Phosphorus-Nitrogen Compounds. Part 49.[1] The Synthesis and Mechanism of Formation of 6-Chloro-5,6,7,12-tetrahydro-2,5,7,10-tetramethyldibenzo-[*d,g*][1,3,2]-diazaphosphocine 6-Oxide and 6-Sulphide

Türsen Demir and Robert A. Shaw*
Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX, U.K.

A reaction mechanism is proposed for the formation of the title compounds in the reactions between *N,N*-dimethyl-*p*-toluidine and phosphoryl and thiophosphoryl chlorides. The synthesis of 2,2'-methylenebis(*p*-toluidine) and 2,2'-methylenebis(*N*-methyl-*p*-toluidine) are described, as are their reactions with phosphoryl and thiophosphoryl chlorides.

We have reported earlier the formation of 6-chloro-5,6,7,12-tetrahydro-2,5,7,10-tetramethyldibenzo[*d,g*][1,3,2]-diazaphosphocine 6-oxide [(**4**)[1,2] and 6-sulphide (**5**)][1,3] in the reaction of *N,N*-dimethyl-*p*-toluidine (**1**) with phosphoryl (**2**) [and thiophosphoryl (**3**)] chloride at 130 °C. The heterocycles were accompanied by acyclic phosphorus compounds (**6**)—(**10**) and by minor amounts of purely organic material (**11**)—(**13**) (Scheme 1). The ethoxy derivatives (**7**), (**8**), and (**10**) are secondary products arising out of the work-up procedure.

The above reaction with phosphoryl chloride [(**1**) + (**2**) ⟶ products] was relatively clean. The reaction with thiophosphoryl chloride was not and the only product isolated from the tarry mixture was the diazaphosphocine 6-sulphide [(**1**) + (**3**) ⟶ (**5**)].

Yields of both heterocycles, (**4**) and (**5**), by this route were poor. To improve the yields, an understanding of the mechanism was desirable. An obvious starting material for a rational synthesis was the diamine (**13**).

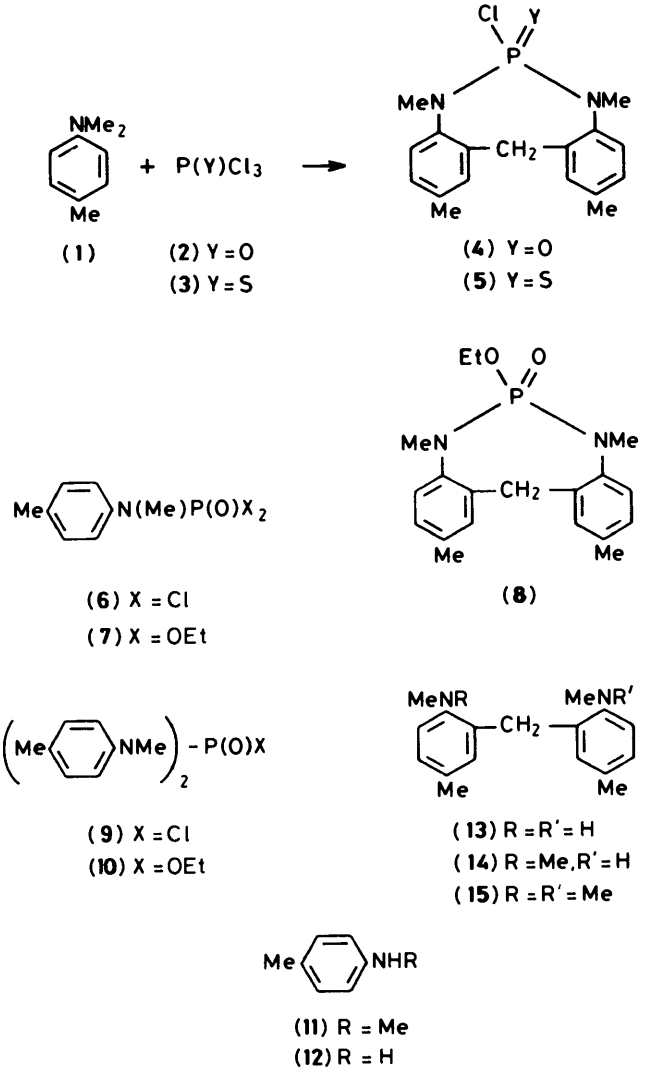
We had obtained this diamine, (**13**), from the hydrolysis of the heterocycle,[1,2] (**4**), and showed that it could be reconverted to it in high yield.[2] Prior to this synthesis, it had been reported only once in the literature, by von Braun[4] and his findings were subsequently disputed by Farrar.[5] We have been able to clarify this anomaly by showing that the above diamine was a secondary product, arising from the high temperature distillation of an *impure primary product*.[6]

We have shown earlier[1] that the acyclic phosphorus compounds are unlikely precursors of the heterocycles. Phosphorus groups,[7] like other acid residues, deactivate aniline derivatives towards electrophilic attack and the structures of our products show clearly *ortho/para* orientations. At this point, we also recall the organic by-products of our earlier studies with *N,N*-dimethylaniline[8] and *N,N*-dimethyl-*m*-toluidine,[1] which gave rise (by *para*-substitution) to diphenyl- and triphenylmethane derivatives. Noteworthy is also the observation of fairly large amounts of secondary amine, *e.g.* *N*-methyl-*p*-toluidine (**11**) even when non-solvolytic work-up procedures were employed. We determined the volatile products in one reaction and showed that they consisted of the tertiary and secondary amines in the molar ratio of 17:10.

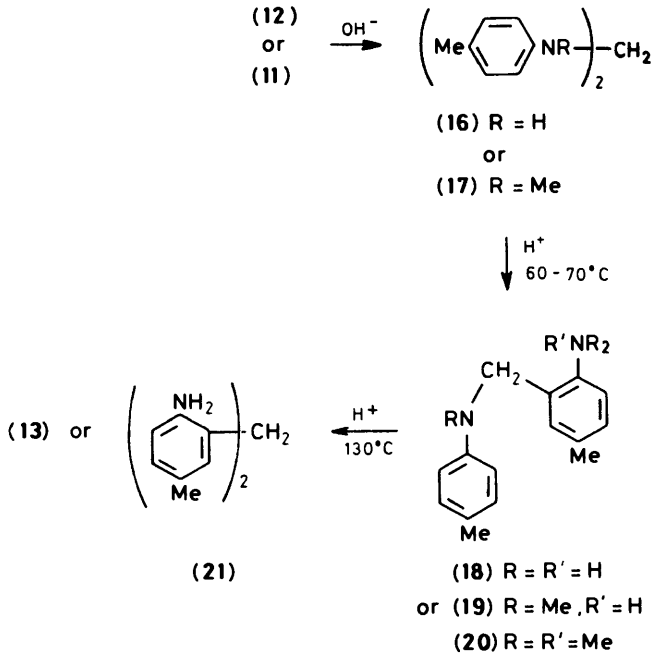
It is well documented in the literature that *p*-toluidine (**12**) and *N*-methyl-*p*-toluidine (**11**) condense with formaldehyde under neutral or basic conditions to give diaminomethane derivatives, (**16**) and (**17**), in near quantitative yields.[9,10]

These then rearrange under acidic conditions at 60—70 °C to the derivatives (**18**) or (**19**) respectively, which rearrange further around 130 °C, again under acidic conditions, to the diamines (**21**) or (**13**) respectively (Scheme 2).

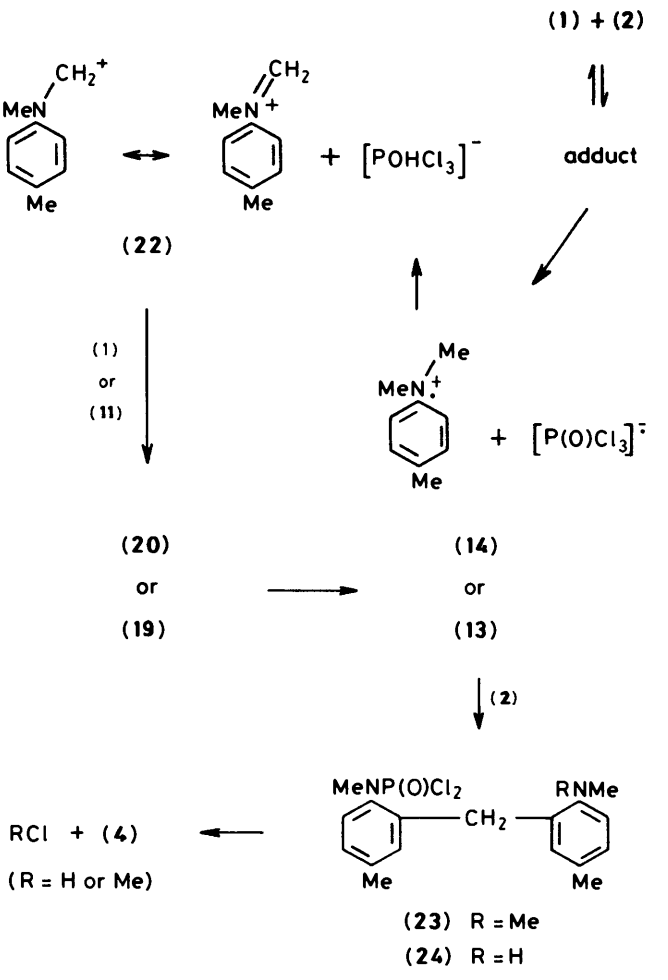
Wagner[11] has suggested that both rearrangements are intermolecular. Both are probably of the Hofmann-Martius type of rearrangements,[12] which normally take place at 200—300 °C. The lower temperatures at which our reactions proceed are probably connected with the fact that in our systems, benzyl groups rather than saturated alkyl groups migrate, which should provide greater ease of reaction with nucleophiles, as well as more stable carbonium ions.



Scheme 1.



Scheme 2.



Scheme 3.

We believe that some parts of the mechanism, which we propose for our reactions (Scheme 3) are closely similar to that proposed for *N,N*-dimethylaniline and tetrachlorobenzoquinone or tetracyanoethylene.[13] Because of the nature of our reaction (multitude of products, high temperature), we are open-minded whether we are dealing with two one-electron or one two-electron oxidation. Evidence for the self-ionisation of phosphoryl chloride has been presented.[14]

$$P(O)Cl_3 \rightleftharpoons [P(O)Cl_2]^+ + Cl^-$$

As tertiary amines, R_3N, give conducting solutions in this solvent, the additional equilibrium below has been suggested.[14]

$$R_3N + P(O)Cl_3 \rightleftharpoons [R_3NP(O)Cl_2]^+ + Cl^-$$

It seems feasible that yet a further equilibrium needs to be considered.

$$[R_3NP(O)Cl_2]^+ + Cl^- \rightleftharpoons R_3NPOCl_3$$

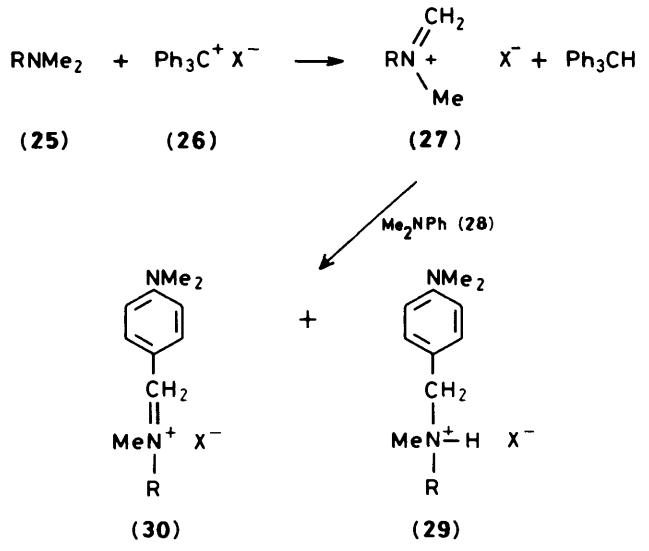
In the ionised form, the nucleophilic chloride ion can attack the methyl group. Dealkylation then would give rise to the acyclic phosphorus chloride derivatives (**6**) and (**9**). A similar dealkylation process would convert (**23**) into (**4**). We have shown previously[1] that *ortho*-substituted *N,N'*-dimethylanilines dealkylate and form products containing phosphorus–nitrogen bonds. The un-ionised form could give by the above mentioned two one-electron or one two-electron oxidations the electrophilic carbonium-imminium species (**22**) postulated above. This species could also arise from the reaction of a secondary amine and formaldehyde under acidic conditions. We have shown that the former, *viz.* *N*-methyl-*p*-toluidine, (**11**), is present in the reaction mixture. Formaldehyde could arise by aerial oxidation or by oxidation involving the phosphoryl chloride. The former can be excluded as the reaction proceeds under an atmosphere of nitrogen, giving rise to the same products as when done in air. The latter mechanism is equally unlikely, as it is well-known that PCl_3 is a powerful de-oxygenation reagent for *N*-oxides.[15]

$$PCl_3 + R_3NO \longrightarrow P(O)Cl_3 + R_3N$$

It is unlikely that the above process would be reversed under our reaction conditions. As Bamberger and Tschirner[16] reported that *N,N*-dimethyl-*p*-toluidine *N*-oxide decomposed thermally to *N*-methyl-*p*-toluidine and formaldehyde, we synthesised this *N*-oxide and pyrolysed it at 130—140 °C: (*a*) by itself, (*b*) in *N,N*-dimethyl-*p*-toluidine, (*c*) in *N,N*-dimethyl-*p*-toluidine, containing an equimolar quantity of the amine hydrochloride, and (*d*) in *N,N*-dimethyl-*p*-toluidine containing an equimolar quantity of phosphoryl chloride. In no case was the formation of formaldehyde, or products arising from it, detected. This is however not completely conclusive, as a great deal of tar was observed.

The oxidation of *N,N*-dimethylaniline and its derivatives at the α-carbon atom has been demonstrated, and a wide range of oxidising agents have been used for this purpose. The most interesting example of such an oxidation, so far as we are concerned, was that reported by Volz and Kiltz,[17] who allowed 2,4,6-trimethyl-*N,N*-dimethylaniline (**25**; R = $C_6H_3Me_3$-2,4,6) to react with triphenylcarbonium perchlorate (**26**; X^- = ClO_4^-) and obtained the carbonium-imminium salt (**27**; R = $C_6H_3Me_3$-2,4,6, X^- = ClO_4^-) (Scheme 4).

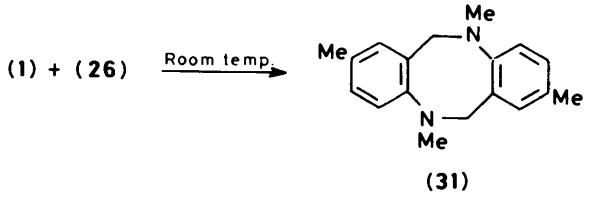
Since the aromatic amine (**25**; R = $C_6H_3Me_3$-2,4,6) was fully substituted in the *ortho*- and *para*-positions, the reaction stopped at this stage. However, when *N,N*-dimethylaniline, (**28**), was added to a solution of (**27**; R = Bu^t), electrophilic attack yielded the salts (**29**) and (**30**) (R = Bu^t, X^- = ClO_4^-).



Scheme 4.

For our purpose, it had to be established whether or not a similar attack at the *ortho*-position of *N*,*N*-dimethyl-*p*-toluidine (**1**) would be successful.

Therefore, *N*,*N*-dimethyl-*p*-toluidine (**1**) was allowed to react with triphenylcarbonium hexafluorophosphate (**26**; $X^- = PF_6^-$). The reaction product was the phenomazine (**31**) (Scheme 5), identical with a sample prepared by another route.[6]



Scheme 5.

This demonstrates clearly that a strong electrophile can remove an hydride ion from the α-carbon atom of *N*,*N*-dimethyl-*p*-toluidine and the resultant carbonium-imminium ion (**22**) can attack the *ortho*-position of the aromatic ring of the tertiary amine, (**1**).

Whilst it shows that under these conditions (room temperature), the acyclic diamine precursor (**20**) of the phenomazine (**31**) has had no opportunity to rearrange to the desired diamines (**14**) or (**13**) for the diazaphosphocine oxide synthesis, it nevertheless proves the existence of the postulated electrophile. Similar mechanistic pathways[13] undoubtedly account for the occurrence of diphenyl- and triphenyl-methane bases in the reactions of the *N*,*N*-dimethyl-aniline and *m*-toluidine.[1,8] In both cases, reactions take place at the preferred *para*-position, whilst if this is blocked, *e.g.* in *N*,*N*-dimethyl-*p*-toluidine (**1**) the *ortho*-position is attacked. Acid-catalysed rearrangement then gives the observed diphenyl- and triphenyl-methane bases. These were not observed for the *p*-toluidine isomer, probably as the *ortho*-effect prevented activation of, and hence electrophilic attack at, the ring.

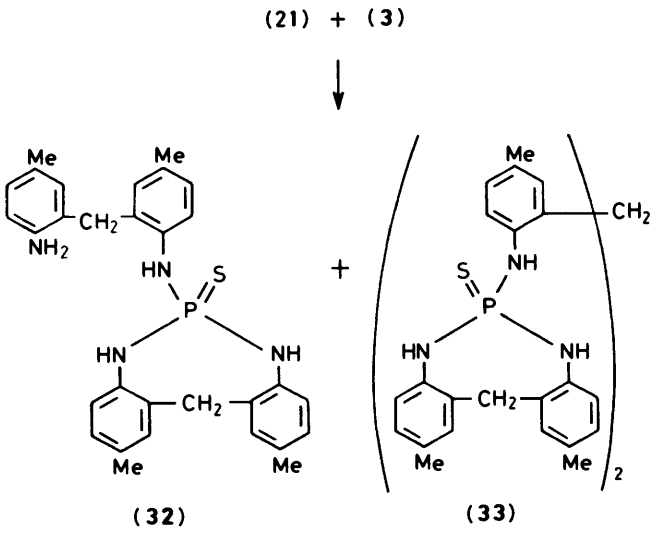
Our postulated mechanism involves oxidation of the dialkylaniline and reduction of phosphoryl chloride. We did not detect phosphorus compounds of lower oxidation states in our reaction mixtures. This does not, however, invalidate our arguments, as such compounds are easily oxidised in acidic (reaction conditions) or basic media (work-up procedures). The reaction mixture contained too many products and their yields were too small to detect trace amounts of P^{III} derivatives by ^{31}P n.m.r. It is probable that similar mechanistic pathways are followed in the formation of the diazaphosphocine sulphide (**5**) from *N*,*N*-dimethyl-*p*-toluidine (**1**) and thiophosphoryl chloride (**3**).

Having proposed a plausible mechanistic route for the diazaphosphocine system we proceeded to a rational exploitation for its synthesis. In our hands, the successive rearrangements (Scheme 2) gave better yields when R = H, than when R = Me. We therefore prepared the required diamine (**13**; R = Me) by preparing its unmethylated derivative (**21**; R = H), which was then successively acetylated, methylated, and hydrolysed to give the diamine (**13**; R = Me). This, it will be shown, gives excellent yields of the diazophosphocine with phosphorus halides. Whilst this diamine (**13**) provides a convenient route to the heterocycles, it is probably not the precursor in the *N*,*N*-dimethyl-*p*-toluidine (**1**) reaction. Initially, only tertiary amine (**1**) is present. The same applies to the initial diamine (**20**). Rearrangement of (**20**) could lead to an *N*,*N*,*N*′-trimethyl- (**14**), as well as to an *N*,*N*,*N*′,*N*′-tetramethyl derivative (**15**), by an intermolecular rearrangement. We have detected the former (**14**) but not the latter (**15**) in the reaction mixture from the *N*,*N*-dimethyl-*p*-toluidine (**1**) and phosphoryl chloride (**2**) reaction. We have made compound (**15**) by an independent route and allowed it to react with phosphoryl chloride. No diazophosphocine derivative was isolated, although all of the diamine was consumed. Similar mechanisms to the ones postulated above might well lead to polymers and the tar observed behaved like a polymeric product. The symmetric diamine (**13**) and some of the *N*-methyl-*p*-toluidine (**11**) may well have arisen out of the work-up procedure. We believe that the bulk of the latter, however, arises from the intermolecular rearrangement discussed above. It is conceivable that in the latter stages of the reaction some symmetric diamine is also formed by the reaction (**19**) + (**11**) ⟶ (**13**). The other likely route is by solvolysis of the heterocycle, (**4**) ⟶ (**13**). We carried out reactions with these diamines, (**21**) or (**13**) and phosphoryl (**2**) and thiophosphoryl chloride (**3**). With the di-secondary amine, (**13**), we obtained in the presence of triethylamine good yields (75%) of the respective heterocycles, (**4**) or (**5**).

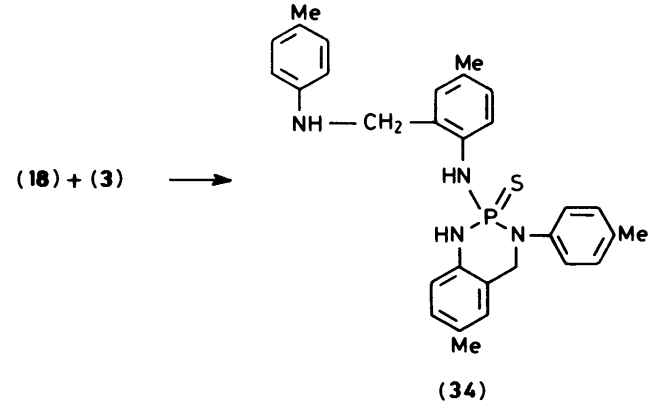
With the di-primary amine (**21**) and phosphoryl chloride (**2**) even at very low temperature, we obtained only a glass-like, probably polymeric, substance insoluble in all common solvents. Hydrolysis with NaOH yielded the parent diamine. The same diamine (**21**) gave, however, with thiophosphoryl chloride (**3**) identifiable products. The major one, m.p. 215 °C, is one with a diamine residue attached at one end to a diazaphosphocine 6-sulphide ring formed from another such residue (**32**) (Scheme 6). The minor one, m.p. 265 °C, which was eluted first in trace amounts, gave a mass spectrum which suggested that the diamine had a heterocycle attached to each of its primary amino groups (**33**). We have reported an analogue (**34**) of the former (**32**) in a related six-membered ring heterocyclic system[18] (Scheme 7). No doubt compounds (**32**) and (**33**) have arisen by a mechanism similar to that proposed for (**34**).[18]

The work described in this paper provides a rationale for the mode of formation of, as well as a convenient synthetic route to, the dibenzo[*d*,*g*][1,3,2]diazaphosphocine 6-oxide (**4**) and 6-sulphide (**5**). Their crystal structures[2,3,19,20] and ^1H n.m.r. spectra[1,2] [except that of (**32**)] have been described previously.

Compound (**32**) has three different NH signals at δ 2.72, 4.23, and 5.34 in the ratio of 2:1:2. That at δ 2.72 is not coupled to phosphorus and is assigned to the NH_2 group, whilst the other



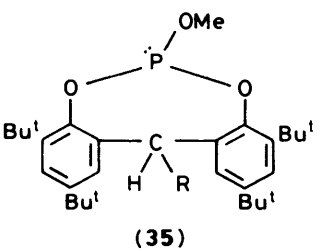
Scheme 6.



Scheme 7.

two show $^2J(PNH)$ coupling constants of 11.0 (4.23) and 12.5 Hz (5.34) and are assigned to the exocyclic and endocyclic NH groups respectively. The aromatic methyl groups are resolved in $CDCl_3$ solution to three signals, in C_6D_6 into four. No attempt was made to assign these. The exocyclic methylene group gives a singlet at δ 3.63. The endocyclic analogue has non-equivalent protons δH_A 3.63, δH_B 4.62 [$^2J(AB)$ 12.0 Hz]. One of these, H_B, is coupled to phosphorus, J = 3.5 Hz.

The related dibenzo[*d*,*g*][1,3,2]dioxaphosphocines have received considerable attention in the scientific and patent literature in recent years.[21] P^{III} As well as P^V derivatives have been investigated.[21] Similar long-range $J(PH)$ values to that for (**32**) have been reported for (**35**) (R = H, 2.9 Hz, R = Me, 2.4 Hz).[22] These authors[21] favour a through-space rather than through-bonds coupling mechanism.



(35)

Experimental

Chemicals and Spectroscopic Techniques.—Phosphoryl chloride (May and Baker Ltd.), thiophosphoryl chloride (Alfa Inorganics Inc.), triethylamine, and *p*-toluidine (Koch Light Ltd.) were purified by conventional methods. ^1H N.m.r. spectra were obtained in $CDCl_3$ solution from a JEOL Model JNM-MH-100 spectrometer ($SiMe_4$ as internal standard). Mass spectra were obtained from an AEI MS9 spectrometer, P.C.M.U., Harwell. Microanalyses were carried out by Dr. Kolbe Laboratories, Mülheim, Ruhr, Germany. Synthesis and characterisation of compounds (**4**)–(**7**), (**9**)–(**11**), (**13**), and (**14**) as products and by-products of the direct interaction of *N*,*N*-dimethyl-*p*-toluidine (**1**) and phosphoryl chloride (**2**) or thiophosphoryl chloride (**3**) have been reported elsewhere.[1-3]

6-*Chloro*-5,6,7,12-*tetrahydro*-2,5,7,10-*tetramethyldibenzo*-[d,g][1,3,2]*diazaphosphocine* 6-*Oxide* (**4**).—2,2′-Methylenebis(*N*-methyl-*p*-toluidine) (**13**) (5 g, 19.7 mmol) and dry triethylamine (3.98 g, 39.4 mmol) were dissolved in NaH-dried benzene (200 ml). While this mixture was stirred at room temperature under nitrogen, phosphoryl chloride (**2**) (3 g, 19.7 mmol) was added dropwise. When addition was complete, the mixture was gently refluxed for 3 h, after which triethylamine hydrochloride was filtered off while hot. The solvent was removed on a rotary evaporator and the resultant oil was crystallised from light petroleum (b.p. 60—80 °C) to give the product (4.5 g, *ca.* 69%), m.p. 172 °C (lit.,[1,2] m.p. 172 °C) (Found: C, 61.1; H, 6.2; Cl, 10.5; N, 8.2; P, 9.4%; M^+, 334.0999. $C_{17}H_{20}ClN_2OP$ requires C, 61.1; H, 6.0; Cl, 10.6; N, 8.4; P, 9.3; *M*, 334.1002).

6-*Chloro*-5,6,7,12-*tetrahydro*-2,5,7,10-*tetramethyldibenzo*-[d,g][1,3,2]-*diazaphosphocine* 6-*Sulphide* (**5**).—2,2′Methylenebis(*N*-methyl-*p*-toluidine) (**13**). (2.2. g, 8.6 mmol), triethylamine (1.75 g, 17 mmol), and thiophosphoryl chloride (**3**) (1.5 g, 8.6 mmol) were allowed to react in dry benzene (50 ml) using the procedure described above for compound (**4**), m.p. 208—210 °C (lit., [1,3] m.p. 209—210 °C); yield 2.07 g (68%) (Found: C, 58.3; H, 5.8; Cl, 10.1; N, 8.0; P, 8.8%; M^+, 350. $C_{17}H_{20}ClN_2PS$ requires C, 58.2; H, 5.8; Cl, 10.1; N, 8.8; P, 8.8%; *M*, 350.)

6-{2-[2-*Amino*-5-*methylbenzyl*]-4-*methylanilino*}-5,6,7,12-*tetrahydro*-2,10-*dimethyldibenzo*[d,g][1,3,2]*diazaphosphocine* 6-*Sulphide* (**32**).—2,2′-Methylenebis(*p*-toluidine)(**21**) (2.26 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) were dissolved in dry benzene (200 ml) and the mixture was cooled in an ice-bath. Thiophosphoryl chloride (**3**) (1.69 g, 10 mmol) was added as described for (**4**). After the solvent was evaporated, the oil left was eluted through a column (silica, benzene–ethyl acetate; 4:1). The first compound was obtained in minute quantities (*ca.* 25 mg) and melted sharply at 265 °C. This was shown by mass spectrometric analysis to be compound (**33**) (Found M^+, 798. $C_{45}H_{48}N_6P_2S_2$ requires *M*, 798). Compound (**32**) was next to be eluted. It was recrystallised from benzene and had m.p. 215 °C; yield 0.4 g (16%) (Found: C, 70.2; H, 6.6; N, 10.9; P, 6.0; S, 6.3%; M^+, 512.2164. $C_{30}H_{33}N_4P_2S_2$ requires C, 70.3; H, 6.5; N, 10.9; P, 6.1; S, 6.3%; *M*, 512.2163).

N,N′-*Methylenebis*(p-*toluidine*) (**16**).—This compound was synthesized by the procedure of Miller and Wagner[9] and had m.p. 88.5 °C (lit.,[9] m.p. 95 °C); yield (minimum 90%) [Found: C, 79.5; H, 8.1; N, 12.4%; no molecular ion (*m*/*z* 121 base peak). Calc. for $C_{15}H_{18}N_2$: C, 79.6; H, 8.0; N, 12.4%; *M*, 226].

N,2′-*Methylenebis*(p-*toluidine*) (**18**).—This compound was synthesized (73% yield) according to Simon's procedure[10]; it had m.p. 88 °C (lit.,[10] m.p. 88 °C) (Found: C, 79.6; H, 8.0; N, 12.4%; M^+, 226.1471. Calc. for $C_{15}H_{18}N_2$: C, 79.6; H, 8.0; N, 12.4%; *M*, 226.1471).

2,2′-*Methylenebis*(p-*toluidine*) (**21**).—This compound was also synthesized (65% yield) according to Simon's procedure[10]; it had m.p. 96 °C (lit.,[10] m.p. 96 °C) (Found: C, 79.6; H, 8.0; N, 12.4%; M^+, 226.1470. Calc. for $C_{15}H_{18}N_2$: C, 79.6; H, 8.0; N, 12.4%; *M*, 226.1471).

2,2′-*Methylenebis*(N-*acetyl*-p-*toluidine*).—Compound (**21**) (4.52 g, 20 mmol) was refluxed in glacial acetic acid (20 ml) for 5 h. When cold, the mixture was neutralised, extracted with ether, and the extract dried and evaporated. The oily residue was taken up with ethanol and upon dilution with water the diamide crystallised (5.37 g, *ca.* 87%), m.p. 226.5 °C (lit.,[10] m.p. 226.5 °C) (Found: C, 73.5; H, 7.1; N, 9.0%; M^+, 310.1681. Calc. for $C_{19}H_{22}N_2O_2$: C, 73.5; H, 7.1; N, 9.0%; *M*, 310.1678).

2,2′-*Methylenebis*(N-*acetyl*-N-*methyl*-p-*toluidine*).—2,2′-Methylenebis(*N*-acetyl-*p*-toluidine) (14.86 g, 48 mmol) and NaH-dried xylene (1 l) was placed in a 3-l flask. While this mixture was gently refluxed under nitrogen, a suspension of NaH (50% dispersion in oil; 4.6 g, 96 mmol) in dry xylene (50 ml) was introduced at short intervals through one side neck. Turbidity was observed almost immediately and the disodium salt of the above diamide was precipitated as an amorphous mass. After 5 h of gentle reflux, the mixture was allowed to cool and a CO_2–acetone condenser was attached to the top of the water condenser. Through this condenser methyl iodide (5 ml, 13.5 g, 96 mmol) was added and the mixture was again brought to gentle reflux. After a period an excess of methyl iodide was added. The solid mass was soon observed to be replaced by a fine precipitate. After a further 7 h, the mixture was filtered whilst hot, the filtrate evaporated under reduced pressure, and the residual oil crystallised from light petroleum (b.p. 60—80 °C) to give the *title compound* (14.7 g, 91%), m.p. 137 °C (Found: C, 74.4; H, 7.7; N, 8.3%; M^+, 338.1974. $C_{21}H_{26}N_2O_2$ requires C, 74.6; H, 7.7; N, 8.3%; *M*, 338.1994).

2,2′-*Methylenebis*(N-*methyl*-p-*toluidine*) (**17**).—*N*-Methyl-*p*-toluidine (**11**) (10 g) was dissolved in ethanol (30 ml) containing sodium hydroxide (0.5 g). A formaldehyde solution (40% soln; 3.25 g) was added at room temperature and the mixture was gently refluxed for 4 h after which time it was diluted with cold water. An oil separated which crystallised in the refrigerator. It was dissolved in ethanol and recrystallised by addition of water to yield the *title compound* (6.82 g, 65%) m.p. 66—68 °C (Found: C, 80.2; H, 8.8; N, 11.1%; M^+, 254.1778. $C_{17}H_{22}N_2$ requires C, 80.3; H, 8.7; N, 11.0%; *M*, 254.1783).

N,2′-*Methylenebis*(N-*methyl*-p-*toluidine*) (**19**).—(*a*) All attempts to obtain this compound by Farrar's method[5] failed. (*b*) Compound (**17**) (4 g, 15 mmol), *N*-methyl-*p*-toluidine (**11**) (45 g, 25 × 15 mmol), and *N*-methyl-*p*-toluidine hydrochloride (2.5 g, 15 mmol) were maintained at 70—80 °C under nitrogen and constantly stirred for 7 h. At the end of this period the mixture was neutralised with aqueous sodium hydroxide and then steam distilled to remove all *N*-methyl-*p*-toluidine (**11**). The remaining oil was recrystallised three times from light petroleum (b.p. 40—60 °C) to yield crystals of the title compound (1.89 g, 47%), m.p. 65 °C (lit.,[5] m.p. 64 °C) (Found: C, 80.3; H, 8.7; N, 11.1%; M^+, 254.1781. Calc. for $C_{17}H_{22}N_2$: C, 80.3; H, 8.7; N, 11.0%; *M*, 254.1783).

2,2′-*Methylenebis*(N-*methyl*-p-*toluidine*) (**13**).—(*a*) Compound (**19**) (0.68 g, 2.68 mmol), *N*-methyl-*p*-toluidine (**11**) (4.87 g, 15 × 2.68 mmol), and *N*-methyl-*p*-toluidine hydrochloride (0.42 g, 2.68 mmol) were maintained at 130 °C for 10 h under nitrogen and stirred. The mixture was then neutralised with aqueous hydroxide, and the *N*-methyl-*p*-toluidine steam distilled off. The residual oil was taken up with a warm dilute HCl solution (1:1), which was again carefully neutralised. The precipitate was extracted with ether and the extract evaporated to yield an oil; this oil solidified on a porous plate and was recrystallised from light petroleum (b.p. 60—80 °C) to yield the title compound (0.16 g, 23%) m.p. 86 °C (lit.,[1] m.p. 86 °C).

(*b*) This compound was obtained in much greater yield by the following procedure. 2,2′-Methylenebis(*N*-acetyl-*N*-methyl-*p*-toluidine) (13.57 g, 40 mmol) was refluxed in a 30% sulphuric acid solution (350 ml) for 30 h. The mixture was then neutralised with a dilute aqueous sodium hydroxide whilst being cooled in ice. The brown oil solidified with time and then was dried and recrystallised from light petroleum (b.p. 60—80 °C) to yield the title compound (9.9 g, 97%), m.p. (sharp) 86 °C.

2,2′-*Methylenebis*(N,N-*dimethyl*-p-*toluidine*) (**15**).—*N,N*-dimethyl-*p*-toluidine (**11**). (13.5 g, 100 mmol) was mixed with paraformaldehyde (3 g, 100 mmol) and formic acid (98—100%; 4.6 g, 100 mmol) and heated on a water-bath until CO_2 evolution ceased as described by Borkowski and Wagner.[23] The mixture was then poured into dilute sodium hydroxide and sodium sulphite. The residual starting amine (**11**) was steam distilled off and the product extracted with ether; the extract was then dried (Na_2SO_4) and evaporated and the remaining oil distilled under reduced pressure to yield the title compound (9.1 g, 65%), b.p. 140—145 °C/1mmHg (lit.,[21] b.p. 205—208 °C/16 mmHg) (Found: C, 80.8; H, 9.2; N, 9.95%; M^+, 282.2098. Calc. for $C_{19}H_{26}N_2$; C, 80.9; H, 9.2; N, 9.9%; *M*, 282.2096).

Reaction between N,N-Dimethyl-p-*toluidine* (**1**) *and Triphenylcarbonium Hexafluorophosphate* (**27**; $X^- = PF_6^-$).—A solution of triphenylcarbonium hexafluorophosphate (**27**; $X^- = PF_6^-$) (3.88 g, 10 mmol) dissolved in dry methylene dichloride (25 ml) was added dropwise to a solution of *N,N*-dimethyl-*p*-toluidine, (**1**) (in excess) at room temperature under nitrogen. After 24 h, the solvent was evaporated off and the oily residue was dissolved in ether; dry HCl gas was then bubbled through this solution for 2 h. The amine hydrochlorides were filtered off, dissolved in distilled water, basified by sodium hydroxide and steam distilled to remove any excess of compound (**1**). The remaining oil was recrystallised from ethanol to give the phenomazine (**31**), m.p. 156 °C (lit.,[5] 149 °C); yield based on (**27**) 0.55 g (41%) (Found: C, 81.2; H, 8.0; N, 10.5%; M^+, 266. Calc. for $C_{18}H_{22}N_2$; C, 81.2; H, 8.3; N, 10.5%; *M*, 266). Compound (**31**) was the only compound obtained by the procedure described by Farrar,[5] m.p. and mixed m.p. showed no change.

N,N-*Dimethyl*-p-*toluidine* N-*Oxide*.—*N,N*-Dimethyl-*p*-toluidine (**1**) (8.5 g, 63 mmol) and hydrogen peroxide (30% w/v; 7.1 g, 63 mmol) were heated at 70—80 °C until the two layers disappeared. When cold the mixture was extracted with ether to remove any unchanged compound (**1**). The aqueous layer was left overnight with a platinum foil to destroy any hydrogen peroxide left. It was then dried *in vacuo* by carefully heating up to 50—60 °C. The extremely hygroscopic colourless crystals were then recrystallised in a dry box from dry benzene under nitrogen, to give the *title compound* (7.3 g, 77%) m.p. 137 °C (Found: C, 71.5; H, 8.7, N, 9.3; M^+, 151.0997. $C_9H_{13}NO$ requires C, 71.5; H, 8.6; N, 9.3%; *M*, 151.0997). Picrate m.p. 110 °C (lit.,[16] 107 °C).

Pyrolysis of N,N-*Dimethyl*-p-*toluidine* N-*Oxide*. The above compound was pyrolysed at 135—140 °C (violent decomposition) under various conditions (see text) and precautions were taken to trap any formaldehyde evolved. Apart from much tar the only product that could be isolated was the parent amine (**1**) showing that the predominant reaction was de-oxygenation. This was also clear from the mass spectrum of the compound.

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