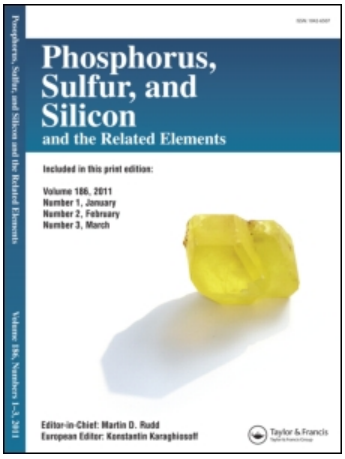

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THE DIHYDROPHENOPHOSPHAZINE RING SYSTEM. 2. THE REACTION OF PHOSPHORUS TRIHALIDES WITH HALO-SUBSTITUTED AND STERICALLY HINDERED DIARYLAMINES

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THE DIHYDROPHENOPHOSPHAZINE RING SYSTEM. 2. THE REACTION OF PHOSPHORUS TRIHALIDES WITH HALO-SUBSTITUTED AND STERICALLY HINDERED DIARYLAMINES[1,2]

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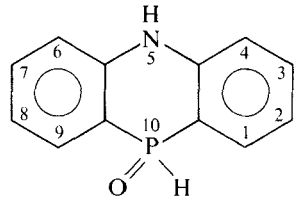
The reaction of phosphorus trichloride with three *p*-chloro-substituted diarylamines gave the expected ring-substituted derivatives of the secondary phosphine oxide **1** and the spirophosphonium chloride **2**. 4,4′-Dibromodiphenylamine was converted in part to a tribromo derivative, but 2,2′,4,4′-tetrabromodiphenylamine did not react at all with phosphorus trichloride or tribromide. *N*-Phenyl-*o*-toluidine and phosphorus trichloride gave a moderate yield of the expected phosphine oxide but no spirophosphonium chloride. Di-*o*-tolyamine gave only a very small yield of phosphine oxide. All of the phosphine oxides obtained in this study were oxidized to the corresponding phosphinic acids.

About ninety years ago Michaelis and Schenk[3] reported that the interaction of diphenylamine and phosphorus trichloride at elevated temperatures (followed by treatment of the reaction mixture with water) yields a phosphorus-containing substance, and they suggested that the phosphorus atom in this substance might be a member of a heterocyclic ring. It was not until 1960 that this substance was unambiguously shown[4] to be the secondary phosphine oxide **1**, and in 1971 it was discovered[5] that the spirophosphonium chloride **2** is also a product of this reaction.



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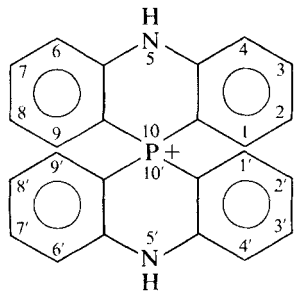


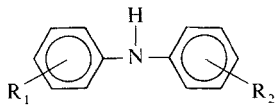
2

More recently, the reaction between phosphorus trichloride and several other diarylamines (di-*p*-tolylamine, 4-methyldiphenylamine, and *N*-phenyl-1-naphthylamine) was studied, and it was found that the expected ring-substituted derivatives of **1** and **2** were formed in each case.[1] The ease with which these heterocyclic substances can be obtained and the recent flurry of interest[6] in the dihydrophenophosphazine ring system have prompted us to report the results that we have obtained with the halo-substituted and sterically hindered diarylamines listed in Table I.

The three chloro-substituted diarylamines reacted with phosphorus trichloride as expected and yielded moderate amounts of secondary phosphine oxides[7] and spirophosphonium chlorides. The in-

TABLE I

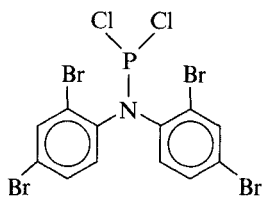
Diarylamines studied



R_1 =	R_2 =
4-Cl	H
4-Cl	4-Me
4-Cl	4-Cl
4-Br	4-Br
2,4-Br_2	2,4-Br_2
2-Me	H
2-Me	2-Me

teraction of 4,4′-dibromodiphenylamine and phosphorus tribromide[8] also appeared to proceed normally, i.e., copious quantities of hydrogen bromide were evolved as the mixture was heated to 220°C. Treatment of the reaction mixture with water in the usual manner yielded a solid, most of which was virtually insoluble in ethanol. Extraction of this solid with ethanol in a Soxhlet apparatus for 26 h gave a residue which could not be recrystallized from the common organic solvents. The IR and mass spectra of the residue indicated that it consisted, at least in part, of the expected secondary phosphine oxide. The mass spectrum, however, exhibited a peak corresponding to a *tribromo* derivative of 5,10-dihydrophenophosphazine 10-oxide (**1**). It was then found that simply heating 4,4′-dibromodiphenylamine alone at 200°C for 24 h produced some tribromodiphenylamine (detected by mass spectrometry). No further investigation of the reaction between 4,4′-dibromodiphenylamine and phosphorus tribromide was undertaken.

Unlike the other diarylamines that we have studied, 2,2′,4,4′-tetrabromodiphenylamine does not appear to undergo any reaction whatever with phosphorus trichloride or tribromide. When this amine was heated with phosphorus tribromide at 205°C in the usual manner, little or no hydrogen bromide was evolved and only the unreacted amine was recovered after treatment of the mixture with water. An attempt was also made to convert the amine to the phosphoramidous dichloride[9] **3** by stirring a solution of the amine in benzene with phosphorus trichloride for 4 h at room temperature.



3

No precipitation of amine hydrochloride occurred, nor was there any other evidence of a reaction. Removal of the benzene and phosphorus trichloride by distillation led to an almost quantitative recovery of 2,2′,4,4′-tetrabromodiphenylamine. It is not clear whether steric or electronic effects (or a combination of both) are responsible for the failure of this amine to react with the phosphorus trihalides.

The interaction of *N*-phenyl-*o*-toluidine and phosphorus trichloride at 200°C gave a reaction mixture from which the expected secondary phosphine oxide and phosphinic acid were isolated in 14% and 31% yields, respectively. To our surprise, none of the corresponding spirophosphonium chloride was obtained. Our failure to isolate this substance cannot be explained simply by the presence of an ortho substituent in the diarylamine, since we had previously[1] obtained a 34% yield of a spirophosphonium chloride via the interaction of *N*-phenyl-1-naphthylamine and phosphorus trichloride. It should be pointed out that we do not yet understand the mechanism of the formation of the spirophosphonium salts from diarylamines and phosphorus trihalides, and it is possible that the yields of these salts depend on factors that we are not adequately controlling.

No dihydrophenophosphazine derivatives were obtained by the interaction of di-*o*-tolylamine and phosphorus trichloride at 200°C. In fact, most of the starting amine could be recovered by treatment of the reaction mixture with water. We were, however, able to synthesize di-*o*-tolylphosphoramidous dichloride, $(o\text{-}MeC_6H_4)_2NPCl_2$(4), by refluxing a benzene solution of di-*o*-tolylamine and phosphorus trichloride for 2 days. Thermal decomposition of the dichloride 4 at 200°C and subsequent treatment of the product with water gave mainly di-*o*-tolylamine together with a small amount of a solid that was oxidized to a phosphinic acid. This acid could not be obtained analytically pure, but its mass and pmr spectra indicated that it was 4,6-dimethyl-10-hydroxy-5,10-dihydrophenophosphazine 10-oxide. The results obtained with di-*o*-tolylamine strongly suggest that the presence of two ortho substituents greatly interferes with the formation of dihydrophenophosphazine derivatives by the interaction of diarylamines and phosphorus trichloride.

EXPERIMENTAL SECTION[10]

Preparation of Diarylamines. *N*-Phenyl-*o*-toluidine, di-*o*-tolylamine, and 4-chlorodiphenylamine were prepared via the Goldberg reaction as previously described.[11] 4-Chloro-4′-methyldiphenylamine was obtained in a similar manner by the interaction of 4′-chloroacetanilide and 4-bromotoluene and subsequent hydrolysis of the resulting amide with alcoholic KOH. The yield was 51%: mp 83.5–87°C (lit.[12] mp 85°C). 4,4′-Dichlorodiphenylamine[13] was prepared via the Chapman rearrangement. 4,4′-dibromodiphenylamine[14] was prepared by bromination of *N*,*N*-diphenylbenzamide and subsequent hydrolysis of the resulting *N*,*N*-bis-(4-bromophenyl)benzamide, and

2,2′,4,4′-tetrabromodiphenylamine[15] was prepared by the bromination of diphenylamine.

2,2′ - Dichloro - 10,10′(5H, 5′H) - spirobiphenophosphazinium chloride; 2 - chloro - 10 - hydroxy - 5,10 - dihydrophenophos - phazine 10 - oxide; and 2 - chloro - 5,10 - dihydrophenophos - phazine 10 - oxide. A mixture of 4-chlorodiphenylamine (30.5 g, 0.150 mol) and PCl_3(22 g, 0.16 mol) was stirred without heating for about 2 h, heated for about 21 h at 200–220°C until the evolution of HCl ceased, and then allowed to cool to room temperature. The brown solid thus obtained was powdered, stirred with about 0.5 L of H_2O, collected by filtration, and then refluxed for 17 h with a mixture of 100 ml of 15% aqueous NaOH and 200 mL of 95% EtOH. The resulting suspension was evaporated to dryness, and the yellow-orange residue was extracted with 250 mL of H_2O. Treatment of the insoluble material with aqueous HCl gave crude 2,2′-dichloro-10,10′ (5H, 5′H)- spirobiphenophosphazinium chloride, which was then recrystallized twice from 95% EtOH: yield 12.6 g (36%): mp > 400°C; UV(MeOH) λ (ε) 218 nm (58,500), 277 nm (20,100), 326 nm (21,900); the mass spectrum contained a peak at *m/e* 432 (55%), which corresponds to a dehydrohalogenated derivative of the spirophosphonium chloride. Anal. Calcd. for $C_{24}H_{16}Cl_3N_2P$: C, 61.37; H, 3.43; N, 5.96. Found: C, 61.24; H, 3.49; N, 5.95.

The alkaline mother liquor from the yellow-orange residue mentioned above was acidified to Congo Red to yield crude 2-chloro-10-hydroxy-5, 10-dihydrophenophosphazine 10-oxide, which was then recrystallized from 95% EtOH: yield 6.4 g (16%); dec 350°C; IR (Nujol) 3300 (O-H) and 1150 cm^{-1} (P=O); base peak in the mass spectrum was the molecular ion, *m/e* 265. Anal. Calcd for $C_{12}H_9ClNO_2P$: C, 54.26; H, 3.42. Found: C, 54.46; H, 3.33.

Attempts to isolate pure 2-chloro-5,10-dihydrophenophosphazine 10-oxide from the reaction mixture have been unsuccessful. In one experiment a small amount of the impure secondary phosphine oxide was obtained by the following procedure. The brown solid obtained by the interaction of 31.5 g of 4-chlorodiphenylamine and 23 g of PCl_3 was treated with H_2O and then dissolved in 400 mL of 95% EtOH. The resulting solution was allowed to evaporate slowly at room temperature, and the substances that crystallized were removed by filtration. The first two crops (totaling 2.0 g) exhibited no P-H absorption in the IR and were discarded. The next two crops (totaling 3.1 g) did exhibit P-H absorption and were purified by extraction with 95% EtOH in a soxhlet apparatus for about 16 h. The material remaining in the thimble proved to be the slightly impure secondary phosphine oxide: yield 1.3 g (3%); mp 370°C dec; IR (KBr) 2320 (P—H) and 1170 cm^{-1} (P=O); the molecular ion (*m/e* 249) was 27% of the base peak (*m/e* 232) of the mass spectrum. Anal. Calcd for $C_{12}H_9ClNOP$: C, 57.74; H, 3.63. Found: C, 58.67; H 3.26.

2 - Chloro - 8 - methyl - 5,10 - dihydrophenophosphazine 10 - oxide; 2,2′ - dichloro - 8,8′ - dimethyl - 10,10′(5H, 5′H) - spirobipheno - phosphazinium chloride; and 2 - chloro - 8 - methyl - 10 - hydroxy - 5,10 - dihydrophenophosphazine 10 - oxide. The reaction of 4-chloro-4′-methyldiphenylamine (42.6 g, 0.196 mol) with PCl_3 (28 g, 0.20 mol) and the treatment of the reaction mixture with H_2O were carried out by the procedure described above. The resulting solid was dissolved in 400 mL of 95% EtOH with the aid of a soxhlet extractor. Cooling this solution gave 0.834 g (1.6%) of crude 2-chloro-8-methyl-5,10-dihydrophenophosphazine 10-oxide. Recrystallization from glacial $MeCO_2H$ gave an analytically pure sample: mp > 400°C; IR(KBr) 2320 (P—H) and 1160 cm^{-1} (P=O); the molecular ion (*m/e* 263) was 97% of the base peak (*m/e* 262) of the mass spectrum. Anal. Calcd for $C_{13}H_{11}ClNOP$: C, 59.22; H, 4.21. Found: C, 58.79; H, 4.32.

The ethanolic mother liquor from the crude secondary phosphine oxide was mixed with 800 mL of 4N aqueous NaOH and refluxed overnight. After the EtOH was removed by distillation, the suspension was cooled and a bright orange solid was collected by filtration. Treatment of this solid with 6N HCl gave 23.5 g (48%) of crude 2,2′-dichloro-8,8′-dimethyl-10,10′ (5H, 5′H)-spirobiphenophosphazinium chloride. Recrystallization from DMF gave an analytically pure sample: mp > 400°C; the mass spectrum contained a peak at *m/e* 460 (78%), which corresponds to a dehydrohalogenated derivative of the spirophosphonium chloride. Anal. Calcd for $C_{26}H_{20}Cl_3N_2P$: C, 62.73; H, 4.05. Found: C, 63.03; H, 4.28.

The alkaline filtrate from the bright orange solid mentioned above was acidified to yield 15.9 g (29%) of crude 2-chloro-8-methyl - 10 - hydroxy - 5,10 - dihydrophenophosphazine 10 - oxide. Recrystallization from 95% EtOH gave an analytically pure sample: mp > 400°C; IR (KBr) 3310 (O—H) and a broad absorption at 1200–1100 cm^{-1} (P=O); the base peak in the mass spectrum was the molecular ion, *m/e* 279. Anal. Calcd for $C_{13}H_{11}ClNO_2P$: C, 55.83; H, 3.96. Found C, 55.70; H, 4.10.

2,8 - Dichloro - 5,10 - dihydrophenophosphazine 10 - oxide; 2,2′,8,8′ - tetrachloro - 10,10′(5H, 5′H) - spirobiphenophos - phazinium chloride; 2,8 - dichloro - 10 - hydroxy - 5,10 - dihydro - phenophosphazine 10 - oxide. The solid obtained by the reaction of 4,4′-dichlorodiphenylamine (20.2 g, 0.085 mol) with PCl_3 (16 g, 0.12 mol) and subsequent treatment of the reaction mixture with H_2O was dissolved in 300 mL of 95% EtOH. Cooling this solution yielded 3.32 g (14%) of crude 2,8-dichloro-5,10-dihydrophenophosphazine 10-oxide. Recrystallization from DMF gave an analytically pure sample: mp > 400°C; IR (KBr) 2320 (P—H) and 1160 cm^{-1} (P=O); the molecular ion, *m/e* 283, was the base peak of the mass spectrum. Anal. Calcd for $C_{12}H_8Cl_2NOP$: C, 50.74; H, 2.84. Found: C, 51.53; H, 3.08.

The ethanolic mother liquor from the crude secondary phosphine oxide was mixed with 300 mL of 4N aqueous NaOH and refluxed overnight. A yellow solid was obtained (after the EtOH was removed by distillation) and was converted by treatment with 6N HCl into 1.77 g (7.7%) of crude 2,2′,8,8′-tetrachloro - 10,10′(5H,5′H) - spirobiphenophosphazinium chloride. Recrystallization from DMSO gave an analytically pure sample: mp > 400°C; the mass spectrum contained a peak at *m/e* 500 (72%), which corresponds to a dehydrohalogenated derivative of the spirophosphonium chloride. Anal. Calcd for $C_{24}H_{14}Cl_5N_2P$: C, 53.52; H, 2.62. Found: C, 53.39; H, 2.67.

The alkaline filtrate from the yellow solid mentioned above was acidified to yield 3.27 g (13%) of crude 2,8-dichloro-10-hydroxy-5,10-dihydrophenophosphazine 10-oxide. Recrystallization from aqueous MeOH gave an analytically pure sample; mp > 400°C; IR(KBr) 3350 (O—H) and a broad absorption at 1200–1050 cm^{-1} (P=O); the base peak in the mass spectrum was the molecular ion, *m/e* 299. Anal. Calcd for $C_{12}H_8Cl_2NO_2P$: C, 48.03; H, 2.69. Found: C, 47.90; H, 2.45.

4 - Methyl - 5,10 - dihydrophenophosphazine 10 - oxide and 4 - methyl - 10 - hydroxy - 5,10 - dihydrophenophosphazine 10 - oxide. The reaction of *N*-phenyl-*o*-toluidine (27.5 g, 0.150 mol) and PCl_3 (21 g, 0.15 mol) was conducted by the same

procedure used in the preparations described above. When the resin reaction kettle[1] used was allowed to cool to room temperature, it was noted that the reaction mixture consisted of a small amount of dark brown solid in the bottom of the kettle and a large amount of a yellow solid that had sublimed to the top and sides. Treatment of the yellow solid with H_2O and subsequent recrystallization from 98% MeOH gave 4.7 g (14%) of pure, white 4-methyl-5,10-dihydrophenophosphazine 10-oxide: mp 240°C dec; IR (Nujol) 2330 (P—H) and 1165 cm^{-1} (P=O); the base peak in the mass spectrum was the molecular ion, *m/e* 229. Anal. Calcd for $C_{13}H_{12}NOP$: C, 68.12; H, 5.28. Found: C, 67.54; H, 5.18.

The dark brown solid from the bottom of the kettle was powdered, stirred with H_2O for several h, and then oxidized with ethanolic NaOH. The resulting mixture was clarified by filtration and then acidified. The solid thus obtained was recrystallized from MeOH to yield 6.9 g (19%) of pure 4-methyl-10-hydroxy - 5,10 - dihydrophenophosphazine 10 - oxide: mp 276–278°C dec; IR (KBr) 1180 cm^{-1} (P=O); the base peak in the mass spectrum was the molecular ion, *m/e* 245. Anal. Calcd for $C_{13}H_{12}NO_2P$: C, 63.67; H, 4.93. Found: C, 62.97; H, 4.82.

An additional 4.4 g (12%) of this phosphinic acid was isolated by oxidation of the solid obtained on evaporation of the methanolic mother liquors from the recrystallization of the secondary phosphine oxide.

Di - o - tolylphosphoramidous dichloride (4) and 4,6 - dimethyl - 10 - hydroxy - 5,10 - dihydrophenophosphazine 10 - oxide. A mixture of di-*o*-tolylamine (16.5 g, 0.084 mol) and PCl_3 (12.7 g, 0.092 mol) in 25 mL of dry benzene was refluxed for 2 days, and then the solvent and excess PCl_3 were stripped off with a rotary evaporator. The residual oil was purified by distillation (150–154°C, 0.15 mm) to give 16.0 g (64%) of di-*o*-tolylphosphoramidous dichloride (4): mp 80–83°C; mass spectrum, *m/e* (relative intensity) 301(2), 299(13.5), 297(M^+, 21), 226(19), 197(64), 196(80), 194(21), 182(32), 181(72), 180(100), 167(15), 78(15), 77(26), 65(46), 63(15), 51(21), 39(31). Treatment of a sample of 4 with H_2O gave a quantitative yield of di-*o*-tolyamine.

Di-*o*-tolylphosphoramidous dichloride (4) (14.5 g, 0.049 mol) was heated at 200°C for 15 h, and the resulting dark oil was allowed to cool to room temperature. The solid thus obtained was powdered and stirred first with H_2O and then with ethyl acetate. Di-*o*-tolylamine (7.0 g) was recovered from the latter solvent, and the material that was insoluble in ethyl acetate was refluxed overnight with a mixture of 95% EtOH and 15% aqueous NaOH. The resulting reaction mixture was then clarified by filtration and acidified to precipitate crude 4,6-dimethyl-10-hydroxy-5,10-dihydrophenophosphazine 10-oxide. Recrystallization from MeOH gave 0.7 g (6%) of the slightly impure phosphinic acid: mp 321–322°C dec; ^1H NMR (TFA-d_1) δ 2.0 (s, 6, CH_3) and 6.4–7.5 (m, 8, N—H, O—H, and aromatic H); the addition of D_2O exchanged two of the protons at δ 6.4–7.5; the base peak in the mass spectrum was the molecular ion, *m/e* 259. Anal. Calcd for $C_{14}H_{14}NO_2P$: C, 64.85; H, 5.44; N, 5.40. Found: C, 63.01; H, 5.38; N, 5.01.

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7. Only a fraction of the phosphine oxide actually formed was isolated as such. Most of it was converted (by oxidation with sodium hydroxide in aqueous ethanol) to the more easily isolated phosphinic acid; see also ref. 1.
8. Phosphorus tribromide rather than the trichloride was used in this reaction in order to avoid the possibility of replacement of the ring bromine atoms by chlorine. We first ascertained that the interaction of diphenylamine and phosphorus tribromide (followed by treatment of the reaction mixture with water) leads to the same products in about the same yields as when the trichloride is used.
9. The interaction of diphenylamine and phosphorus trichloride at room temperature yields diphenylphosphoramidous dichloride, Ph_2NPCl_2; cf. G. P. Sollott and W. R. Peterson, Jr., *J. Organomet. Chem.*, **19**, 143 (1969). We have previously noted[1] that this type of compound is probably an intermediate in the high temperature reaction between a diarylamine and phosphorus trichloride.
10. Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. IR spectra were obtained with either a Beckman IR 8 or Perkin–Elmer Model 521 spectrophotometer. Mass spectra were taken at 70 eV with a solid injection probe on an Associated Electrical Industries MS12, a Varian MAT, or a Varian MAT 731 mass spectrometer. Elemental analyses were performed by either Integral Microanalytical Laboratories, Raleigh, N. C. or Galbraith Laboratories, Inc., Knoxville, Tenn. The reactions between the diarylamines and phosphorus trihalides were carried out in "resin reaction kettles" as previously described.[1]
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