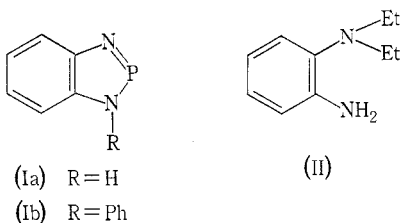


THE REACTION BETWEEN TRIETHYL PHOSPHITE AND SOME AROMATIC AMINES

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According to a review,¹ triethyl phosphite and *o*-phenylenediamine give the heterocycle (Ia). This statement appears to be based on a misreading of the original literature,² in which Pilgram and Korte reported that *N*-phenyl-*o*-phenylenediamine and triphenyl phosphite gave a compound, m.p. 350° (dec.), for which the elemental composition corresponded to (Ib). Its low solubility and high melting point are compatible with a cyclic trimeric structure. Pilgram and Korte did not report any such reactions with alkyl phosphites.



In our hands, triethyl phosphite and *o*-phenylenediamine gave a mixture of all possible *N*-ethylated phenylenediamines in which the diethyl compounds predominated. Examination of the crude reaction product by mass spectrometry showed no evidence of a peak at *m/e* 408 (trimer of (I)) or at *m/e* 272 (dimer). The peak at *m/e* 136 was shown by precision mass measurement to consist only of C₈H₁₂N₂. No C₆H₅N₂P was detected.

The reaction mixture exhibited an intense blue colour which became red immediately on acidification or red-brown slowly on standing. These colours are thought to be associated with the Wurster salt-like oxidation product of the unsymmetrical *N,N*-diethylphenylenediamine (II).

Triethyl phosphate is known to be an effective alkylating agent for aromatic amines,^{3,4} and the above result shows that triethyl phosphite alkylates also. We examined the reaction of both esters with aniline and found that triethyl phosphite is not as efficient as phosphate. The maximum yield with phosphite was 85% diethylaniline and 11% monoethylaniline when equimolar amounts were heated

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¹ Hudson, R. F., "Structure and Mechanism in Organophosphorus Chemistry." p. 40. (Academic Press: London 1965.)

² Pilgram, K., and Korte, F., *Tetrahedron*, 1963, **19**, 137.

³ Thomas, D. G., Billman, J. H., and Davis, C. E., *J. Am. chem. Soc.*, 1946, **68**, 895.

⁴ Billman, J. H., Radike, A., and Mundy, B. W., *J. Am. chem. Soc.*, 1942, **64**, 2977.

at 165° for 8 hr. The maximum yield with phosphate was 97% diethylaniline and 3% monoethylaniline from 2 moles of ester and 1 mole of amine after heating for 8 hr at 165°. Heating for shorter periods gave lower yields with both esters.

Billman reported⁴ that the reaction of triethyl phosphite with *p*-nitroaniline led to decomposition. We attempted the reaction of phosphite and phosphate with both *o*- and *p*-nitroaniline; starting material and monoethylnitroaniline were obtained with only small amounts of diethylnitroaniline and of an unidentified substance. Although no decomposition was observed, neither phosphite nor phosphate can be recommended for the alkylation of nitroanilines.

Experimental

Gas chromatography was carried out with an F&M 810 instrument using a 6 ft by $\frac{1}{8}$ in. column packed with 10% silicone gum rubber on Diatoport S at 120°. Mass spectrometry was carried out with an Atlas CH4 instrument and precision mass measurement at *m/e* 136 on a CEC 21-110. We are indebted to J. L. Occolowitz for this determination.

(a) *o*-Phenylenediamine

o-Phenylenediamine (5.4 g, 0.05 mole) and triethyl phosphite (8.4 g, 0.05 mole) were heated under reflux on an oil-bath at 160–165° for 1.5 hr. A deep blue colour developed. (This crude product was examined for the composition of *m/e* 136, and for the presence of *m/e* 272 and 408.) Remaining phosphite was hydrolysed by refluxing with sodium hydroxide (6.6 g) in water (50 ml) for 1 hr. The reaction products were extracted with ether and their composition determined by gas chromatography, giving the following results: *o*-phenylenediamine 12%, ethylphenylenediamine 10%, diethylphenylenediamine 37%, triethylphenylenediamine 36%, tetraethylphenylenediamine 4%. The mass spectrum of the mixture was consistent with this result.

(b) Aniline

(i) *Triethyl phosphite*.—Aniline (4.6 g, 0.05 mole) and triethyl phosphite were refluxed on an oil-bath at 160–170°. The reaction mixture was cooled and then remaining phosphite hydrolysed by refluxing for 1 hr with 25% sodium hydroxide solution (40 ml). After cooling, the anilines were extracted with ether and the composition of the mixture was determined by gas chromatography.

The procedure was repeated using various mole ratios of phosphite to aniline and for different periods of reflux at 160–165°. With 8.3 g (0.05 mole) of phosphite, the product composition was diethylaniline 66%, monoethylaniline 33%, aniline 1%, after heating for 4 hr, and diethylaniline 85%, monoethylaniline 11%, aniline 4% after heating for 8 hr.

(ii) *Triethyl phosphate*.—Aniline (4.6 g, 0.05 mole) and triethyl phosphate were treated as in (i) above. The procedure was repeated using various mole ratios of phosphate to aniline and for different reflux times. With 9.1 g (0.05 mole) of phosphate, the product composition was diethylaniline 65%, monoethylaniline 29%, aniline 4% after heating for 4 hr, and diethylaniline 66%, monoethylaniline 32%, and aniline 2% after heating for 8 hr.

(c) *o*-Nitroaniline

o-Nitroaniline (3.4 g, 0.025 mole) and triethyl phosphite (4.15 g, 0.025 mole) were refluxed for 8 hr as in (b) above. Reaction products were determined by gas chromatography. Ethylnitroaniline and *o*-nitroaniline were present in approximately equal amounts. A small amount of diethylnitroaniline was present as well as an unidentified product. Poor resolution by gas chromatography did not allow accurate evaluation. With triethyl phosphate similar results were obtained except that the proportion of diethylnitroaniline was increased.

(d) *p*-Nitroaniline

p-Nitroaniline (3.4 g, 0.025 mole) and triethyl phosphite (4.15 g, 0.025 mole) were treated as in (c) above, giving similar results.