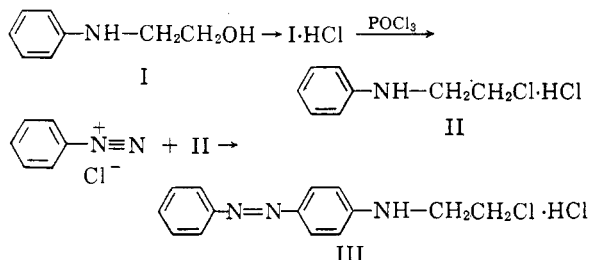


Preparation of *N*-(2-Chloroethyl)-4-(phenylazo)aniline

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In the course of other work, a specimen of the title compound (III) was desired. It was therefore synthesized by the following sequence of reactions.



2-Anilinoethanol (I) was first converted to its hydrochloride, as Ward² has shown that hydrochlorides of such compounds are more readily chlorinated than are the free bases. Compound I·HCl was treated with phosphoryl chloride, to give *N*-(2-chloroethyl)aniline hydrochloride (II) in a yield of 99.5% (lit. yield,³ 9.2%, using thionyl chloride). (Compound II had previously been prepared, in poor yield, by a variety of methods.³⁻⁷) Compound II was then condensed with benzenediazonium chloride, to afford III.

EXPERIMENTAL

N-(2-Chloroethyl)aniline hydrochloride (II). 2-Anilinoethanol (I, 137 g., 1 mole) was dissolved in 86 ml. (101 g.) of concentrated hydrochloric acid, and the solution was evaporated under diminished pressure (standard-taper joints) to a thick sirup which was dissolved in 100 ml. of absolute ethanol and the solution evaporated to dryness. Treatment with absolute ethanol (100 ml.) was repeated, followed by addition of 100 ml. of benzene and evaporation. Final traces of solvent were removed⁸ at 0.1 mm., to give a quantitative yield of a thick, pale brown gum (I·HCl).

To this hydrochloride (173.7 g.; 1 mole) was added 173 ml. of chloroform, the solution was cooled in ice, a boiling stone and 25 ml. of fresh phosphoryl chloride were added, and the solution was gradually heated under a reflux condenser (standard-taper joints; Drierite tube) until, after 30 min., vigorous gas evolution occurred (bath temp., 51°). The temperature was gradually raised to 58–61° (30 min.) and three 25-ml. portions of phosphoryl chloride were added at

45-min. intervals (through the condenser), followed by the addition of 80 ml. of phosphoryl chloride and gradual raising of the bath temperature to 84° (2 hr.). The resulting clear solution was kept overnight at room temperature, and the solvents were removed in three steps: (a) at atmospheric pressure (bath temp., 28–160°); (b) at 15 mm.; and (c) at⁸ 0.25 mm. (bath temp., 80–98°), affording 270 g. of brown gum. This was dissolved in 200 ml. of chloroform, the flask was closed by a stopper bearing a pentane thermometer, and the solution was cooled to 0° in ice-salt. Absolute ethanol (45 ml.) was now added (in portions, at 5-min. intervals) so that the temperature did not exceed 2°, and the solution was evaporated under diminished pressure, with addition of six 25-ml. portions of absolute ethanol, to give an almost solid mass of colorless crystals. The suspension was refrigerated, filtered with suction (rubber dam), and the crystals dried in a vacuum desiccator; wt., 117.2 g. The mother liquor afforded a further 74.0 g. of colorless crystals (total yield, 191.2 g. or 99.5%). For recrystallization, the salt was dissolved in 3 vol. of boiling absolute ethanol under reflux, the hot solution filtered, and the filtrate cooled; m.p. 159–160° (lit. m.p., 155–157°, ³ 158°, ⁴ 156–158°, ⁵ 155–158°).

Anal. Calcd. for C₈H₁₁Cl₂N: C, 50.02; H, 5.77; Cl, 36.92; N, 7.29. Found: C, 49.96; H, 5.97; Cl, 36.30; N, 7.62.

N-(2-Chloroethyl)-4-(phenylazo)aniline hydrochloride (III). Aniline (9.3 g.; 0.1 mole) in 125 ml. of 2 *N* hydrochloric acid at 0° was diazotized with 6.9 g. of sodium nitrite in 100 ml. of water at 0°. The solution of benzenediazonium chloride (at 0°) was slowly added (10 min.), with stirring, to a solution of 19.2 g. of II in 250 ml. of absolute methanol at 0°. The mixture was then stirred during a further 4 hr.; after 1 hr. at 0°, the temperature was allowed to rise slowly to room temperature. Dark-red crystals gradually separated; these were removed by filtration and dried to constant weight at 0.1 mm. at 25°; wt., 10.0 g. The mother liquor, kept overnight at 0°, afforded a further 2.7 g. of crystals. A portion (8.6 g.) of the crystals was shaken with 258 ml. (30 vol.) of absolute ethanol, the suspension was filtered, and to the filtrate was added 3.0 ml. of concentrated hydrochloric acid, giving 7.2 g. of dark red crystals, m.p. 178–179°.

Anal. Calcd. for C₁₄H₁₅Cl₂N₂: C, 56.77; H, 5.11; Cl, 23.94; N, 14.19. Found: C, 56.39; H, 5.34; Cl, 23.88; N, 14.13.

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The Reaction of Phosphorus Pentachloride with *N*-Methyltrifluoroacetamide. *N*-Methyltrifluoroacetimidoyl Chloride and 1,3-Dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine

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The reaction of mono-*N*-substituted amides with phosphorus pentachloride is a much used and general preparative method for imidoyl chlorides.¹ In the various sources investigated the only products mentioned were the imidoyl chloride,

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(8) Using a potassium hydroxide trap and a chloroform-Dry Ice trap.