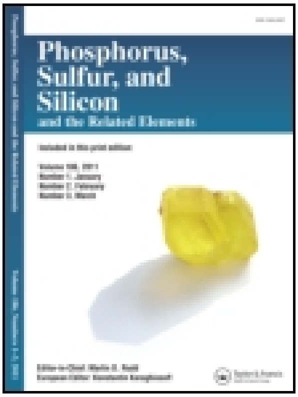

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THE SYNTHESIS AND REACTION OF HETEROCYCLIC THIOPHOSPHORYL CHLORIDES WITH ALCL$_3$ OR CF$_3$SO$_3$Ag. AN ATTEMPT TO OBTAIN $\delta^5\delta^3$-THIOPHOSPHORYL CATIONS

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THE SYNTHESIS AND REACTION OF HETEROCYCLIC THIOPHOSPHORYL CHLORIDES WITH ALCL$_3$ OR CF$_3$SO$_3$Ag. AN ATTEMPT TO OBTAIN $\lambda^5\sigma^3$-THIOPHOSPHORYL CATIONS

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Two new heterocyclic thiophosphoryl chlorides (**2**), derivatives of 1,3,2-benzodiazaphosphole, are synthesized. The reaction of respective thiophosphoryl chlorides (**1**) and (**2**) with $AlCl_3$ affords dimeric heterocyclic diphosphonium dications **3**and **4**. The reaction of **2a** with CF_3SO_3Ag gives rise to dimeric anhydride **5** instead of the expected $\lambda^5\sigma^3$-thiophosphoryl cations. The results show that $\lambda^5\sigma^3$-thiophosphonium cations incorporated into a thiadiazaphospholic system (**1**) or benzodiazaphospholic system (**2**) are not stable, and undergo a structural rearrangement to give a $\lambda^4\sigma^4$-phosphorus-centre products.

Keywords: $\lambda^5\sigma^3$-Phosphonium cation; phosphoryl cation; 1; 3; 4; 2-thiadiazaphoaphole; 1; 3; 2-benzodiazaphosphole

INTRODUCTION

$\lambda^5\sigma^3$-Phosphonium cations include oxo-, thio- or seleno-phosphoryl cation, imino-phosphonium cations and methylene-phosphonium cations. Phosphoryl cations have been invoked as reactive intermediates for thirty years,[1] but only one selenophosphoryl cation has been fully characterized.[2] The formation of iminophosphonium cation was still in debate.[3,4] The first identification of alkenic $\lambda^5\sigma^3$-methylenephosphonium salts were reported by

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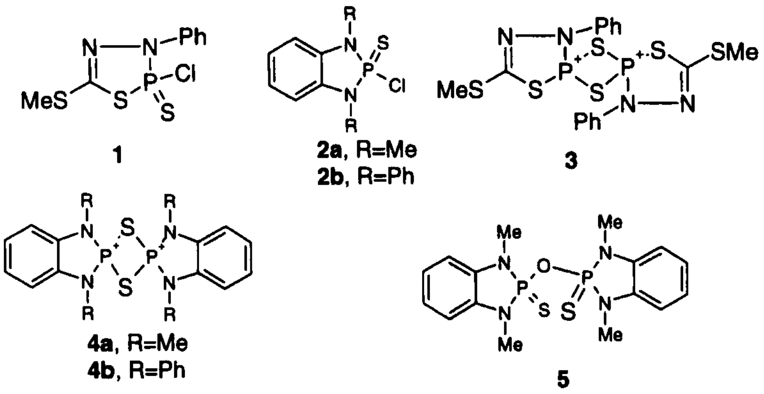
Grutzmacher[5a] in 1989, and near a dozen of them were known.[5] These $\lambda^5\sigma^3$-Phosphonium cations are thought to be stabilized by the steric shielding from the very much sterically hindered substitutes, such as $(Ph_3P{=})(Ph{-})C$[2], *i*-Pr_2N[5] *t*-Bu,[4,5]and Me_3Si,[4,5] etc. group. In principle, Huckel (6π- and 10π) delocalization should also afford a stabilization to allow $\lambda^3\sigma^5$-phosphonium cation to be persistent in solution. The principal objective of our work was to explore the possibility of the stabilization of $\lambda^5\sigma^3$-phosphonium cations when phosphonium unit is incorporated into a heterobenzenic system (**1**) or heteronaphthalenic system (**2**). We have shown that 2,3-dihrdro-1,3,4,2-thiadiazaphosphole ring as well as N-phenyl group can afford a sufficient stabilization for an $\lambda^3\sigma^2$-phosphenium ($N{-}P^+{-}S$) cation.[6] Furthermore, in the view of the structure, 2,3-dihrdro-benzodiazaphosphole-2-thion skeleton, whose di-, tri, quadra- and penta- coordinated derivatives were known,[7] should be suited for a $\lambda^5\sigma^3$-Phosphonium cation. Therefore we synthesized the known 2-chloro-2-thiono-3-N-phenyl-5-methylthio-2,3-dihydro-1,3,4,2-thiadiazaphosphole (**1**)[8] and two new compounds, 2-chloro-2-thiono-2,3-dihydro-1,3,2-benzodiazaphosphole-1,3- bismethyl (**2a**) and –1,3-bisphenyl (**2b**), and performed the reaction of these thiophosphoryl chlorides (**1** and **2**) with $AlCl_3$, and the reaction of **2a** with CF_3SO_3Ag. Unexpectedly, none of them afforded an $\lambda^5\sigma^3$-thiophosphoryl cationic product, the former resulted in dimeric heterocyclic diphosphonium dicationic **3** and **4**, the latter gave rise to dimeric anhydride **5**. These demonstrated that the heterobenzenic and heteronaphthalenic $\lambda^5\sigma^3$-phosphoryl cations are not persistent at room temperature.



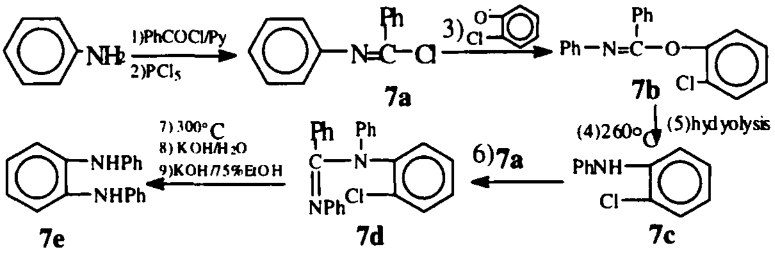
SCHEME 1

RESULTS AND DISSCUSION

Preparation of Precursor Heterocyclic Thiophosphoryl Chloride 1 and 2

2-chloro-2-thiono-3-N-phenyl-5-methylthio-2,3–2(H)-1,3,4,2-thiadiaza-phosphole (**1**)[8] was synthesized according to a procedures by Huang *et al.*, Jennings[7a] and Gloede[7c] found that 2-chloro-2,3-dihydro-1,3,2-benzodiazaphosphole-1,3-dimethyl and –1,3-diethyl could be prepared by refluxing the mixture of *o*-phenylenediamine-N,N'-dimethyl or -N,N'-diethyl with PCl_3. We treated the respective *o*-phenylenediamine-N,N'-dimethyl (**6**) and -N,N'-diphenyl (**7e**) with $PSCl_3$ in toluene at 110 °C to give 84% yield of 2-chloro-2-thiono-1,3-bismethyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (**2a**) and 45.8% yield of 2-chloro-2-thiono-1,3-bisphenyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (**2b**). The structures of **1** and **2** were confirmed by MS, IR, ^{1}H, ^{13}C, ^{31}P NMR and microanalyses. The data is listed in the experimental part.

o-Phenylenediamine-N,N'-dimethyl (**6**) was prepared according to reported method.[9] We failed to obtain N,N'-diphenyl-*o*-phenylenediamine (**7e**) from *o*-phenylenediamine and *o*-chlorobenzoic acid according to procedure by Clemo.[10a] We synthesized **7e** by 9 steps (SCHEME II) from aniline and *o*-chlorophenol on basis of the modifying Chapman's method.[10b–c] The data were described in details in the experimental part.



SCHEME 2

Reaction of 1 with $AlCl_3$

Chloride abstraction from a phosphoryl chloride system has been proved to be a useful approach toward tricoordinate phosphonium cations.

Burford[4a] showed that the reactions of diaminothiophosphinic chlorides and $AlCl_3$ have at least two modes of reactivity, either to form Lewis acid-base complexes or to produce dimeric $\lambda^4\sigma^4$-diphosphonium compounds. Here, the reaction of 2-chloro-2-thiono-3-N-phenyl-5-methylthio-2,3-dihydro-1,3,4,2-thiadiazaphosphole (**1**)[7] with $AlCl_3$ at −20 °C for 1–2 hr produce exclusively dimeric cation **3** (SCHEME III) in solution and in solid state, as indicated by IR, ^1H, ^{27}Al, ^{31}P NMR, the equivalent conductivity, ESCA and FAB-MS data, which were listed in experimental part and Table I.

$$\mathbf{1} + AlCl_3 \longrightarrow \mathbf{3}\bullet\ [AlCl_4^-]_2$$

SCHEME 3

The IR ($487cm^{-1}$) and ^{27}Al NMR (102.4 ppm) confirmed the formation of anion $AlCl_4^-$. The phosphorus nucleus of **3** give rise to a signal at 60.4 ppm, slightly shielded from that in **1** (δp=82.0 ppm), indicative of absence of low coordinate phosphorus species. The ^1H NMR exhibits peaks at 2.98 ppm (s, 3H, MeS) and 7.65 to 7.85 ppm (m, 5H, Ph) which are downfield from those of **1** (2.60 ppm, MeS; 7.01–7.60 ppm, Ph). The equivalent conductivity for **1**, **3** $\bullet[AlCl_4^-]_2$ and $Ph_3P^+CH_2Ph\bullet Br^-$ are 46.7, 6177.6 and 1270 $uScm^2M^{-1}$, respectively. These data disclose the ionic character of **3**.

Since ESCA is capable of telling charged compounds from neutral, we performed ESCA spectra of **1** and **3**, the Cl (2p) binding energy in **3** are 199.30 and 199.21ev, P (2p) binding energy are 133.78 and 134.1 ev, respectively, these imply that phosphorus in **3** has partial positive charge. FAB-MS spectrum of **3** give M^+ peak at 518 (16%) confirming of dimeric diphosphonium dicationic structure.

The expected thiophosphoryl cation is observed as dicationic phosphetane dimer **3**. While it is tempting to assign a monomeric cation as an intermediate in the reaction, there is no evidence for such a species.

The reaction of 2 with $AlCl_3$

The reactions of 2 with $AlCl_3$ afforded 4 $\bullet[AlCl_4^-]_2$, shown in the SCHEME IV. The mode of the reaction was similar to those of **1**. No signal for $\lambda^5\sigma^3$-phosphoryl cation could be found in ^{31}P NMR spectroscopy of the solution of the reaction of respective 2-chloro-2-thiono-1, 3-bismethyl-2, 3-dihrdro-1,3,2-benzodiazaphosphole (**2a**) and 2-chloro-2-thiono-1,3-bisphenyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (**2b**) with $AlCl_3$. The structures of **4** were supported by IR, ^{27}Al and ^{31}P NMR, the equivalent conductivity and FAB-MS, which were listed in experimental part and Table I.

$$\mathbf{2} + AlCl_3 \longrightarrow \mathbf{4}\bullet\ [AlCl_4^-]_2$$

SCHEME 4

The reaction of 2a with Silver Trifluoromethanesulfonate (CF_3SO_3Ag)

The dimeric anhydride 5, not a monomeric cation, was observed in the reaction of **2a** with CF_3SO_3Ag. The CF_3SO_3Ag was selected as the chloride scavenger because of the low nucleophilicity of its anion. We allow a mixture of **5** and a stoichiometric quantity of dry CF_3SO_3Ag in CH_2Cl_2 to stir in a dry evacuated dual compartment vessel shielded from light at 0°C. A white precipitate, found to be AgCl, was isolated in nearly quantitative yield. The ^{31}P NMR spectrum of the reaction mixture showed after 24 hours two signals at 69.0 ppm (**2a**) and 58.7 ppm, after 48 hours a sole peak at 59.1 ppm. Product **5** was isolated in yield of 87.3% by chromatography on silica gel with centrifugal TLC using petroleum ether/ether (8:1) as the eluent. The MS show M^+ peak at 418 (30.2%). The ^{31}P NMR give a single signal at 59.2 ppm, the absence of $^2J_{P\text{-}X\text{-}P}$ implies that **5** has a symmetric structure.

$$\mathbf{2a} + CF_3SO_3Ag \longrightarrow \mathbf{5} + AgCl + CF_3SO_2Cl\uparrow$$

SCHEME 5

From above discussion it is concluded that $\lambda^5\sigma^3$-thiophosphonium cations corporated into a Huckel thiadiazaphospholic system (**1**) or benzodiazaphospholic system (**2**) are not stable, and undergo a structural rearrangement to give a $\lambda^4\sigma^4$-phosphorus-centre products.

TABLE I Data of ^{31}P NMR, the equivalent conductivity and ESCA

Compound		$\delta\ ^{31}P$ *(ppm)*	Λ_m *(uS•cm^2•M^{-1})*	*ESCA (ev)*	
No	*R*			*Cl (2p)*	*P (2p)*
1		82.0	46.7	199.30	133.78
2a	Me	68.8	131.1	199.31	133.74
2b	Ph	59.0	286.3	199.31	133.73
3		60.4	7177.6	199.21	134.10
4a	Me	59.3	7954.4	199.27	134.07
4b	Ph	54.5	6821.3	199.25	134.00
5		58.7	547.5		
$Ph_3P^+CH_2Ph•Br^-$			1270.0		

Considering that thiazaphosphenium[6,11] and diazaphosphenium[12] cations are stable for hours and even are somewhat aromatic, it is tempting to conclude that the $\lambda^5\sigma^3$-thiophosphonium cation is more active than the corresponding $\lambda^3\sigma^2$-phosphenium cation.

EXPERIMENTAL

Elemental analyses were obtained with a Carlo Erba 1106 elementary analyzer for C, H and N or with the chemical method for P and Cl. Mass spectra were recorded with a HP 5988A spectrometer at 20 ev ionization energy and with VG-7070-HF spectrometer in *glycerol medium*. The ^1H, ^{27}Al, ^{13}C and ^{31}P NMR were recorded with Brucker AM 300 MHz spectrometer. The chemical shifts were reported in ppm relative to the internal standard TMS for ^1H and ^{13}C NMR, and external standard $[Al(H_2O)_6]^{3+}[(NO_3)_3]^{3-}$ and 85% H_3PO_4 for ^{27}Al and ^{31}P NMR. IR were recorded on PE-983G spectrometer. ESCA (xps) was obtained on XSAM 800 at 1253.6 ev (MgKα). The equivalent conductivity was measured on DDS-11 conductor at 0.01M, 0°C under dry N_2, reported in $uScm^2M^{-1}$. Toluene were dried with sodium. CH_2Cl_2, CD_2Cl_2(Aldrich) and $CDCl_3$ were dried over P_2O_5 and stored over CaH_2. All manipulations were carried out under an atmosphere of dry nitrogen. Standard Schlenk technology was applied.

2-Chloro-2-thiono-3-n-phenyl-5-methylthio-2,3–2(H)-1,3,4,2-thiadiazaphospholes (1)

Were synthesized according to the reported procedure.[8] The equivalent conductivity and ESCA data were listed in Table I.

2-Chloro-2-thiono-1,3-bismethyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (2a)

The mixture of 6 (14.9 g, 0.11 mol) in 300 ml of toluene and $PSCl_3$ (11.0 ml, 0.12 mol) were refluxed for 10 hrs. Completion was indicated by the disappearance of **6** on silica gel TLC. The clear filtrate was concentrated at reduced pressure. The residue was purified on a flash silica gel column using petroleum ether/ether (8:1) as the eluent to give **2a**, white crystal, m.p. 84.5–86.0 °C (ether), 27.25 g (84.3%). IR (KBr, cm^{-1}): 639, 739, 920, 1047, 1116, 1201, 1216, 1276, 1446,1465, 1484,1599, 2853, 2924, 3059. δ ^1H ($CDCl_3$, ppm): 3.26 (d, 6H, J=14 Hz, 2Me), 6.82~7.05 (m, 4H, C_6H_4). δ ^{13}C ($CDCl_3$, ppm): 27.57 (d, $^2J_{PNC}$=14.5 Hz, Me), 109.1 (d, $^2J_{PNC}$=8.8 Hz), 122.0 and 134.2 (Ph). δ ^{31}P ($CDCl_3$, ppm): 68.8. MS (20ev, m/e, %): 232 (M^+, 67.5), 197 (M-Cl, 27.4), 165 (100, M-Cl-S), 15 (Me, 41.7). Anal. Calcd. For $C_8H_{10}ClN_2PS$: C, 41.30; H, 4.30; N, 12.05; Cl, 15.25; P, 13.33. Found: C, 41.41; H, 4.50; N, 12.03; Cl, 14.96; P, 12.89.

2-Chloro-2-thiono-1,3-bisphenyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (2b)

The mixture of 7e (4.00 g, 0.015 mol) in 150 ml of toluene, 5.0 ml of Et_3N (0.036 mol) and $PSCl_3$ (2.50 ml, 0.28 mol) were refluxed for 32 hrs. Completion was indicated by the disappearance of **7e** on silica gel TLC. The clear filtrate was concentrated at reduced pressure. The residue was purified on a flash silica gel column using petroleum ether to give **2b**, white crystal, m.p. 98.0 °C (ether), 2.55 g (45.8%). IR (KBr, cm^{-1}): 661, 690, 739, 757, 899, 920, 927, 993, 1038, 1072, 1218, 1280, 1287, 1298, 1347, 1447, 1489,1588, 3037. δ ^1H ($CDCl_3$, ppm): 6.67–6.94 (m, 4H, C_6H_4), 7.49–7.65 (m, 10H, 2Ph). δ ^{13}C ($CDCl_3$, ppm): 109.2–134.3 (m, 2Ph and C_6H_4). δ ^{31}P ($CDCl_3$, ppm): 59.0. MS (20ev, m/e, %): 356 (M^+, 100), 321 (M-Cl, 35.2), 289 (72.5, M-Cl-S), 212 (M-Ph-S-Cl, 5.2). Anal. Calcd. For $C_{18}H_{15}ClN_2PS$: C, 60.60; H, 4.21; N, 7.86; Cl, 9.94; P, 8.70. Found: C, 60.47; H, 4.26; N, 7.84; Cl, 9.61; P, 8.35.

Reaction of heterocyclic thiophosphoryl chloride 1, 2a and 2b with $AlCl_3$ resulting in 3, 4a and 4b

These reactions were performed in dual compartment vessels, which were flame-dried before used. Typically, a mixture of respective heterocyclic thiophosphoryl chloride (ca. 1 mmol) and $AlCl_3$(ca. 3 mmol of each) in 10 ml of CH_2Cl_2 was stirred for 4–6 hr. at –20 °C. A transparent solution was formed. In the cases of **1** and **2b**, the reaction solution is red. In the instances of **2a**, they were green. The solvent was removed slowly from the clear pale yellow solution to yield crystals. The supernatant liquid was decanted and the crystals were washed twice with small aliquots of cool CH_2Cl_2, to characterize **3**, **4a** *and* **4b**.

For **3**: Red crystal, m.p. 143–145 °C (CH_2Cl_2-Hexane), 86.5%. IR (KCl, cm^{-1}): 295, 487s, 686, 762, 963, 1099, 1423, 1491, 1596. δ ^1H ($CDCl_3$, ppm): 2.98 (s, 6H, 2MeS), 7.655–7.85 (m, 10H, $2C_6H_5$). δ ^{13}C ($CDCl_3$, ppm): 22.5 (MeS), 123.8, 125.4, 128.2, 132.9 (d, $^2J_{PNC}$=13.5 Hz) (Ph), 170.5 (d, $^2J_{PNC}$=21.8 Hz, C=N). δ ^{27}Al ($CDCl_3$, ppm): 102.23. δ ^{27}Al ($CDCl_3$, ppm): 102.43 ($\nu_{1/2}$=12.5 Hz). δ ^{31}P ($CDCl_3$, ppm): 60.42. FAB-MS (glycerol, m/e, %): M^+ 518 (M^+, 16%), 259 (3%), 227 (83), 164 (11), 122 (6), 77 (100). Anal. Calcd. For $C_{16}H_{16}N_4P_2S_2\bullet[AlCl_4^-]_2$: C, 22.44; H, 1.87; N, 6.55; Cl, 33.15; P, 7.25. Found: C, 22.43; H, 1.85; N, 6.36; Cl, 33.33; P, 7.55. The equivalent conductivity and ESCA data were listed in Table I.

For **4a**: Green crystal, m.p. 161–162 °C (CH_2Cl_2-Hexane), 43%. IR (KCl, cm^{-1}): 294, 490s, 695, 742, 964, 1092, 1165, 1220,1310,1420, 1440, 1475, 1516, 1610, 2950, 3030. δ ^1H ($CDCl_3$, ppm): 3.38 (d, 15.8Hz, 12H, 4Me), 7.29~7.45 (m, 8H, $2C_6H_4$). δ ^{27}Al ($CDCl_3$, ppm): 102.71 ($\nu_{1/2}$=12.0Hz). δ ^{31}P ($CDCl_3$, ppm): 59.3. FAB-MS (glycerol, m/e, %): 394 (M^+,6%), 379 (3), 364 (6), 232 (16), 227 (13), 197 (11), 165 (100). Anal. Calcd. For $C_{16}H_{20}N_4P_2S_2\bullet[AlCl_4^-]_2$: C, 26.24; H, 2.74; N, 7.65; Cl, 38.76; P, 8.47. Found: C, 26.43; H, 2.57; N, 7.88; Cl, 38.27; P, 8.31. The equivalent conductivity datum was listed in Table I.

For **4b**: Purple crystal, m.p. 178–179 °C (CH_2Cl_2-Hexane), 33%. IR (KCl, cm^{-1}): 295, 490s, 690, 736, 760, 896, 920, 995, 1040, 1290, 1350, 1480, 1491, 1588, 3030. δ ^1H ($CDCl_3$, ppm): 7.21–7.95 (m, Ar-H). δ ^{27}Al ($CDCl_3$, ppm): 102.36 ($\nu_{1/2}$=11.4 Hz). δ ^{31}P ($CDCl_3$, ppm): 54.5. FAB-MS (glycerol, m/e, %): M^+ 642 (21), 356 (25), 321 (7), 289 (100), 212 (3.5), 77 (90). Anal. Calcd. For $C_{36}H_{30}N_4P_2S_2\bullet[AlCl_4^-]_2$: C, 44.10; H, 3.06; N, 5.71; Cl, 28.95; P, 6.33. Found: C, 43.99; H, 2.97; N, 5.57; Cl, 28.66; P, 6.29. The equivalent conductivity datum was listed in Table I.

Reaction of 2-chloro-2-thiono-1,3-bismethyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (2a) with CF_3SO_3Ag resulting in 5

A solution of 2-chloro-2-thiono-1,3-bismethyl-2,3-dihrdro-1,3,2-benzodiazaphosphole (**2a**) (98.6 mg, 0.42 mmol) and dry CF_3SO_3Ag (117.9 mg, 0.46 mmol) in 10 ml of CH_2Cl_2 is stirred at 0 °C for 48 hr from light. White AgCl is filtered off. The filtrate is evaporated and vacuum to remove the solvent. The residue is chromatographed on silica gel by centrifugal TLC using petroleum ether/ether (8:1) as the eluent to afford **5**, 75.16 mg (87.3%), colorless crystal, m.p. 68–69 °C (ether). δ ^1H ($CDCl_3$, ppm): 3.24 (d, 12H, J=12.4 Hz, 4Me), 6.65~7.10 (m, 8H, $2C_6H_4$). δ ^{31}P ($CDCl_3$, ppm): 59.28 (single). MS (20ev, m/e, %): 418 (M^+, 30.2%), 197 (76.6), 165 (100), 133 (29.4). Anal. Calcd. For $C_{16}H_{20}N_4OP_2S_2$: C, 46.83; H, 4.88; N, 27.30; P, 15.12. Found: C, 48.64; H, 4.76; N, 27.15; P, 15.11.

o-Phenylenediamine-N,N'-dimethyl (6)

Was prepared according to reported method.[9]

N,N'-Diphenyl-o-phenylenediamine (7e)

Was prepared from **7a** on the basis of the modifying Chapman's method.[10b–c]

(1) (N-Phenyl)(benzyliden)(chloro)imine (7a)

(1) Under vigorous agitation, to a solution of 91 ml of aniline in 300 ml of pyridine, 120 ml of PhCOCl was dropwise added. The mixture was refluxed for an hour, cooled to 60 °C, poured it into 1000 ml of vigorously stirring water, stirred for 1 hr. The solid collected by filtration was crystallized from 95 % EtOH to afford N-phenyl benzoyl amide (PhNHCOPh, 184 g, 93.4%, m.p. 161). (2) The solution of 40 g of N-phenyl benzoyl amide (0.2 mol) and 42.0 g of PCl_5 (0.2 mol) in 300 ml of toluene was refluxed until the disappearance of HCl for ca. 2 hrs. The $POCl_3$ and the solvent was removed off under vacuum. The residue was distilled under

vacuum to give pure **7a**, bp 150–158/1 mmHg, 38.0 g (88.0%), at room temperature oil becomes pale yellow-green crystal, m.p. 57.0–57.6 °C. Anal. Calcd. for $C_{13}H_{10}ClN$: Cl, 16.45. Found: Cl, 16.13.

(2) (N-Phenyl)(benzyliden)(o-chlorophenoxy)imine (7b)

The mixture of **7a** (8.5 g, 0.039 mol), Et_3N (5.5 ml, 0.04 mol) and *o*-chlorophenol (5.1 g, 0.04 mol) in 100 ml of ether was stirred at room temperature for 24 hours. Triethylamine hydrochloride is filtered off. The filtrate is evaporated under vacuum to remove the solvent. The residue is crystallized from 95 % EtOH to afford light yellow solid, (N-Phenyl)(benzyliden)(*o*-chlorophenoxy)imine (**7b**), 10.5 g, 85.4%, m.p. 161 °C. Anal. Calcd. For $C_{19}H_{14}ClNO$: Cl, 11.53. Found: Cl, 11.06.

(3) N-(o-Chlorophenyl)aniline (7c)

The 10.0 g of **7b** was heated at 260for 1.5 hrs, cooled to room temperature. To it, 50 ml of 50 % KOH and 120 ml of 95 % EtOH was added, the mixture was refluxed for 2 hrs, and was concentrated to one third of the volume, then poured it into 500 ml of water. The water solution was extracted with 4×150 ml of ether. The ether solution was dried and evaporated to obtain oily residue which was distilled under vacuum to give pure **7c**, colorless oil, 5.0 g (67.6%), bp 138°C/10 mm Hg. Anal. Calcd. For $C_{12}H_{10}ClN$: Cl, 17.42. Found: Cl, 17.73.

(4) (N-Phenyl)(N'-phenyl)[N'-(o-chloro)phenyl]carboxamidine (7d)

The mixture of 5.0 g of **7c** (0.025 mol) and 5.5 g of **7a** (0.025 mol) was heated at 100 for 3 hrs, added 30 ml of pyridine and refluxed for half an hour. Poured the warm solution into 200 ml of water, the solid collected by filtration was crystallized from EtOH to obtain ***(N-Phenyl)(N'-phenyl)[N'-(o-chloro)phenyl]carboxamidine*** (**7d**), 2.34 g(24.5%), yellow crystal, m.p. 168 °C (benzene). Anal. Calcd. For $C_{25}H_{19}ClN_2$: Cl, 9.27. Found: Cl, 9.17.

(5) N,N'-Diphenyl-o-phenylenediamine (7e)

(1) The 2.0 g of **7d** was heated at 300 for 2 hrs, cooled to room temperature, added 60 ml of ice water, stirred and refluxed for a quarter of an hour. The pale green filtrate was adjusted to PH=13. The white solid obtained by filtration was crystallized from EtOH to afford N,N'-bisphenyl-N-ben-

zoyl-o-phenylenediamine (1.4 g, 73.5%, m.p. 151). (2) The mixture of 1.0 g of N,N'-bisphenyl-N-benzoyl-o-phenylenediamine in 15 ml of EtOH, and 5 ml of 50% KOH-H_2O was refluxed for 2.5 hrs, cooled to room temperature. The crystal obtained by filtration crystallized from petroleum ether (60–90°) to afford N,N'-diphenyl-*o*-phenylenediamine (**7e**), 4.0 g (70%), m.p. 105.5 °C (108°C[10c]). IR (KBr, cm-1): 690, 744, 759, 1074, 1155, 1172, 1184, 1226, 1243, 1257, 1280, 1301, 1316, 1408, 1420, 1455, 1465, 1494, 1513, 1590, 1601, 3039, 3047, 3388. δ ^1H ($CDCl_3$, ppm): 5.33–5.90 (br, 2NH), 6.78–7.32 (m, 14H, C_6H_4 and 2Ph). Anal. Calcd. For $C_{18}H_{16}N_2$: C, 83.08; H, 6.15; N, 10.77. Found: C, 83.44; H, 6.31; N, 10.52.

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