CXCVI.—*The Action of Nitrous Acid on Substituted* p-*Phenylenediamines. Part I. Benzyl*-n-*butyl*-p-*phenylenediamine.*

By JOSEPH REILLY and PETER J. DRUMM.

BUTYL-*p*-PHENYLENEDIAMINE behaves normally on diazotisation (Reilly and Hickinbottom, J., 1917, **111**, 1034). According to Hantzsch (*Ber.*, 1902, **35**, 896), methyl-*p*-phenylenediamine cannot be readily diazotised in hydrochloric acid solution, nitrogen being evolved even below 0°; the present authors have found, however, that a much more stable diazo-solution is obtained if sulphuric acid is used. Substituents in aromatic diamines therefore have a marked influence on the stability of the diazo-solutions produced from them, and in view of this the authors have commenced an investigation on the nature of the reaction between nitrous acid and various mono- and di-substituted diamines and on the stability of the resulting solutions.

Benzyl-n-*butyl*-p-*phenylenediamine*, $NH_2\cdot C_6H_4\cdot N(C_4H_9)\cdot CH_2Ph$, the first diamine to be investigated, was obtained from *benzyl*-n-*butylaniline* through the p-*nitroso*-compound and also by reduction of the azo-compound formed by coupling this tertiary amine with diazosulphanilic acid. It diazotises readily to give a comparatively stable diazo-solution.

EXPERIMENTAL.

Benzyl-n-*butylaniline*.—Benzylaniline (1 mol.) and *n*-butyl iodide (1 mol.) were heated together at 100° for 6 hours, the excess of *n*-butyl iodide was removed under diminished pressure, and the residue made alkaline with aqueous sodium hydroxide. The resulting oil was dissolved in ether and dried with potassium carbonate. The fraction, b. p. 190—200°/17 mm., on refractionation gave *benzyl*-n-*butylaniline* as a pale yellow oil, b. p. 193—195°/17 mm., $d^{16\cdot5^\circ}$ 1·005 (yield, 20%). It possesses feebly basic properties and is very sparingly soluble in dilute acids. The *picrate* forms bright yellow prisms, m. p. 129° (Found: $C_6H_3O_7N_3$, 49·3. $C_{17}H_{21}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 48·9%), and is decomposed by boiling water. The *chloroplatinate* is only slightly soluble in alcohol, from which it separates in biscuit-coloured prisms, m. p. 185—186° (decomp.) [Found: Pt, 21·8. $(C_{17}H_{22}N)_2PtCl_6$ requires Pt, 21·9%].

p-*Nitrosobenzyl*-n-*butylaniline*.—A well-cooled solution of benzyl-*n*-butylaniline in glacial acetic acid was slowly treated with a solution of the theoretical quantity of sodium nitrite in the minimum of water. The mixture was stirred for 3 hours and then diluted with ice-water, and the precipitated green oil was dissolved in benzene. From the dried, cooled benzene solution, hydrogen chloride precipitated p-*nitrosobenzyl*-n-*butylaniline hydrochloride;* this, after being washed with benzene, dissolved in absolute alcohol, and reprecipitated by ether, was obtained in greenish-yellow, glistening plates, m. p. 138° with previous darkening (Found: Cl, 11·8. $C_{17}H_{20}ON_2,HCl$ requires Cl, 11·6%). It is readily hydrolysed by water.

The *base* was obtained by decomposing the hydrochloride with aqueous sodium carbonate; it crystallised from ether in green, glistening plates, m. p. 48—49°, which appeared steel-blue by reflected light (Found: N, 10·0. $C_{17}H_{20}ON_2$ requires N, 10·4%). When it was heated with concentrated hydrochloric acid, a pronounced odour of benzaldehyde was observed. On reduction with zinc dust and dilute sulphuric acid, it gave *benzyl*-n-*butyl*-p-*phenylenediamine*, which is described below.

4-p-*Sulphobenzeneazobenzyl*-n-*butylaniline*.—Solid diazosulphanilic acid was gradually added to a glacial acetic acid solution of benzyl-*n*-butylaniline. The mixture was shaken for 3 hours and diluted with water; the *azo*-compound then separated in well-defined, violet crystals (Found: S, 7·7. $C_{23}H_{25}O_3N_3S$ requires S, 7·6%). It forms a very soluble, orange *sodium* salt.

Benzyl-n-*butyl*-p-*phenylenediamine*.—Reduction of the preceding azo-compound (20 g.) by ammonium sulphide solution proceeded in the cold and was complete at the end of 24 hours. The precipitated oil was dissolved in ether, the solution washed with an aqueous suspension of lead carbonate to remove traces of ammonium sulphide, and the ether distilled off; *benzyl*-n-*butyl*-p-*phenylenediamine* was then obtained at 220—224°/12 mm. as a pale yellow oil (yield, 75%) (Found: N, 10·6. $C_{17}H_{22}N_2$ requires N, 11·0%), which slowly became red in the air.

The *sulphate* was obtained as a white solid from sulphuric acid and the amine in ethereal solution [Found: S, 5·6. $(C_{17}H_{22}N_2)_2,H_2SO_4$ requires S, 5·3%]. It is very soluble in alcohol and water. The *hydrochloride* was similarly prepared and obtained as a very hygroscopic, viscous precipitate. The *benzoyl* compound, prepared by the Schotten–Baumann reaction, was obtained in colourless needles, m. p. 131° (Found: N, 8·1. $C_{24}H_{26}ON_2$ requires N, 7·8%).

p-*Benzyl*-n-*butylaminobenzeneazo*-β-*naphthol*.—The green solution obtained by diazotising benzyl-*n*-butyl-*p*-phenylenediamine (prepared in either of the two ways mentioned above) in hydrochloric acid solution was freed from nitrous acid by means of carbamide and added to an alkaline solution of β-naphthol. The brown precipitate thus produced crystallised from alcohol in stout, dark red prisms with a greenish lustre; m. p. 133—134° (Found by the micromethod: N, 10·3. $C_{27}H_{27}ON_3$ requires N, 10·3%). With concentrated sulphuric acid, it developed a magenta colour, which changed to yellowish-orange on dilution.

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UNIVERSITY COLLEGE, CORK. [*Received, April 7th,* 1927.]