XCII.—*The Nitration of Phenylbenzylamine Derivatives.*

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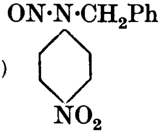
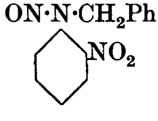
IN a recent paper (J., 1928, 563) the authors showed that, on nitration of benzylaniline and dibenzylaniline under similar conditions, the former yielded only the nitrate of the base. Nitration of the secondary amine in sulphuric acid solution led to the formation of phenyl-3-nitrobenzylamine together with a smaller amount of the corresponding 4-nitro-derivative.

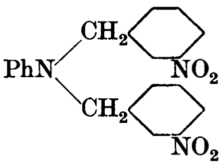
That work is now extended to include the nitration of phenylbenzylamine derivatives in which the imino-hydrogen is replaced by acidic and other groups. Unlike the parent substance, nitrosobenzylaniline is nitrated directly or in acetic acid solution with remarkable ease, giving nitroso-4-nitrophenylbenzylamine (I) as the main product and a small amount of the nitroso-2-nitro-compound (II).

(I.)





(II.)



(III.)

There are conflicting views in the literature with regard to the orientation of the nitration products of benzylalkylanilines. Schultz, Rohde, and Bosch (*Annalen*, 1904, **334**, 242) state that benzylethylaniline in sulphuric acid solution is nitrated in the benzyl ring, whereas Gnehm and Scheutz (*J. pr. Chem.*, 1901, **63**, 426), who worked under identical conditions, assign the nitro-group to the aniline ring. The nitration of benzyl-*n*-butylaniline is in line with the results of the former workers, the main product isolated being phenyl-3-nitrobenzyl-*n*-butylamine.

Nitration of dibenzylaniline in acetic acid solution gives mainly 2 : 4-dinitrophenyldibenzylamine and a very small amount of the 2 : 6-dinitro-compound (Desai, *J. Indian Chem. Soc.*, 1928, **5**, 425). Evidence of the formation of either of these nitro-derivatives in the hitherto unrecorded nitration of dibenzylaniline in sulphuric acid solution has not been obtained, but instead the authors have isolated a new dinitro-derivative, which has been shown by direct synthesis to be *phenyldi*-m-*nitrodibenzylamine* (III).

The experimental evidence supports the view that nitration of phenylbenzylamine derivatives directly (*i.e.*, as bases) leads to the formation of nitro-derivatives substituted in the aniline ring, whereas nitration through the salt promotes substitution in the benzyl nucleus.

EXPERIMENTAL.

Nitration of Nitrosobenzylaniline.—Nitrosobenzylaniline (5 g.) was slowly added, with stirring, to nitric acid (*d* 1·42; 25 c.c.) at 0—5°. When the mixture was poured on ice, a reddish, partly solid product was obtained, from a solution of which in hot alcohol there separated, on cooling, yellow needles (3·4 g.), m. p. 108—109°, of nitroso-4-nitrophenylbenzylamine (Found : N, 16·1. Calc. for $C_{13}H_{11}O_3N_3$: N, 16·3%). This constitution follows from the fact that, on heating with an alcoholic solution of either hydrochloric acid or potassium hydroxide, the nitroso-group was eliminated and a substance obtained, m. p. 143—144°, a mixture of which with the 4-nitrophenylbenzylamine of Meldola and Streatfeild (*Ber.*, 1886, **19**, 3250) showed no depression in melting point.

The alcoholic mother-liquor, on dilution with water, gave an oil which did not crystallise. This was boiled with alcoholic hydrochloric acid : from the solution, on standing, orange-coloured plates (1 g.), m. p. 74·5°, separated, which showed no depression in melting point when mixed with 2-nitrophenylbenzylamine (m. p. 74·5°).

On adding nitric acid (*d* 1·42; 20 g.) to a solution of nitrosobenzylaniline (10 g.) in glacial acetic acid (60 c.c.), considerable heat was evolved, the temperature rising from 18° to 40°. From the reddish solution, nitroso-4-nitrophenylbenzylamine (7 g.) was obtained on cooling. From the mother-liquor, 2-nitrophenylbenzylamine (1·5 g.) was obtained in the manner already described.

*Nitration of Phenylbenzyl-*n*-butylamine in Mixed Acids.*—To a well-cooled solution of phenylbenzyl-*n*-butylamine (9 g.) in concentrated sulphuric acid (100 c.c.) was added, with stirring, a solution of nitric acid (*d* 1·51; 2·2 g.) in concentrated sulphuric acid (30 c.c.), the temperature being maintained at 0°. The mixture was stirred for 6 hours at 0° and poured on ice. The clear solution, when made alkaline in the cold with sodium carbonate solution, gave a dark oil, which was extracted with chloroform and dried with anhydrous potassium carbonate. The chloroform on evaporation left a viscous oil which, after inoculation with a crystal of *phenyl-3-nitrobenzyl-*n*-butylamine* and standing in the ice-chest for a week, set to a semi-solid mass. This, drained on a porous plate, left a solid (6 g.), which was obtained from alcohol in bright yellow plates, m. p. 44—45° (Found : N, 9·8. $C_{17}H_{20}O_2N_2$ requires N, 9·9%).

The above nitro-compound was identical in all respects with phenyl-3-nitrobenzyl-*n*-butylamine synthesised by heating 3-nitrobenzyl chloride (1 mol.) and *n*-butylaniline (2 mols.) for 3 hours at 130—140°. The product was made alkaline by addition of sodium hydroxide solution and distilled in steam. The residual oil slowly solidified, and separated from alcohol in yellow plates, m. p. 44—45° (Found : N, 9·9%), readily soluble in chloroform, ether, and benzene and moderately easily soluble in cold ethyl alcohol.

Nitration of Dibenzylaniline in Mixed Acids.—In the nitration of dibenzylaniline the use of one molecular proportion of nitric acid left much initial material unchanged and gave substantially the same product as when two molecular proportions were used. Potassium nitrate gave more satisfactory results than fuming nitric acid.

To a solution of dibenzylaniline [recrystallised from alcohol; m. p. 69—70° as against 67° recorded by Matzudaira (*Ber.*, 1887, **20**, 1611) and 71° by Wedekind (*Ber.*, 1899, **32**, 522)] (10 g.) in sulphuric acid (100 c.c.), potassium nitrate (7·4 g.) was slowly added at room temperature with stirring. There was no appreciable rise in temperature. After 12 hours, the mixture was poured on ice. The sulphate of the nitro-compound which separated was converted into the base by means of sodium hydroxide solution. The yellow residue (10 g.) obtained after trituration with ether was separated into two parts by repeated fractional crystallisation from ethyl alcohol–ethyl acetate. The less soluble portion (2·8 g.) consisted of canary-yellow prisms, m. p. 128—129° (Found: N, 11·5. $C_{20}H_{17}O_4N_3$ requires N, 11·6%), and was identified as *phenyldi*-m-*nitrodibenzylamine* (III) by the synthesis described below. The second fraction melted at 100—105°. No other definite substance was isolated. The melting point of the fraction m. p. 100—105° was not depressed by addition of phenyldi-*m*-nitrodibenzylamine. Repeated extraction of this fraction with ethyl alcohol–ethyl acetate removed small amounts of phenyldi-*m*-nitrodibenzylamine, but the other nitro-compounds present were not identified. It melted at 80—90° when mixed with 2 : 4-dinitrophenyldibenzylamine (m. p. 107°).

Synthesis of Phenyldi-m-*nitrodibenzylamine* (III).—Aniline (1 mol.) and *m*-nitrobenzyl chloride (2 mols.) were heated in alcoholic solution for 2 hours. The alcohol was removed, a concentrated aqueous solution of sodium carbonate added, and the mixture boiled for 8 hours. The product, which solidified on cooling, was extracted with warm alcohol; the yellow insoluble portion separated from alcohol–ethyl acetate in canary-yellow prisms, m. p., alone or mixed with the above nitro-compound, 129—130°. Phenyldi-*m*-nitrodibenzylamine is readily soluble in chloroform, benzene, and ethyl acetate and sparingly soluble in cold alcohol, acetic acid, and ether.

We wish to thank Mr. William Rintoul, F.I.C., of Imperial Chemical Industries, Ltd. (Nobel's Explosive Co.) for providing the dibenzylaniline, and the Chemical Society for a grant which has partly defrayed the cost of this work.

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