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Dihydrophenophosphazine Ring System[1]

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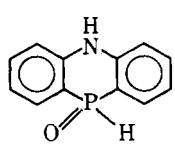
The reaction of diarylamines with phosphorus trichloride followed by treatment of the reaction mixtures with water has been employed to synthesize the secondary phosphine oxides **1**, **3**, **5**, and **7** and the spirophosphonium chlorides **2**, **4**, **6**, and **8**. A mechanism for the formation of the oxides has been proposed. Phosphinic acids have been prepared by oxidation of the oxides. The *N*-methyl derivative **12** has been obtained by a variant of the Friedel-Crafts reaction in which *N*-methyl-di-*p*-tolylamine and phosphorus trichloride were heated together in the presence of aluminum chloride and the reaction mixture was then hydrolyzed and oxidized.

It has long been known that the reaction of diphenylamine with phosphorus trichloride followed by treatment of the reaction mixture with water yields a heterocyclic phosphorus compound with the empirical formula $C_{12}H_{10}NOP$.[2] In 1960 Häring[3] published detailed directions for this reaction and showed that the heterocyclic compound is a secondary phosphine oxide, viz. 5,10-dihydrophenophosphazine 10-oxide (**1**). On attempting to repeat Häring's method of preparation, we found[4] that the phosphine oxide **1** was invariably admixed with a chlorine-containing compound $C_{24}H_{18}ClN_2P$. The chemical and spectral properties of the latter substance showed that it did not contain a P–H bond and that it was not a derivative of trivalent phosphorus. The structure of the unknown substance was unambiguously shown by an X-ray study[4,5] to be 10,10′(5*H*,5′*H*)-spirobiphenophosphazinium chloride (**2**). This was the first spirophosphonium compound re-



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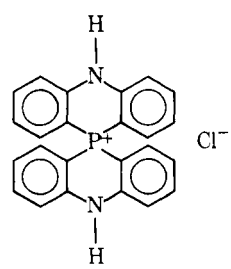

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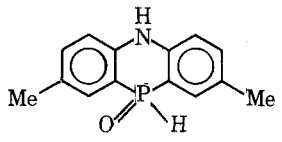
ported in which the phosphorus atom was a member of a ring that also contained nitrogen; it was, in fact, one of the relatively few spirophosphonium compounds known. The X-ray data showed that the C–N and C–P bond distances in this compound were unusually short and suggested that the central rings had aromatic character. A ^{31}P nmr study[5] also indicated that there was extensive electron delocalization in these rings. The ease of formation of the phosphine oxide **1** and the spirophosphonium compound **2**, in addition to the inherent interest in such substances, has prompted us to investigate the reaction of phosphorus trichloride with diarylamines other than diphenylamine and to inquire into the mechanism of formation of the dihydrophenophosphazine ring system.

No special difficulties were encountered in preparing ring-substituted derivatives of **1** and **2**. Thus, di-*p*-tolylamine yielded the phosphine oxide **3** and the spirophosphonium chloride **4**; 4-methyldiphenylamine gave **5** and **6**; and *N*-phenyl-1-naphthylamine gave **7** and **8**. The phosphine



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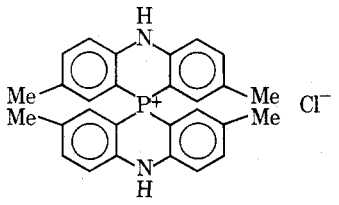

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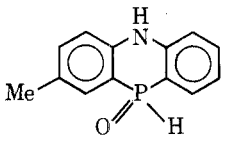

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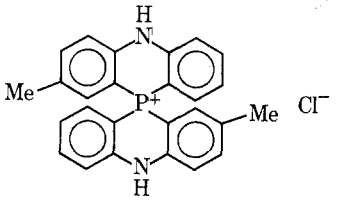

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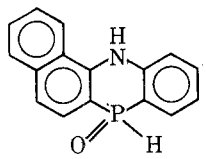

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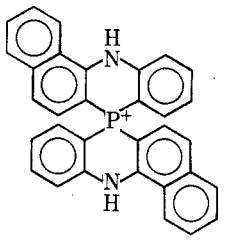

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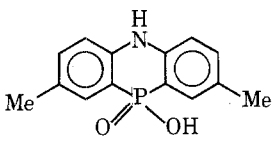
oxides **3**, **5**, and **7** were readily oxidized to the corresponding phosphinic acids **9**, **10**, and **11**. It seems clear, therefore,



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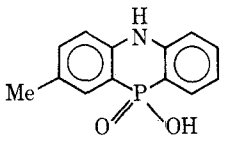

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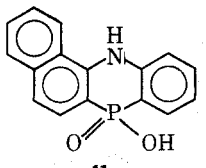
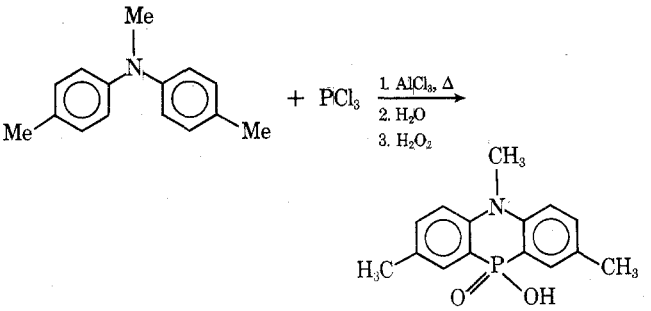


11

that a variety of dihydrophenophosphazine derivatives can be obtained *via* the interaction of diarylamines and phosphorus trichloride.

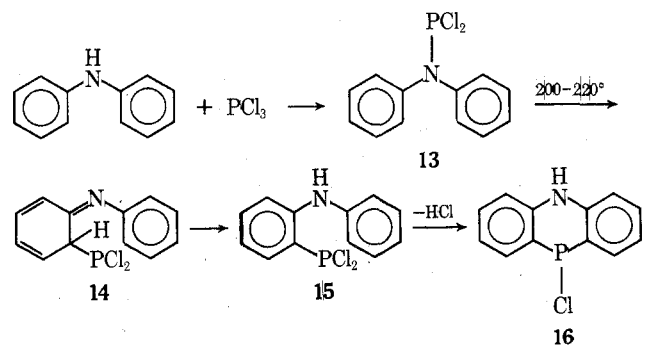
In contrast to the results discussed above, the reaction of *N*-methyldiphenylamine and phosphorus trichloride does not lead to the formation of heterocyclic derivatives of phosphorus. Thus, Michaelis and Schenk[2b] in 1890 reported that the aluminum chloride catalyzed condensation of *N*-methyldiphenylamine and phosphorus trichloride gives the phosphonous dichloride $PhN(Me)C_6H_4PCl_2$. Although the orientation of the dichlorophosphino group has apparently not been established, it has been generally assumed that the group enters para to the nitrogen.[6a] We have found that no reaction whatever occurred when a mixture of *N*-methyldi-*p*-tolylamine and phosphorus trichloride was refluxed for 12 hr.[7] In the presence of aluminum chloride, however, the ortho positions were attacked, and the *N*-methyl derivative **12** was obtained. This reaction



12

represents the first synthesis of an *N*-methylphenophosphazine derivative by the condensation of phosphorus trichloride and an aromatic amine.[8]

In the first edition of his monograph, Kosolapoff[9] suggested that the primary product of the interaction of diphenylamine and phosphorus trichloride is diphenylphosphoramidous dichloride, Ph_2NPCl_2 (**13**), which subsequently undergoes rearrangement and further condensation to yield a heterocyclic substance. We have prepared the dichloride **13** by the method of Sollott and Peterson[10] and have found that this compound at 200–220° does indeed rearrange and lose hydrogen chloride to give, after treatment with water, the same mixture of **1** and **2** obtained *via* the interaction of diphenylamine and phosphorus trichloride. The failure of the *N*-methyldiarylamines to react with phosphorus trichloride (except in the presence of aluminum chloride) would seem to be a consequence of the inability of these amines to form phosphoramidous dichlorides. The formation of the dihydrophenophosphazine ring by the interaction of diphenylamine and phosphorus trichloride appears to be consistent with the following sequence of reactions.



13

14

15

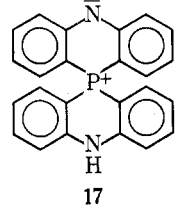
16

In the above mechanism, the rearrangement of **13** to **14** involves the transfer of the PCl_2 group to an ortho position and the formation of the type of intermediate usually postulated in electrophilic aromatic substitution. (Pearson and Buehler[11] have discussed other examples of enhanced ortho substitution in which the attacking reagent first forms a bond with the side chain and is then transferred to the aromatic ring.) Rearomatization of **14** accompanied by trans-

fer of aoton from carbon to nitrogen yields the phosphonous dichloride **15**, which would be expected[12] to readily undergo cyclodehydrohalogenation to give the phosphinous chloride **16**. And, finally, hydrolysis of **16** would certainly yield the phosphine oxide **1**.[13]

The aluminum chloride catalyzed interaction of the *N*-methyldiarylamines and phosphorus trichloride requires little comment, since the reaction of aromatic compounds with phosphorus trihalides under Friedel–Crafts conditions is well known.[6b] When the aromatic compound contains an alkyl, alkoxy, phenoxy, or halo substituent, the entering dihalophosphino group goes mainly para to the substituent already present. In the case of *p*-tolyl ether and *p*-tolyl sulfide (which, of course, have no available para positions), the phosphorus attacks positions ortho to the oxygen or sulfur and heterocyclic compounds are formed.[14] Thus, the reactions of the *N*-methyldiarylamines with phosphorus trichloride appear to be normal Friedel–Crafts reactions.

The most interesting and surprising finding noted in this investigation is the formation (albeit in low yields) of the spirophosphonium chlorides **2, 4, 6,** and **8**. Treatment of alcoholic solutions of these chlorides with aqueous sodium hydroxide yields fine yellow precipitates, which have not been purified since they are insoluble in water and the common organic solvents (except for glacial acetic acid, which apparently converts them to acetates). These yellow substances contain no chlorine, but their ir and mass spectra are virtually identical with the spectra of the corresponding chlorides, and they can be reconverted to the chlorides by treatment with hydrochloric acid. It seems likely that the yellow substances have zwitterionic structures like **17** and are resonance stabilized through canonical forms of type **18**.



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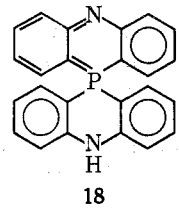

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Although the insolubility of the yellow substances discussed above has thus far prevented us from ascertaining their structures, we have made use of their properties in the isolation of both the phosphine oxides and the phosphonium chlorides from the mixtures obtained by the interaction of diarylamines and phosphorus trichloride. For example, when diphenylamine and phosphorus trichloride are allowed to a react by Häring's procedure[3] and the reaction mixture is treated with water, a solid is obtained which is soluble for the most part in cold 95% ethanol. Addition of aqueous sodium hydroxide to the ethanolic solution precipitated the yellow substance that could be converted to the phosphonium chloride **2**; the phosphine oxide **1** could then be isolated by evaporation of the filtrate from the yellow precipitate to a small volume. Adaptations of this technique were used in separating **3** from **4** and **5** from **6**. The separation of the naphthalene derivatives **7** and **8**, however, was more conveniently accomplished by column chromatography.

Molecular models[15] of the spirophosphonium chlorides **6** and **8** show that these molecules do not possess a plane of symmetry and are indeed chiral. Attempts to resolve these racemic mixtures are now in progress.

Experimental Section

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Ir spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer. Mass spectra were taken at 70 eV with an Associated Electrical Industries MS 12 recording mass spectrometer using a solid injection probe. Detailed fragmentation patterns deduced from metastable studies and accurate mass measurements will be published elsewhere. Elemental analyses on samples dried in vacuo at 140° were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The reactions between phosphorus trichloride and the aromatic amines can be carried out in conventional round-bottom flasks equipped with a thermometer, magnetic stirrer, and reflux condenser protected with a drying tube. The reaction mixtures were, however, much more easily removed from similarly equipped "resin reaction kettles" (Fisher Scientific Co., Cat. No. 11-847). Performing the reactions in a atmosphere of dry nitrogen appeared to have no effect on the yields of the organophosphorus compounds.

5,10-Dihydrophenophosphazine 10-Oxide (1), 10,10′-(5*H*,5′*H*)-Spirobiphenophosphazinium Chloride (2), and 5,10-Dihydro-10-hydroxyphenophosphazine 10-Oxide. A mixture of diphenylamine (20 g, 0.12 mol) and PCl_3 (18 g, 0.13 mol) was stirred without heating for 2 hr, heated at 200–220° for at least 9 hr, and then treated cautiously with water as previously described.[3,5] The solid thus obtained was powdered and extracted with 300 ml of 95% ethanol. The resulting solution was filtered to remove about 1 g of an unidentified solid and then treated with 10% aqueous NaOH to precipitate a yellow substance believed to be 10,10′(5*H*)-spirobiphenophosphazine (**17** ↔ **18**). Treatment of this material with dilute hydrochloric acid yielded a slightly off-white solid, which on recrystallizaton from glacial acetic acid gave 8.2 g (8.3%) of analytically pure chloride **2**. Ir spectrum in Nujol exhibited N–H absorption at 3215 and 3125 cm^{-1} but no absorption near 2300 cm^{-1} characteristic of P–H stretching. The base peak of the mass spectrum was at *m/e* 364, which corresponds to a dehydrohalogenated derivative of **2**.

The basic ethanolic filtrate from the yellow substance **17** ↔ **18** was evaporated to about 75 ml and cooled, whereupon crude phosphine oxide **1** crystallized from solution. After recrystallization from glacial acetic acid, the yield of **1** was 6.2 g (24%): mp 214–216° (lit.[3] mp 214–216°); ir spectrum (Nujol) agreed well with that reported by Häring;[3] mass spectrum exhibited the molecular ion, *m/e* 215 (92%).

The original mother liquor from the crude **1** was evaporated to dryness, and the residue was oxidized by refluxing for 24 hr in a mixture of 40 ml of 95% ethanol and 60 ml of 4 *N* aqueous NaOH.[16] The crude phosphinic acid obtained by acidification of the resulting solution to Congo Red was recrystallized from 95% ethanol to yield 3.4 g (12%) of 5,10-dihydro-10-hydroxyphenophosphazine 10-oxide: mp 270–274° dec (lit.[3] mp 274–275°); ir spectrum (Nujol) in good agreement with Häring;[3] molecular ion, *m/e* 231, was the base peak of the mass spectrum.

2,2′,8,8′-Tetramethyl-10,10′(5*H*,5′*H*)-spirobiphenophosphazinium Chloride (4), 2,8-Dimethyl-5,10-dihydrophenophosphazine 10-Oxide (3), and 2,8-Dimethyl-10-hydroxy-5,10-dihydrophenophosphazine 10-Oxide (9). The reaction of di-*p*-tolylamine[17] (39.4 g, 0.21 mol) with PCl_3 (30.2 g, 0.22 mol) and the hydrolysis of the reaction mixture were carried out by the procedure described above. Extraction of the resulting solid with 400 ml of 95% ethanol at room temperature yielded a residue of 22.2 g, which was shown by its ir spectrum to consist mainly of the phosphine oxide **3**. This material could be purified or oxidized to the phosphinic acid **9**; the procedures used are described in the paragraphs below. Treatment of the ethanolic extract with 4 *N* aqueous NaOH gave a yellow precipitate, which was converted to a whitish solid by the addition of concentrated hydrochloric acid. Recrystallization from 95% ethanol gave 1.5 g (3%) of the phosphonium chloride **4**: mp >400°; base peak of the mass spectrum was *m/e* 420, corresponding to the loss of HCl.

Anal. Calcd for $C_{28}H_{26}ClN_2P$: C, 73.60; H, 5.74; Cl, 7.76; N, 6.13; P, 6.78. Found: C, 71.50; H, 6.07; Cl, 7.55; N, 6.10; P, 6.70.

Although the crude phosphine oxide mentioned above was only slightly soluble in 95% ethanol, it could be recrystallized from this solvent with the aid of a Soxhlet extraction apparatus. The yield of pure **3** was 30% (based on di-*p*-tolylamine), mp >400°, but sample turned yellow at about 245°: ir (KBr) 3260 and 3150 (NH), 2320 (PH), and 1150 cm^{-1} (P=O); mass spectrum exhibited the molecular ion, *m/e* 243 (90%).

Anal. Calcd for $C_{14}H_{14}NOP$: C, 69.13; H, 5.80; P, 12.73. Found: C, 69.33; H, 5.94; P, 12.74.

A 2.0-g sample of the crude phosphine oxide was oxidized by refluxing for 4 hr in a mixture of 30% H_2O_2 (20 ml), 4 *N* aqueous

NaOH (25 ml), 95% ethanol (15 ml), and water (100 ml). After the reaction mixture was cooled, a yellow precipitate was removed by filtration, treated with concentrated hydrochloric acid, and then recrystallized from 95% ethanol to yield 0.30 g (8%) of the phosphonium chloride **4**; thus, the total yield of **4** was 11%. Acidification of the filtrate from the yellow precipitate gave the crude phosphinic acid **9**, which was recrystallized from 95% ethanol: yield 1.5 g (33%); mp 289° dec; ir (KBr) 3180 (NH) and 1120 cm^{-1} (P=O); base peak of the mass spectrum was the molecular ion, *m/e* 259.

Anal. Calcd for $C_{14}H_{14}NO_2P$: C, 64.86; H, 5.44. Found: C, 64.85; H, 5.53.

2-Methyl-5,10-dihydrophenophosphazine 10-Oxide (5), 2,2'-Dimethyl-10,10'(5*H*,5'*H*)-spirobiphenophosphazinium Chloride (6), and 2-Methyl-10-hydroxy-5,10-dihydrophenophosphazine 10-Oxide (10). The reaction of 4-methyldiphenylamine[18] (8.2 g, 0.045 mol) with PCl_3 (6.2 g, 0.045 mol) and the subsequent hydrolysis were conducted by the same procedure used in the preparations above. Extraction of the resulting solid with 150 ml of 95% ethanol at room temperature yielded a residue, which was recrystallized from 95% ethanol to give 0.30 g (2%) of the oxide **5**: mp 205–206°; ir (KBr) 3250 and 3160 (NH), 2320 (PH), and 1155 cm^{-1} (P=O); the molecular ion, *m/e* 229 (95%), was prominent in the mass spectrum.

Anal. Calcd for $C_{13}H_{12}NOP$: C, 68.12; H, 5.28. Found: C, 68.38; H, 5.31.

The ethanolic extract mentioned above was treated with 4 *N* aqueous NaOH to yield a yellow precipitate, which was converted to the phosphonium chloride **6** by treatment with concentrated hydrochloric acid. After two recrystallizations from aqueous ethanol, the yield of pure **6** was 1.0 g (10%): decomposed at 270–280° with the evolution of a gas and finally melted with darkening at 375–385°; ir (Nujol) 3220 and 3130 cm^{-1} (NH); base peak of the mass spectrum was at *m/e* 392, corresponding to the loss of hydrogen chloride.

Anal. Calcd for $C_{26}H_{22}ClN_2P$: N, 6.53; P, 7.22. Found: N, 6.45; P, 7.19.

The filtrate from the yellow precipitate was evaporated to dryness, and the residue was oxidized by refluxing for 6 hr in a mixture of 30% H_2O_2 (25 ml), 4 *N* aqueous NaOH (30 ml), 95% ethanol (2 ml), and water (50 ml). The reaction mixture was filtered, the filtrate was acidified, and the precipitated phosphinic acid **10** recrystallized twice from MeOH. The yield was 2.7 g (25%): mp 270–272°; ir (Nujol) 3320 (OH), 3260 and 3170 (NH), and 1100 cm^{-1} (P=O); base peak of the mass spectrum was the molecular ion, *m/e* 245.

Anal. Calcd for $C_{13}H_{12}NO_2P$: C, 63.68; H, 4.93. Found: C, 63.90; H, 4.88.

7,12-Dihydrobenzo[*c*]phenophosphazine 7-Oxide (7), 7,7'(12*H*,12'*H*)-Spirobi[benzo[*c*]phenophosphazinium] Chloride (8), and 7-Hydroxy-7,12-dihydrobenzo[*c*]phenophosphazine 7-Oxide (11). The reaction of *N*-phenyl-1-naphthylamine[19] (43.8 g, 0.20 mol) with PCl_3 (27.5 g, 0.21 mol) was carried out and the reaction mixture was hydrolyzed as in the procedures above. The solid thus obtained weighed 50.0 g after being dried in vacuo. A 1.0-g sample of this material was dissolved in 30 ml of $CHCl_3$ and added to a column packed with 50 g of silicic acid (Bio-Sil A, 100–200 mesh) suspended in $CHCl_3$. The column was washed with 1 l. of $CHCl_3$, and 1 l. of 5% MeOH in $CHCl_3$ was then used as the eluent. The first band to separate was collected and proved to be the phosphine oxide **7**: yield, 0.40 g (36%); mp, after recrystallization from 95% ethanol, 238–240°; ir (KBr) 3280 and 3180 (NH), 2300 (PH), and 1160 cm^{-1} (P=O); base peak of the mass spectrum was the molecular ion, *m/e* 265.

Anal. Calcd for $C_{16}H_{12}NOP$: C, 72.45; H, 4.56; N, 5.28; P, 11.68. Found: C, 72.17; H, 4.57; N, 5.30; P, 11.36.

The second band that separated on the column yielded an oily material, which was not identified. Complete removal of the third band (which contained the phosphonium chloride **8**) from the column required 1 l. of 10% MeOH in $CHCl_3$: yield, 0.30 g (34%); mp, after recrystallization from 95% ethanol, >400°; ir (KBr) 3250 and 3160 cm^{-1} (NH); base peak of the mass spectrum was at *m/e* 464, corresponding to the loss of HCl.

Anal. Calcd for $C_{32}H_{22}ClN_2P$: C, 76.72; H, 4.43; N, 5.59; P, 6.18. Found: C, 76.43; H, 4.54; N, 5.82; P, 5.96.

A 5.0-g sample of the 50.0-g crude reaction product was oxidized by refluxing for 6 hr in a mixture of 30% H_2O_2 (30 ml), 4 *N* aqueous NaOH (20 ml), and water (100 ml). The reaction mixture was filtered, and the filtrate was acidified to precipitate the phosphinic acid **11**: yield 1.0 g (18%); mp, after recrystallization from glacial acetic acid, 290–295°; ir (KBr) 3220 and 3180 cm^{-1} (NH); base peak of the mass spectrum was the molecular ion, *m/e* 281.

Anal. Calcd for $C_{16}H_{12}NO_2P$: C, 68.33; H, 4.30. Found: C, 68.17; H, 4.32.

2,5,8-Trimethyl-10-hydroxy-5,10-dihydrophenophosphazine 10-Oxide (12). A mixture of *N*-methyl-di-*p*-tolylamine[20] (5.0 g, 0.024 mol), PCl_3 (6.5 g, 0.047 mol), and anhydrous $AlCl_3$ (1.3 g, 0.0098 mol) was stirred and refluxed for 24 hr. On pouring the reaction mixture over 200 g of cracked ice, a heavy oil was obtained, which solidified on standing. The solid was washed thoroughly with water, added to a mixture of 20% aqueous NaOH (50 ml) and 30% H_2O_2 (20 ml), and then heated at 100° for 1 hr. On cooling the resultant mixture, 2.2 g of a solid was obtained, which was removed by filtration and identified as unreacted *N*-methyldi-*p*-tolylamine. Acidification of the filtrate precipitated the phosphinic acid **12**, which was recrystallized from 95% ethanol: yield, 0.70 g (12%); mp 276–277°; pmr (CF_3CO_2H) τ 8.07 (s, 6, $ArCH_3$), 6.87 (s, 3, NCH_3), 3.04 (m, 6, aromatic H); ir (KBr) 1200–1150 cm^{-1} (P=O); base peak of the mass spectrum was the molecular ion, *m/e* 273.

Anal. Calcd for $C_{15}H_{16}NO_2P$: C, 65.93; H, 5.90. Found: C, 65.89; H, 5.96.

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Registry No.—**1**, 53778-28-2; **2**, 34283-79-9; **3**, 53778-29-3; **4**, 53778-30-6; **5**, 53778-31-7; **6**, 53778-32-8; **7**, 53798-59-6; **8**, 53778-33-9; **9**, 53798-60-0; **10**, 53798-61-1; **11**, 53798-62-2; **12**, 53798-63-3; 5,10-dihydro-10-hydroxyphenophosphazine 10-oxide, 53778-28-2; diphenylamine, 122-39-4; PCl_3, 7719-12-2; di-*p*-tolylamine, 620-93-9; 4-methyldiphenylamine, 620-84-8; *N*-phenyl-1-naphthylamine, 90-30-2; *N*-methyl-di-*p*-tolylamine, 3480-97-5.

References and Notes

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