LXXIII.—*The Nitration of Benzylaniline.*

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MATZUDAIRA (*Ber.*, 1887, **20**, 1613), by nitrating dibenzylaniline in acetic acid solution, obtained 4-nitrophenyldibenzylamine, $NO_2{\cdot}C_6H_4{\cdot}N(CH_2Ph)_2$. Under such conditions we have found that benzylaniline does not nitrate in either ring, the nitrate of the base only being formed. On nitration with nitric and sulphuric acids, however, benzylaniline yields phenyl-3-nitrobenzylamine, $C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, and a small quantity of phenyl-4-nitrobenzylamine. Further work on this interesting result—unexpected in view of recent theories on substitution, which indicate that nitration should occur in the *o*- and *p*-positions of the aniline ring—will be undertaken as soon as possible.

EXPERIMENTAL.

Nitric acid (*d* 1·5; 6·7 g.) was added to benzylaniline (18·3 g.) in acetic acid (500 c.c.); crystals of benzylaniline nitrate, m. p. 142° (decomp.), slowly separated (Found: N, 11·8. Calc. for $C_{13}H_{13}N,HNO_3$: N, 11·4%).

To a well-cooled solution of benzylaniline (10 g.) in concentrated sulphuric acid (150 c.c.) was added, with stirring, a solution of nitric acid (*d* 1·5; 3·7 g.) in concentrated sulphuric acid (20 c.c.), the temperature being maintained at about − 3°. The mixture was stirred for an hour at 0° and poured on crushed ice. The clear solution, when made alkaline in the cold with sodium carbonate solution, gave a reddish-orange precipitate (10 g.) which, crystallised from alcohol and finally from light petroleum (b. p. 60—80°), formed deep orange needles (6·5 g.), m. p. 84·5—85° (Found: N, 12·3. Calc. for $C_{13}H_{12}O_2N_2$: N, 12·3%). The residue obtained by evaporation of the alcoholic mother-liquor, on repeated crystallisation from light petroleum (b. p. 60—80°), gave yellow plates (1 g.), m. p. 70—72°, which were identified as phenyl-4-nitrobenzylamine by the melting point of a mixture with an authentic specimen.

The identity of the above substance (m. p. 84·5—85°) with phenyl-3-nitrobenzylamine was established by the mixed melting-point method and by comparison of their acetyl and benzoyl derivatives.

Acetophenyl-3-nitrobenzylamide was prepared by Purgotti and Monti (*Gazzetta*, 1900, **30**, 257) by heating phenyl-3-nitrobenzylamine with acetic anhydride in a sealed tube at 130° for 3 hours, and obtained as yellow needles, m. p. 48°. It is more conveniently obtained by heating the nitroamine and acetic anhydride at the ordinary pressure in presence of anhydrous sodium acetate. It crystallised from benzene–light petroleum (b. p. 60—80°) in colourless plates (Found: N, 10·4. Calc. for $C_{15}H_{14}O_3N_2$: N, 10·4%), which melted, alone or when mixed with the acetyl derivative of the main product of nitration of benzylaniline, at 66—67°.

Benzophenyl-3-nitrobenzylamide, prepared in the usual manner, crystallised from benzene–light petroleum (b. p. 60—80°) in colourless prisms (Found: N, 8·6. $C_{20}H_{16}O_3N_2$ requires N, 8·4%). Specimens prepared from phenyl-3-nitrobenzylamine and from the main product of nitration of benzylaniline melted, alone or when mixed, at 103°.

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