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SYNTHESIS OF 2-AMINOMETHYLPYRIDINE DERIVATIVES OF PHOSPHAZENES

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Abstract- Novel cyclophosphazenes **(5-8)** with pyridine side groups have been synthesized by the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ **(1)**, with 2-amino-3-methylpyridine **(2)**, 2-amino-4-methylpyridine **(3)** and 2-amino-5-methylpyridine **(4)**. Di- and monosubstituted products **(5, 6)** were obtained from the reaction of **1** with **2** and **3**, respectively. Both di- and monosubstituted products **(7, 8)** were obtained from 2-amino-5-methylpyridine with **1**. The structures of the compounds **(5-8)** were defined by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and elemental analyses.

INTRODUCTION

Cyclophosphazenes are probably the best known and most intensively studied phosphorus-nitrogen compounds. Up to date numereous compounds have been reported from the interactions of cyclophosphazenes with amines,[1] alcohols,[2] aryl oxides.[3] The reactions of compound (**1**) with pyridine derivatives is highly limited in the literature.[4,5] So, in this paper; we report the reactions of hexachlorocyclotriphosphazatriene with 2-aminopyridine derivative ligands **(2-4)**. White crystal compounds **(5-8)** were obtained from these reactions. The partial replacement of chlorine atoms has been achieved from reactions of compound **(1)** with aminomethylpyridine derivatives **(2-4).**

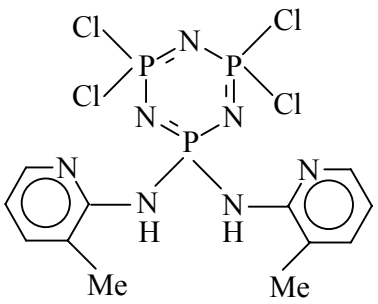
RESULTS AND DISCUSSION

Compound **(1)** was reacted with 2 equiv. of pyridine derivatives **(2-4)** in THF. Excess of pyridine derivatives being used in all these reactions as hydrogenechloride acceptor. The partially substituted products **(5-8)** could be isolated from these reactions. In all cases, thin layer chromatography results

should that reaction mixtures would contain two products. But, only major products **(5-8)** were isolated from the reaction mixtures by column chromatography. No other product could be isolated. In all these reactions, the yield of reactions ranged from 42 to 20 %. Therefore, unreacted **1** was recovered from all these cases. The fully substituted products could not be obtained from these reactions.

The di- and monosubstituted products **(5**, **6)** were obtained from the reaction of compound (**1**) with **2** and **3**, respectively.

Both di- and monosubstituted products **(7**, **8)** were obtained from the reaction of compound (**1**) with **4**. All these compounds are stable in air and moisture.



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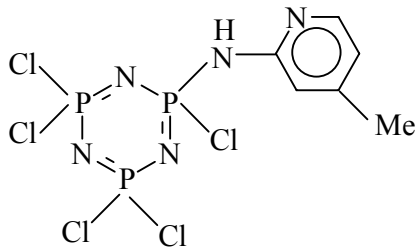

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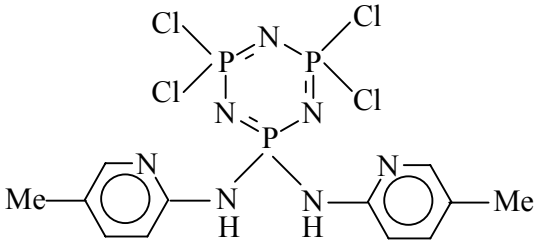

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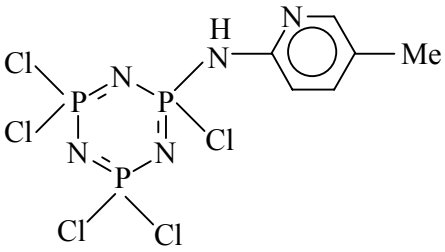

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The structures of compounds **(5-8)** were determined by their characteristic spectroscopic data and elemental analyses. In the IR spectra of **5-8**, the characteristic $\nu_{P=N}$ vibrations occur between 1167 and 1186 cm^{-1}. These data are in accordance with the reported values for phosphazene derivatives.[6] The indication of the partially substitutions for compounds **(5-8)** is given by the ν_{P-Cl} streching bands observed at 580, 589, 566, and 579 cm^{-1}, respectively. In the FTIR spectra of the compounds **(5-8),** C-H (aryl) and C-C (aryl) streching bands are observed between 2933–2967 and 1435–1644 cm^{-1}, respectively.

The NH-streching frequencies of compounds **(5-8)** were observed at 3318, 3436, 3255 and 3436 cm^{-1}, respectively. In the ^1H NMR spectra the pyridinic protons was observed at δ = 6.81-8.12, 6.69-8.28, 6.79-8.14 and 6.73-8.27 as multiplets for compounds **(5**, **6**, **7**, and **8)** respectively. The protons of the

methyl groups in compounds **(5, 6, 7** and **8)** give singlets at δ = 2.19, 2.47, 2.26 and 2.29 ppm, respectively. The signal for each carbon atom can be seen in the ^{13}C NMR spectra. It is noticed that the carbon atoms nearest to the phosphorus atoms are generally observed at the lowest downfield in the NMR spectra. The carbons of the methyl groups in compounds **(5**, **6**, **7** and **8)** give singlets at δ= 28.6, 22.3, 28.6 and 27.2 ppm, respectively.

The ^{31}P NMR spectra of the compounds **(5-8)** have AB_2 spin system due to two different phosphorus environments within the molecules. The compounds show a typical five-line resonance pattern which has a triplet and doublet that are assigned to P_A and P_B, respectively. The P_A signals are shifted to lower values than those of P_B. Chemical shifts were δ $P(NHR)_2$ = 5.39 and δ PCl_2 = 26.22 in **5**, δ PCl(NHR) = 7.43 and δ PCl_2 = 21.65 in **6**, δ $P(NHR)_2$ = 4.08 and δ PCl_2 = 24.19 in **7**, δ PCl(NHR) = 8.14 and δ PCl_2 = 22.02 in **8**. The ^{31}P NMR spectrum (AB_2) of compounds **(5** and **7)** reveals the geminal substitution pattern with chemical shifts of P_A 5.39 (t), 4.08 (t) and P_B 26.22 (d), 24.19 (d) ; J_{AB} 55.8, 56.23 Hz, respectively. According to the ^{31}P NMR spectra of compounds **(5** and **7)** it is concluded that the only geminal structures are possible. Two bond coupling constants of compounds **(5-8)**, J_{AB}, are between 38.79-56.23 Hz. These data are in good with the literature.[13,15] J_{AB} values of compounds **(6)** (38.79 Hz) and **(8)** (39.08 Hz) compound are lower than others.

EXPERIMENTAL

General Remarks

All synthetic steps were carried out under an inert atmosphere of N_2 or Ar in predried glassware by using the Schlenk techniques.

Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, was provided by Aldrich Co. before use it was recrystallized from *n*-hexane. Other chemicals were used as purchased. Tetrahydrofuran was used as solvent and distilled over a sodium-potassium alloy in presence of benzophenone under an atmosphere of dry argon. IR spectra were recorded on an ATI Unicam Mattson 1000 FT-IR spectrophotometer, in KBr disks and were reported in cm^{-1} units. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker DPX-300 spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C), and 121.49 MHz (^{31}P). All data were recorded for solutions in $CDCl_3$. The ^1H and ^{13}C chemical shifts were measured using $SiMe_4$ (δ=0) as an internal standard, and the ^{31}P chemical shifts using 85% H_3PO_4 as an external standard. Coupling constants were given (*J*) in Hz. Microanalysis was carried out by LECO 932 CHNS-O apparatus. For column chromatography silica gel (230-400 mesh Merck) was used. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and were uncorrected.

Preparation of 4,4,6,6-pentachloro-2-(3-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (5). Compound **(2)** (1.86 g; 17.2 mmol) was added dropwise at rt to a solution of **1** (3 g; 8.62 mmol) in 50 mL THF. The reaction mixture was stirred for 6 days and was then filtered to remove 2-amino-3-methylpyridine hydrochloride which precipitated from the solution. After removal of the solvent and chromatography using *n*-hexane eluent, unreacted $(NPCl_2)_3$ was isolated. Further elution with CH_2Cl_2 / *n*-hexane (1:1) gave 4,4,6,6-tetrachloro-2,2-di-(3-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene **(5)** was obtained. Compound **(5)** is white solid. (R_f = 0.352 CH_2Cl_2 / *n*-hexane 2:1). Yield: 0.80 g, 20 %. mp 167-168 ^{0}C. IR (KBr, cm^{-1}), ν= 3318 (NH), ν= 2959 (CH aryl), ν= 1589, 1458, 1435 (CC aryl), ν= 1191 (P=N), ν= 580 (P-Cl). ^{1}H NMR ($CDCl_3$) δ: 6.81-8.12 (m, 4H, pyridinic H), 5.54 (s, 1H, NH), 2.19 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 151 (s, 1C, C-ipso), 145, 138, 118, 117 [pyridinic C], 28.6 (s, 1C, CH_3). ^{31}P NMR ($CDCl_3$) δ: 5.39 (t, 1P, $P(NH\text{-}Ar)_2$, $^2J_{AB}$: 55.8 Hz), 26.22 (d, 2P, PCl_2), $^2J_{AB}$ = 55.8 Hz). Anal. Calcd for $C_{12}H_{14}N_7Cl_4P_3$: C, 29.35; H, 2.87; N, 19.96. Found: C, 29.09 ; H, 3.02 ; N, 19.70.

Preparation of 2,4,4,6,6-pentachloro-2-(4-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (6).

Hexachlorocyclotriphosphazatriene **(1)** (3 g; 8.62 mmol) and compound **(4)** (1.86 g ; 17.2 mmol) were used for the preparation of **6** as for **3**. Reaction mixture was filtered to remove 2-amino-4-methylpyridine hydrochloride which precipitated from the solution. After removal of the solvent and chromatography using hexane eluent, unreacted $(NPCl_2)_3$ was isolated. Further elution with acetone / *n*-hexane (1:3) gave 2,4,4,6,6-pentachloro-2-(4-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene **(6)**. Compound **(6)** is white crystal. (R_f= 0.297 acetone / *n*-hexane 1:3). Yield: 0.85 g, 23 %, mp > 300 ^{0}C. IR (KBr, cm^{-1}), ν= 3436 (NH), ν= 2963 (CH aryl), ν= 1632, 1608, 1516 (CC aryl) ν= 1187 cm^{-1} (P=N) , ν= 589 (P-Cl). NMR ($CDCl_3$) : ^{1}H NMR ($CDCl_3$) δ: 6.69-8.28 (m, 4H, pyridinic H), 4.85 (s, 1H, NH), 2.47 (s, 3H, CH_3), ^{13}C NMR ($CDCl_3$) δ: 156 (s, 1C, C-ipso), 137, 118, 114 [pyridinic C], 22.32 (s, 1C, CH_3). ^{31}P NMR ($CDCl_3$) δ: 7.43 (t, 1P, PCl(NH-Ar), $^2J_{AB}$: 38.79 Hz), 21.65 (d, 2P, PCl_2), $^2J_{AB}$: 38.79 Hz) Anal. Calcd for $C_6H_7N_5Cl_5P_3$: C, 17.17; H 1.67; N, 16.70. Found: C, 17,69; H, 1.78; N, 16.22.

Preparation of 4,4,6,6-tetrachloro-2,2-di-(5-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (7) and 2,4,4,6,6-pentachloro-2-(5-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (8). Compound **(7)** and **(8)** were prepared in the same way as **5** from 2-amino-5-methylpyridine (1.86 g; 17.2 mmol) and hexachlorocyclotriphosphazatriene (3 g; 8.62 mmol). The

reaction mixture was filtered to remove the 2-amino-5-methylpyridine hydrochloride which precipitated and the solvent removed under reduced pressure. The resulting white solid was subjected to column chromatography. First, to remove $(NPCl_2)_3$ *n*-hexane used as eluent in column chromatography. After, *n*-hexane : CH_2Cl_2 (1:1) used as eluent and 4,4,6,6-tetrachloro-2,2-di-(5-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene **(7)** was obtained. Compound **(7)** is a white colored crystal. (R_f = 0.435 Acetone / *n*-hexane 1:3).Yield: 0.5 g, 24 %. mp 134-135 ^{0}C. IR (KBr, cm^{-1}) : ν= 3255 (NH) ν= 2967 (CH aryl), ν= 1607,1492, 1435 cm^{-1} (CC aryl), ν= 1211 (P=N), ν= 566 (P-Cl). ^{1}H NMR ($CDCl_3$) δ: 6.79-8.14 (m, 4H, pyridinic H), 6.41 (s, 1H, NH), 2.26 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 150 (s, 1C, C-ipso), 147, 139, 126, 110 [pyridinic C], 28.6 (s, 1C, CH_3). ^{31}P NMR ($CDCl_3$) δ: 4.08 (t, 1P, P(NH-Ar)$_2$, $^2J_{AB}$: 56.23 Hz), 24.19 (d, 2P, PCl_2), $^2J_{AB}$: 56.23 Hz) Anal. Calcd for $C_{12}H_{14}N_7Cl_4P_3$: C, 29.35; H, 2.87; N, 19.96. Found: C, 28.44; H, 3.12; N, 20.01.

Further elution with dichloromethane gave **8** which was obtained. Compound **(8)** is a white colored crystal. (R_f = 0.604 CH_2Cl_2 / *n*-hexane 1:1). Yield: 0.75 g, 42 %. mp > 300 ^{0}C (decomp. The color of the compound changed from white to brown). 2,4,4,6,6-pentachloro-2-(5-methyl-2-pyridylamino)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene. IR (KBr) : ν= 3436 cm^{-1} (NH), ν= 2933 cm^{-1} (CH aryl) ν= 1644, 1613, 1542 cm^{-1} (CC aryl), ν= 1179 cm^{-1} (P=N), ν= 579 (P-Cl). ^{1}H NMR ($CDCl_3$) δ: 6.73-8.27 (m, 4H, pyridinic H), 4.85 (s, 1H, NH), 2.29 (s, 3H, CH_3), ^{13}C NMR ($CDCl_3$) δ: 154, 144, 137, 122, 118 [pyridinic C], 155 (s, 1C, C-ipso), 17.27 (s, 1C, CH_3). ^{31}P NMR ($CDCl_3$) δ: 8.14 (t, 1P, PCl(NH-Ar), $^2J_{AB}$: 39.08 Hz), 22.02 (d, 2P, PCl_2), $^2J_{AB}$: 39.08 Hz) Anal. Calcd for $C_6H_7N_5Cl_5P_3$: C, 17.17; H 1.67; N, 16.70. Found: C, 17.28; H, 1.72; N, 15.98.

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