compounds can be readily formed from *o*-aminodiphenylmethane, it seemed desirable to prepare 2-*o*-aminobenzylpyridine, with a view to synthesising similar compounds from it.

Bryans and Pyman (J., 1929, 549) have reported that direct nitration of 2-benzylpyridine gives only 2-*m*-nitro- and 2-*p*-nitrobenzylpyridines. It was found that heating pyridine with *o*-nitrobenzyl chloride, either alone or in the presence of copper powder or aluminium chloride, gave only black tars from which no *o*-nitrobenzylpyridine could be isolated.

2-*o*-Nitrobenzylpyridine was obtained by reducing the 4-nitro-group of 2-(2′ : 4′-dinitrobenzyl)pyridine (Tschitschibabin, Kuindshi, and Benewolenskaja, *Ber.*, 1925, **58**, 1584) and eliminating the resulting amino-group. The intermediate 2-o-*nitro*-p-*aminobenzylpyridine* was identical with that produced by nitrating 2-*p*-aminobenzylpyridine in concentrated sulphuric acid, whence the orientation of the amino-group is known.

Reduction of 2-*o*-nitrobenzylpyridine gave 2-*o*-aminobenzylpyridine, and oxidation with potassium permanganate gave first 2-o-*nitrobenzoylpyridine*, and then *o*-nitrobenzoic acid, whence the orientation of the nitro-group is known, and the configuration of 2-(2′ : 4′-dinitrobenzyl)pyridine assumed by Tschitschibabin and his co-workers is shown to be correct.

EXPERIMENTAL.

2-o-*Nitro*-p-*aminobenzylpyridine*.—2 - (2′ : 4′ - Dinitrobenzyl)pyridine (5 g.) was suspended in alcohol (25 c.c.), and ammonia (*d* 0·880; 3 c.c.) added. Hydrogen sulphide was passed in for 2 hours at 0° and 1 hour at 80°. The product was evaporated to dryness, the residue extracted three times with hydrochloric acid, and the extract made alkaline and extracted with much ether. The *base* crystallised from alcohol in reddish-brown prisms, m. p. 118·5°, 3·5 g. (Found : C, 63·0; H, 4·9. $C_{12}H_{11}O_2N_3$ requires C, 62·9; H, 4·8%).

2-o-*Nitrobenzylpyridine*.—2-*o*-Nitro-*p*-aminobenzylpyridine (10 g.) was dissolved in hydrochloric acid (20%; 30 c.c.), and diazotised at 0°. The resulting solution was treated with sodium hypophosphite (20 g.) dissolved in hydrochloric acid (10%; 60 c.c.) for 12 hours, and the product basified and extracted with ether. The base was distilled at 165—185°/0·06 mm. (2·6 g.). The *hydrochloride* crystallised from alcohol in pale yellow plates, m. p. 204° (Found: C, 57·5; H, 4·4; Cl, 14·4. $C_{12}H_{10}O_2N_2,HCl$ requires C, 57·5; H, 4·4; Cl, 14·2%). The base regenerated from the hydrochloride had m. p. 29·5°.

2-o-*Nitrobenzoylpyridine* was prepared by heating the above base (0·2 g.) with potassium permanganate (0·4 g.) in 1% aqueous solution for 2 hours at 80°, evaporating the product to dryness, and extracting the residue with alcohol. It crystallised from water in needles, m. p. 118°, the yield being 0·06 g. (Found: C, 63·0; H, 3·7. $C_{12}H_8O_3N_2$ requires C, 63·2; H, 3·5%). By 5 hours' heating with potassium permanganate at 90°, a small yield of *o*-nitrobenzoic acid was obtained (m. p. 145°; mixed m. p. 144°).

2-o-*Aminobenzylpyridine*.—2-(2′ : 4′-Dinitrobenzyl)pyridine (40 g.) was reduced as above. The product was evaporated to dryness, the residue extracted with hydrochloric acid, and the extract evaporated to dryness. The solid product was dissolved in water, hydrochloric acid (50 c.c.) added, and the solution diazotised with 10·7 g. of sodium nitrite and treated with sodium hypophosphite (120 g.) in hydrochloric acid (10%; 300 c.c.) over-night. Stannous chloride (120 g.) and concentrated hydrochloric acid (100 c.c.) were then added, and the whole was heated for 4 hours on a water-bath, basified, and extracted with ether. The base distilled at 138—165°/0·1 mm. or 185—210°/10 mm., the yield being 8—12 g. The *dihydrochloride* crystallised from water in needles (decomp. 280°) (Found: C, 56·3; H, 5·6; Cl, 27·5. $C_{12}H_{12}N_2,2HCl$ requires C, 56·0; H, 5·5; Cl, 27·6%); the base regenerated therefrom had m. p. 69—70°.

2-(2′ : 4′-*Diaminobenzyl*)*pyridine* was prepared by reducing 2-(2′ : 4′-dinitrobenzyl)pyridine with stannous chloride. It crystallises from alcohol in white prisms, m. p. 161° (Found: C, 72·4; H, 6·6. $C_{12}H_{13}N_3$ requires C, 72·4; H, 6·5%), and is almost insoluble in other solvents.

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