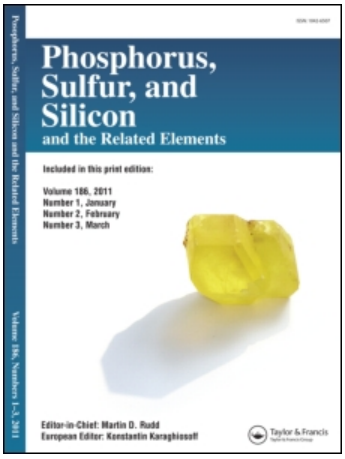

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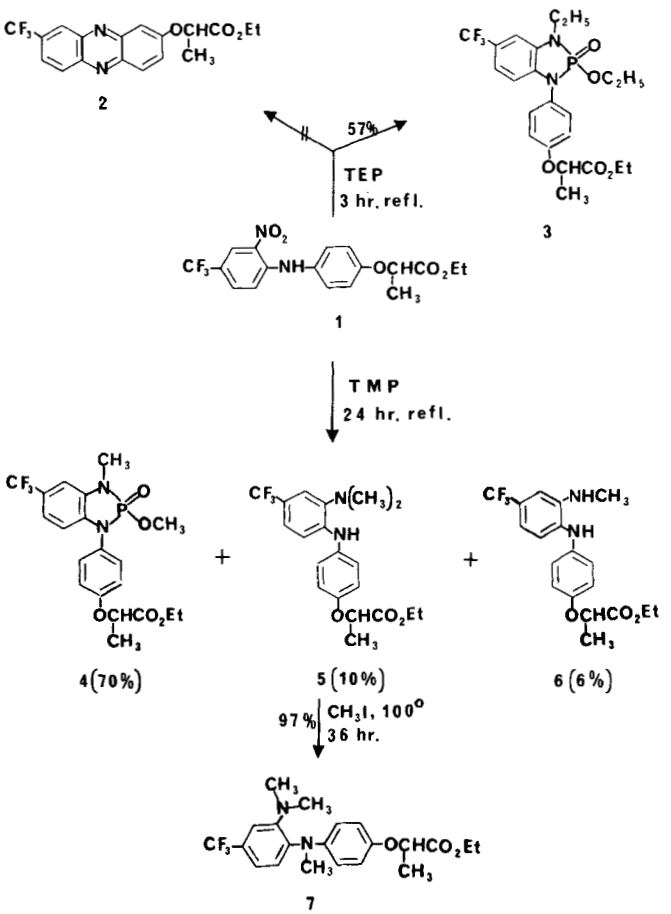
Reductive cyclization of 2-nitrodiphenylamines with trialkyl phosphites provides an efficient one-pot synthesis of 1,3-dihydro-1,3,2-diazaphosphole 2-oxides. Further exhaustive alkylation at elevated temperature is accompanied by rupture of both P—N bonds, leading to N-alkylated 2-aminodiphenylamines.

Key words: 2-Nitrodiphenylamines; trialkyl phosphites; deoxygenation; 1,3-dihydro-1,3,2-diazaphosphole 2-oxides; rupture of phosphorus-nitrogen bonds; N-alkylated 2-aminodiphenylamines.

1. INTRODUCTION

Prior to the present investigation, 2,3-dihydro-1H-1,3,2-benzodiazaphosphole 2-oxides have been prepared by refluxing an addition product of phenylphosphonic dichloride with ortho-phenylenediamines in bromobenzene.[1] Under similar conditions, a corresponding pyridine derivative was also prepared, but attempts to synthesize the corresponding pyrimidine derivative were unsuccessful. The condensation of 4,5-diaminopyrimidines with phenylphosphonodiamide gave a number of 3- and 7-substituted pyrimidinodiazaphosphole derivatives.[2] Attempted synthesis of the 8-phospha-substituted purine isostere by reaction of 4,5-diaminopyrimidine with phosphorus trichloride and subsequent dehydrochlorination was not successful. However, when PCl_3 was replaced by triphenyl phosphite,[3] reaction proceeded smoothly with elimination of three equivalents of phenol to give monomeric pyrimidino(4,5-d)-1H-1,3,2-diazaphosphole[4] in 52% yield.

Our interest in heteroaryloxypropionates as herbicides[5,6] prompted us to approach the synthesis of phenazines by intramolecular cyclization of nitrenes derived from 2-nitrodiphenylamine derivatives. The chemistry of nitrenes has been the subject of considerable interest in recent years. Nitrenes are generally obtained (a) by loss of nitrogen (N_2) from an azide, or (b) by removal of oxygen from nitroso or nitro compounds. An elegant phenothiazine synthesis[7] from 2-nitrophenyl sulfides is based upon approach (b). However, the reaction of the analogous 2-nitrodiphenylamine **1**[8] with excess triethyl phosphite (TEP), at elevated temperature, did not yield the desired phenazine **2**. Instead, an alternative nitrogen to phosphorus ring closure was achieved leading to the substituted 2,3-dihydro-1H-1,3,2-diazaphosphole 2-oxide **3** in 57% yield (Scheme



SCHEME 1 Reaction of **1** with TMP and TEP.

1). In view of this, the present study was undertaken to examine the scope of this one-pot reaction.

RESULTS AND DISCUSSION

The reaction of **1** with an excess of TEP proceeded smoothly at 150° (reflux). After three hours, no starting material was detectable by TLC-techniques. The reaction mixture was concentrated under reduced pressure (80°, 1.0 mm) and the residue was subjected to silica chromatography to give 57% of **3** as an amber syrup (Scheme 1). Its structure is based on correct analytical (C, H, N) and spectral data. The infrared spectrum (CH_2Cl_2) shows a strong carbonyl band at 1748 cm^{-1}, and bands at 1219 (P→0) and 1036 (P—O—C), but no apparent NH-absorption. In the EI/MS, the molecular ion is observed at m/z 486 (M^+).

TABLE I

^{1}H NMR spectral data of **4**

Group/assignment	δ, ppm	No. of H's
CH—$\underline{CH_3}$	1.65 (d)	3
$\underline{CH}$—CH_3	4.76 (m)	1
O—CH_2—$\underline{CH_3}$	1.28 (t)	3
O—$\underline{CH_2}$—CH_3	4.25 (q)	2
N—CH_3	3.22 (s)	3
P—O—CH_3	3.66 (d)	3
CH=	6.5–7.5 (m)	7

The fragmentation pattern agrees with the proposed structure (see "Experimental").

When the procedure was extended to include trimethyl phosphite (TMP), the reaction proceeded more sluggishly (24 hrs, reflux) to give **4** as the major reaction product, isolated in 70% yield by silica chromatography. Again, the infrared spectrum (CH_2Cl_2) shows no NH-absorption, but one band at 1748 (C=O) cm^{-1} and bands between 1350–1000 (P=O, P—O—C, CF_3, C—O—C) cm^{-1}. In the ^{1}H NMR-spectrum, all protons have been assigned and are accounted for (Table I).

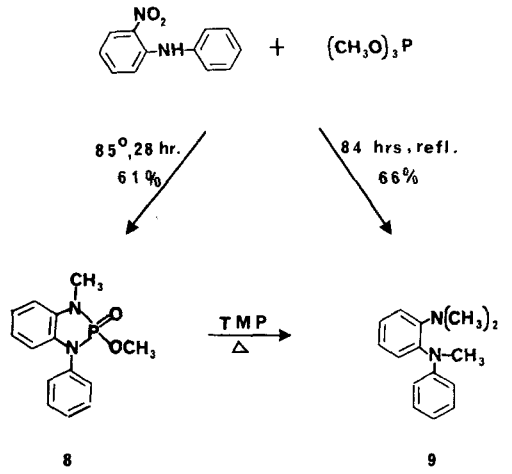
Two additional reaction products, namely, the *ortho*-(dimethylamino)-diphenylamine derivative **5** and the *ortho*-(methylamino)-diphenylamine **6** also were isolated in 10% and 6%, respectively, by silica chromatography. The mass spectra (EI/MS), which show the parent molecular ion, and the ^{1}H NMR spectra were instrumental in the structure assignment: **5**, δ 2.69 (6H, s, $N(CH_3)_2$); **6**, δ 2.87 (3H, d, NCH_3).

Treatment of **5** with methyl iodide gave the N-methylated derivative **7** in almost quantitative yield as evidenced by its mass and NMR spectra: EI/MS (m/z) 410 (M^+), ^{1}H NMR ($CDCl_3$) δ 2.75 (6H, s, $N(CH_3)_2$) and 3.14 (3H, s, NCH_3).

In order to gain a better insight into the mechanism for this simple one-pot reaction leading to 2,3-dihydrobenzo-1H-1,3,2-diazaphosphole 2-oxides, 2-nitrodiphenylamine was allowed to react with TMP at elevated temperature. When a solution containing 0.1 mol of 2-nitrodiphenylamine in 105 g (0.85 mole) of TMP was heated to reflux, the reaction leading to **8**, as monitored by GLC and TLC, proceeded smoothly, trimethyl phosphate and methyl dimethylphosphonate being the only reaction products detected. Only after all of the 2-nitrodiphenylamine had been converted into **8** was the formation of trimethyldiphenylamine **9** noticeable. After 84 hrs at 190–210° (reflux), all of the 2,3-dihydrobenzo-1H-1,3,2-diazaphosphole 2-oxide, **8**, had been converted into **9** (Scheme 2).

The structure of **8** follows from correct analytical (C, H, N) and spectral measurements. In the EI/MS, the molecular ion is observed at m/z 274 (M^+). The peak at m/z 259 corresponds to the loss of CH_3 from the molecular ion. The very prominent peak at m/z 195 is due to the loss of the fragment $P(OH)OCH_3$ from the molecular ion.

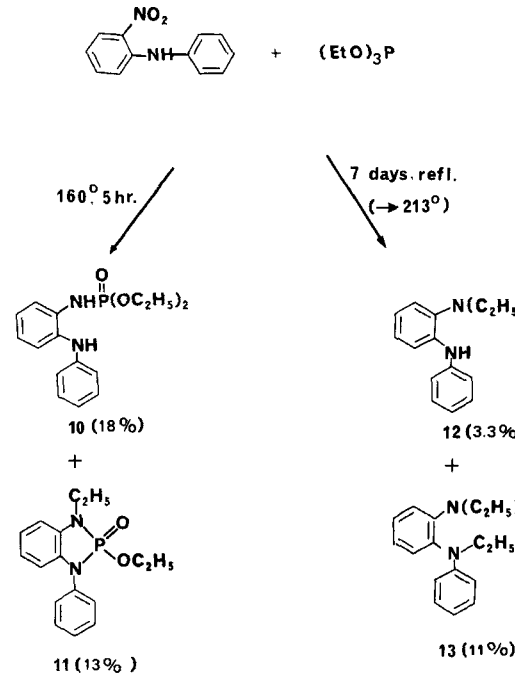
The structure of the degradation product of **8**, namely, **9**, follows from correct elemental analysis (C, H, N), the ^{1}H NMR spectrum ($CDCl_3$) δ 2.72 (6H, s,



SCHEME 2 Reaction of 2-nitrodiphenylamine with TMP.

$N(CH_3)_2$), 3.16 (3H, s, NCH_3), and 6.5–7.5 (9H, m, $(CH{=})_9$) and the mass spectrum, obtained upon electron-impact, which shows the molecular ion (M^+) at m/z 226.

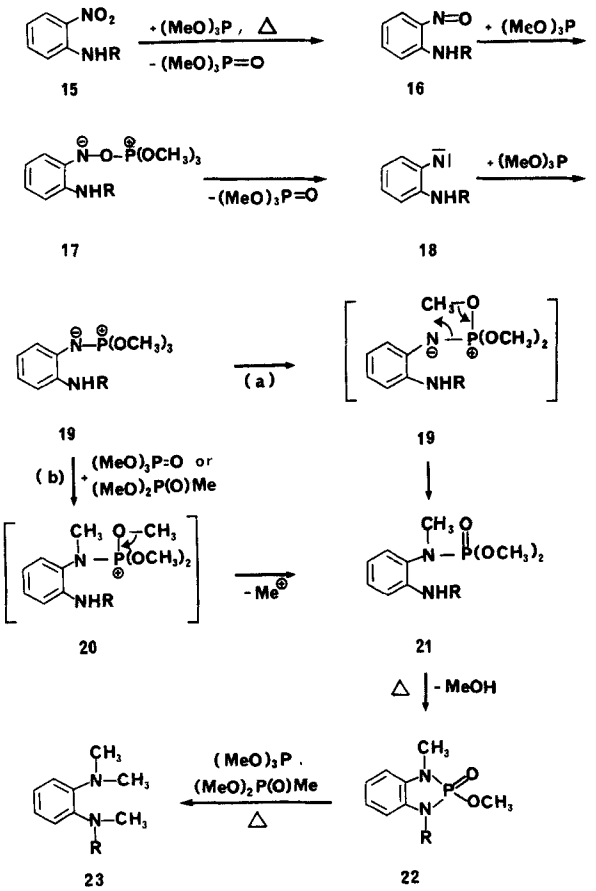
By contrast, the reaction of 2-nitrodiphenylamine with TEP was much more sluggish at 160° (5 hrs), leading to the formation and isolation of the phosphoramidate **10** (m/z 320 (M^+)), in 19% yield, and the 2,3-dihydrobenzo-1H-1,3,2-diazaphosphole 2-oxide derivative, **11** (m/z 302 (M^+)), in 13% yield. When



SCHEME 3 Reaction of 2-nitrodiphenylamine with TEP.

the reaction temperature was raised to reflux (213°, 7 days), the only products formed and isolated were 2-(diethylamino)-diphenylamine **12**, m/z 240 (M^+), the triethyl-2-aminodiphenylamine **13**, m/z 268 (M^+); δ 0.96 (6H, t, $N(CH_2\underline{CH_3})_2$) and 1.16 ppm (3H, t, $N—CH_2—\underline{CH_3}$), and a mixture of tetraethylated 2-aminodiphenylamines **14**, m/z 296 (M^+). Isomeric tetraethyl compounds proved very difficult to separate by chromatographic techniques. The ratio of the various isomers of **14** could not be determined by ^1H NMR techniques.

The efficient conversion of the 2-nitrodiphenylamines of general structure **15** into dihydrobenzo-1,3,2-diazaphosphole-2-oxides **23** is thought to occur via 2-nitroso-diphenylamine **16** and an intermediate of the type **17** which may decompose to give a nitrene **18**. Subsequent reaction of the nucleophile TMP with electrophilic nitrene **18** would give the ylide-like phosphine-imine **19** for which several canonical forms may be written. The N-methylation of **19** may proceed via two possible mechanisms. One process may involve a four-membered transition state of **19** (path **a**). Alternatively, trimethyl phosphate, formed in the deoxygenation steps or methyl dimethylphosphonate, formed by the thermal isomerization of trimethyl phosphate, may methylate **19**, leading to **21** via intermediate **20**.



SCHEME 4 Reaction mechanism.

At elevated temperature, both trimethyl phosphate and methyl dimethylphosphonate are powerful alkylating agents.[9] The phosphoramidate **21** may undergo thermal elimination of methanol (aminolysis) to the 2,3-dihydro-1H-1,3,2-diazaphosphole-2-oxide derivative **22**. Finally, exhaustive methylation of **22** at elevated temperature is accompanied by rupture of both P—N bonds, leading to a trimethyl- 2-phenylenediamine of general structure **23** (Scheme 4).

EXPERIMENTAL

General Methods. Melting points were determined with a Thomas–Hoover capillary melting point apparatus and are uncorrected, as are boiling points. Routinely, reaction courses and product mixtures were monitored by thin layer chromatography (TLC) or gas–liquid chromatography (GLC). Thin layer separations were accomplished on silica gel GF^{254} plates with visualization by iodine vapor, phosphomolybdic acid spray, or UV light. Infrared (IR) spectra were measured on a Digilab FTS-15E or Beckman Acculab I spectrophotometer, and only pertinent and other strong absorptions are listed. Bruker WN-360 or General Electric QE-300 spectrometers were used to obtain nuclear magnetic resonance (NMR) data. Peak positions are given in ppm downfield from tetramethylsilane as an internal standard. Mass spectra were determined at 70 eV on a Finnigan 4000 spectrometer, either through gas chromatographic (GC/MS) or solid probe (SP/MS) sample introduction, and only the pertinent or more abundant fragment peaks are recorded. In the absence of clearly detectable molecular ions (chemical ionization, CI) using CH_4 was employed on the same instrument.

Propionic acid, 2-[4-(2-*Ethoxy*-3-*ethyl*-2,3-*dihydro*-2-*oxo*-5-*trifluoromethylbenzo*-1*H*-1,3,2-*diazaphosphol*-1-*yl*)*phenoxy*]-, *ethyl ester,* **3**. A solution of 10.4 g (0.025 mol) of **1** in 50 ml of triethyl phosphite was heated at 150° (reflux) for 3 hrs until TLC showed the disappearance of starting material. The mixture was concentrated under reduced pressure (1 mm Hg, 80°). The residue was purified by silica chromatography (solvent #3)[10] to give 7.0 g (57%) of **3** as an amber syrup; IR (CH_2Cl_2):ν 1748 (C═O), 1616, 1510 (aromat. CH), no apparent NH, 1219 (P═O), 1036 (P—O—C) cm^{-1}; EI/MS (m/z) 486 (M^+), 467 (M^+-F), 458 (M^+-C_2H_4), 441 (M^+-C_2H_5O), 413 (M^+-$CO_2C_2H_5$), 385 (M^+-$CH(CH_3)CO_2C_2H_5$), 369 (M^+-$OCH(CH_3)CO_2C_2H_5$), 357 (m/z 369-C_2H_4).

Anal. Calcd. for $C_{22}H_{26}F_3N_2O_5P$ (486.43): C, 54.3; H, 5.4; N, 5.8. Found: C, 54.3; H, 5.6; N, 6.2.

Propionic acid, 2-[4-(2-*Methoxy*-3-*methyl*-1,3-*dihydro*-2-*oxo*-5-*trifluoro-methyl-benzo*-1*H*-1,3,2-*diazaphosphol*-1-*yl*]*phenoxy*)-, *Ethyl Ester,* **4**; *Propionic Acid,* 2-[4-(2-*Methyl-amino*)-4-*trifluoromethyl-phenylamino*)-*phenoxy*]-, *Ethyl Ester,* **6**; *and Propionic Acid,* 2-[4-(2-*Dimethylamino*)-4-*trifluoromethyl-phenylamino*)*phenoxy*]-, *Ethyl Ester,* **5**. A solution of 10.4 g (0.025 mol) of **1** in 50 ml of trimethyl phosphite was refluxed for 24 hrs, concentrated under rotary evaporation (90°, 0.5 mm Hg), and purified by silica chromatography (solvent #2)[10] to give a fraction consisting of 1.0 g (10%) of **5**; an amber syrup, $R_f = 0.63$. A second fraction consisted of 0.6 g (6%) of **6**, an amber syrup, $R_f = 0.48$. A third fraction consisted of 8.0 g (70%) of **4**, an amber syrup, $R_f = 0.20$.

5: ^{1}H NMR ($CDCl_3$): δ 1.26 (3H, t, $OCH_2\underline{CH_3}$), 4.23 (2H, m, OCH_2), 1.63 (3H, d, $OCH\underline{CH_3}$), 4.71 (1H, m, $O\underline{CH}CH_3$), 2.69 (6H, s, $N(CH_3)_2$), 6.66 (1H, s, NH), 6.8–7.3 (7H, m, $(CH═)_7$); EI/MS (m/z) 396 (M^+), 377 (M^+-F), 351 (M^+-OC_2H_5), 336, 323 (M^+-C_2H_5OCO), 295 (M^+-$CH(CH_3)CO_2C_2H_5$), 281 (m/z 295-C_6H_5OH); IR (CH_2Cl_2): ν 3350 (NH), and 1748 (C═O) cm^{-1}.

Anal. Calcd. for $C_{20}H_{23}F_3N_2O_3$ (396.40): C, 60.6; H, 5.8; N, 7.1. Found: C, 60.9; H, 5.9; N, 7.2.

6: ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, $OCH_2\underline{CH_3}$), 4.21 (2H, m, OCH_2), 2.87 (3H, d, NCH_3), 5.08 (1H, m, NH), *ca.* 7.0 (7H, m, $(CH═)_7$), 1.59 (3H, d, $OCH\underline{CH_3}$), 4.66 (1H, m, $O\underline{CH}CH_3$); IR (CH_2Cl_2): ν 3400 (NH), 1748 (C═O), 1325 (CF_3) cm^{-1}; EI/MS (m/z) 382 (M^+), 363 (M^+-F), 336 (M^+-C_2H_5OH), 281 (M^+-$CH(CH_3)CO_2C_2H_5$), 187 (m/z 281-C_6H_5OH).

Anal. Calcd. for $C_{19}H_{21}F_3N_2O_3$ (382.38): C, 59.7; H, 5.5; N, 7.3. Found: C, 59.8; H, 5.8; N, 7.4.

4: ^{1}H NMR ($CDCl_3$): δ 1.28 (3H, t, $OCH_2\underline{CH_3}$), 4.25 (2H, q, OCH_2), 3.22 (3H, s, NCH_3), 3.66 (3H, d, $POCH_3$), 6.5–7.5 (7H, m, $(CH═)_7$), 1.65 (3H, d, $OCH\underline{CH_3}$), 4.76 (1H, m, $O\underline{CH}CH_3$); EI/MS (m/z) 458 (M^+), 439 (M^+-F), 427 (M^+-OCH_3), 385 (M^+-$CO_2C_2H_5$), 357 (M^+-

$CH(CH_3)CO_2C_2H_5$), 249; IR (CH_2Cl_2) 1748 (C=O), no NH, 1350–1000 (P=O), (P—O—C, CF_3, C—O—C) cm^{-1}.

Anal. Calcd. for $C_{20}H_{22}F_3N_2O_5P$ (458.38): C, 52.4; H, 4.8; N, 6.1. Found: C, 52.0; H, 5.1; N, 6.0.

Propionic Acid, 2-[(4-(2-(Dimethylamino)-4-trifluoromethyl-phenyl)-methylamino)phenoxy]-, Ethyl Ester, **7**. A solution of 0.6 g (1.51 mmol) of **5** in 25 ml of methyl iodide was sealed in a glass bomb and the bomb placed for 36 hrs in a steam bath. The reaction mixture was concentrated and purified by silica chromatography (solvent 1)[10] to give 0.6 g (97%) of an amber liquid; IR (CH_2Cl_2): ν 1748 (C=O) cm^{-1}, no NH; ^1H NMR ($CDCl_3$): δ 1.26 (3H, t, $OCH_2\underline{CH_3}$), 4.21 (2H, m, OCH_2), 2.75 (6H, s, $N(CH_3)_2$), 3.14 (3H, s, NCH_3), 6.5–7.3 (7H, m, $(CH=)_7$), 1.58 (3H, d, $OCH\underline{CH_3}$), 4.63 (1H, m, $O\underline{CH}CH_3$); EI/MS (m/z) 410 (M^+), 391 (M^+-F), 378, 364 (M^+-C_2H_5OH), 337 (M^+-$CO_2C_2H_5$), 315, 309 (M^+-$CH(CH_3)CO_2C_2H_5$), 215 (m/z 309-C_6H_5OH).

Anal. Calcd. for $C_{21}H_{25}F_3N_2O_3$ (410.43): C, 61.5; H, 6.1; N, 6.8. Found: C, 61.6; H, 6.3; N, 7.1.

Benzo-1H-1,3,2-Diazaphosphole, 2,3-Dihydro-2-methoxy-3-methyl-2-oxo-1-phenyl-, **8**. A solution of 10.7 g (0.05 mol) of 2-nitrodiphenylamine in 150 ml of trimethyl phosphite was heated at reflux for 28 hrs. The cooled mixture was poured into 200 ml of 10% hydrochloric acid and extracted with 3 × 200 ml of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica chromatography (solvent #3)[10] to give 9.0 g of syrup that crystallized from ether-hexane (1:1) to give 8.5 g (61%) of colorless solid; mp 109–111°; IR (KBr): 2800 (NCH_3) no NH, 1271 (P=O), 1032 (P—O—C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.19 (3H, d, NCH_3)(J_{PH} = 9.35 Hz), 3.60 (3H, d, $POCH_3$)(J_{PH} = 12.81 Hz), 6.6–7.6 (9H, m, $(CH=)_9$). EI/MS (m/z) 274 (M^+), 259 (M^+-CH_3), 195 (M^+-$HOPOCH_3$).

Anal. Calcd. for $C_{14}H_{15}N_2O_2P$ (274.26): C, 61.3; H, 5.5; N, 10.2. Found: C, 61.3; H, 5.6; N, 10.2.

Diphenylamine, 2-(Dimethylamino)-N-methyl-, **9**. A solution of 21.4 g (0.1 mol) of 2-nitrodiphenylamine in 125 ml of trimethyl phosphite was refluxed. The reaction proceeded sluggishly for the first two days as evidenced by TLC. After 72 hrs, the mixture turned dark, all TMP had isomerized to dimethyl methylphosphonate, and starting 2-nitrodiphenylamine and product **8** had disappeared. A fluorescing spot on a silica gel TLC plate having an R_f value higher than that for starting material was the only detectable reaction product. The cooled reaction mixture was treated (1) with hydrochloric acid, (2) aqueous sodium hydroxide, and extracted with 3 × 200 ml of ether. The usual work up gave 18.0 g of a crude oil that was purified by distillation to give 15.0 g (66%) of **9** as a colorless oil, bp 108–110° (2 mm Hg) (short path), which darkens when exposed to light; IR (CH_2Cl_2): no NH; ^1H NMR ($CDCl_3$): δ 2.72 (6H, s, $(CH_3)_2N$), 3.16 (3H, s, NCH_3), 6.5–7.5 (9H, m, $(CH=)_9$); EI/MS (m/z) 226 (M^+), 211 (M^+-CH_3), 195, 77 ($C_6H_5^+$).

Anal. Calcd. for $C_{15}H_{18}N_2$ (226.31): C, 79.6; 8.0; N, 12.4. Found: C, 79.4; H, 7.7; N, 12.7.

Phosphoramidate, N-(2-[Phenylamino)phenyl]-, Diethyl Ester, **10**, *and Benzo-1H-1,3,2-Diazaphosphole, 2-ethoxy-3-ethyl-1,3-dihydro-2-oxo-1-phenyl-,* **11**. A solution of 10.7 g (0.05 mol) of 2-nitrodiphenylamine in 50 ml of triethyl phosphite was heated to reflux (160 ± 5°). The course of the reaction was monitored by TLC. After 5 hrs, the reaction mixture was concentrated by rotary evaporation (0.5 mm Hg, 90°). The residual oil was purified by silica chromatography (solvent #3)[10] to give 4.6 g (fraction 1) of red syrup. A second fraction consisted of 2.0 g (13%) of **11** as a red oil. The third fraction consisted of 1.5 g of a white solid.

1st and 3rd Fraction: Recrystallization from ether gave 3.0 g (19%) of **10**; mp 107–109°; R_f = 0.15 (solvent #3)[10]; EI/MS, (m/z) 320 (M^+), 274 (M^+-C_2H_5), 246 (m/z 274-C_2H_4), 184 (C_6H_5NH-$C_6H_4NH_2$ +); Ir (KBr) 3400–3000 (NH), 1225 (P=O), 1026–984 (P—O—C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.26 (6H, m, $(OCH_2\underline{CH_3})_2$), 4.1 (4H, m, $(O\underline{CH_2}CH_3)_2$), 5.81 (1H, s, NH), 6.18 (1H, m, PNH), 6.5–7.5 (9H, m, $(CH=)_9$).

Anal. Calcd. for $C_{16}H_{21}N_2O_3P$ (320.33): C, 60.0; H, 6.6; N, 8.7. Found: C, 59.9; H, 6.7; N, 8.7.

2nd Fraction. Amber red oil, **11**; EI/MS (m/z) 302 (M^+), 274 (M^+-C_2H_4), 259, 246, 181, 77 (C_6H_5 +).

Anal. Calcd. for $C_{16}H_{19}N_2O_2P$ (302.31): C, 63.6; H, 6.3; N, 9.3. Found: C, 63.8; H, 6.5; N, 9.6.

2-(Diethylamino)diphenylamine, **12**, *N-Ethyl-2-(diethylamino)diphenylamine,* **13**; *and N-Ethyl-2-(diethylamino)-x-ethyl-diphenylamine,* **14**. When the reaction of 2-nitrodiphenylamine, 10.7 g (0.05 mol), was carried out in refluxing TEP, 100 ml, over a 7-day period, none of the above **10** and **11** was detectable. The mixture was concentrated at 90° (0.5 mm). The residue was taken in 150 ml of 14% hydrochloric acid, heated on a steam bath for 0.5 hour, chilled to 0° and made basic with 50% sodium hydroxide. Extraction with 3 × 200 ml of ether gave an extract that was washed with cold water, dried, and concentrated to give 12.0 g of an amber syrup. This syrup consisted of a mixture of compounds as evidenced by GLC and TLC. Separation by silica chromatography gave 1.5 g (11%) of **13** as an amber syrup (1st fraction), $R_f = 0.53$ in solvent #1[10]. EI/MS (m/z) 268 (M^+), 253 (M^+-CH_3), 239 (M^+-C_2H_5), 233, 209, 195, (M^+-NH(C_2H_5), 163, 77. ^{1}H NMR ($CDCl_3$: δ 0.96 (6H, t, $N(CH_2\underline{CH_3})_2$), 1.16 (3H, t, $NCH_2\underline{CH_3}$), 3.08 (4H, q, $N(\underline{CH_2}\text{-}CH_3)_2$), 3.69 (2H, q, $N\underline{CH_2}\text{-}CH_3$), 6.5–7.5 (9H, (CH=)$_9$).

Anal. Calc. for $C_{18}H_{24}N_2$ (268.39): C, 80.6; H, 9.0; N, 10.4. Found: C, 80.8; H, 9.5; N, 10.7.

The second fraction consisted of 6.0 g (40.5%) of **14**, a mixture of isomers. A reverse phase C_{18} prep. columns (20mm × 25 cm) was used in the attempted separation, eluent 72% acetonitrile containing 0.5% of triethylamine and 28% of water. EI/MS (m/z) 296 (M^+), 281, 267, 251, 237, 223, 208, 194, 100, 163, 147, 133, 119, 105, 91, 77, 72, 65, 44.

Anal. Calcd. for $C_{20}H_{28}N_2$ (296.44): C, 81.0; H, 9.5; N, 9.5. Found: C, 80.9; H, 9.3; N, 9.8.

The third fraction consisted of 0.4 g (3.3%) of an amber oil which was tentatively assigned structure **12**. EI (MS (m/z) 240 (M^+), 225, 211, 195, 181, 167, 119, 92 ($C_6H_5NH^+$), 77 ($C_6H_5^+$), 65, 51.

Anal. Calcd. for $C_{16}H_{20}N_2$ (240.34): C, 80.0; H, 8.4; N, 11.7. Found: C, 79.7; H, 8.6; N, 11.5.

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10. Solvent System (by volume): No. 1, THF (4), hexane (96); No. 2, THF (4), ethyl acetate (16), hexane (80); No. 3, THF (4), ethyl acetate (30), hexane (66).