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The Reactions of Hexachlorocyclotriphosphazatriene with Pyridine Derivatives

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ABSTRACT: *The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (**1**), with 2-hydroxypyridine (**2**), 2-aminopyridine (**3**), 2-amino-6-methyl-pyridine (**4**), and 2-hydroxy-4-methylquinoline (**5**) have been investigated. The products were identified by elemental analyses, IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:57–60, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20185

INTRODUCTION

Cyclophosphazenes $(PNX_2)_n$ are an important class of inorganic heterocyclic compounds. In which tetracoordinated phosphorus atoms alternate with the nitrogen atoms. Six- and eight-membered phosphazene rings have been studied intensively. The chlorophosphazene rings, especially $(PNCl_2)_3$ (**1**) are important precursors of phosphazene polymers. Although a number of cyclic phosphazenes with amino [1–7], aryloxy [8–13], aryl [14] groups have been prepared and studied, discussion on a substitution with pyridine derivatives is relatively limited in the literature [15–20]. In this article, we report the reactions of **1** with pyridine derivatives **2–5**. White crystal compounds **6–10** were obtained from these reactions.

RESULTS AND DISCUSSION

Compound **1** was reacted with all reagents **2–5** in ratios of 1:1, 1:2, and 1:6. The partially substituted products **6–10** could be isolated from these reactions. Thin layer chromatography studies indicated that reaction mixtures would contain more than one product. However, only major products (**6–10**) were isolated from the reaction mixtures by column chromatography. In all these cases, the yield of reactions ranged from 43 to 6%. Compounds **6** and **10** were obtained in good yield, that is 43 and 31%, respectively. But products **7, 8, 9** were obtained in low yields, that is 13, 9, and 6%, respectively. Therefore, unreacted **1** was recovered especially in the case of low yields. The fully substituted products could not be obtained from these reactions. Since the nature of the reagents affect the yield, the steric hindrance also plays an important role in such reactions.

The monosubstituted products **7, 8** were obtained from the reaction of compound **1** with **3** and **5**, respectively. The disubstituted product **9** was obtained from the reaction of **1** with **4**. Surprisingly, the monosubstituted derivative could not be isolated from this reaction and TLC gave no indication of its presence. Both mono- and di-substituted products **6, 10** were obtained from the reaction of compound **1** with **2**. All compounds **6–10** are stable in air and moisture.

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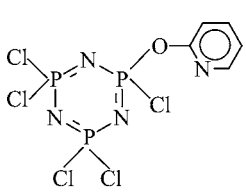

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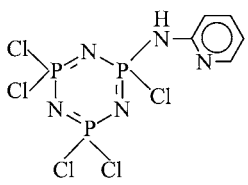

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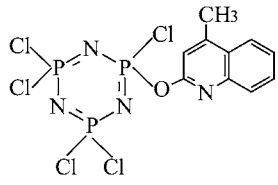

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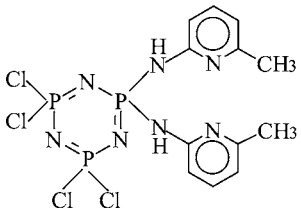

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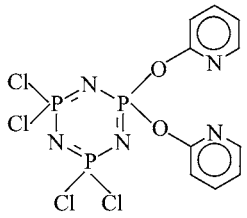

(10)

The structures of compounds **6–10** were determined by using elemental analyses, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. These results are given in the experimental. In the IR spectra of **6–10**, the characteristic $\nu_{P=N}$ vibrations occur between 1194 and 1226 cm^{-1}. These data are in accordance with the reported values for phosphazene derivatives [21–23]. The indication of the partially substitutions for compounds **6–10** is given by the ν_{P-Cl} stretching bands observed at 592, 588, 592, 583, and 556 cm^{-1}, respectively. In the FTIR spectra of the compounds **6–10**, C—H (aryl) and C—C (aryl) stretching bands are observed between 3046–3090 and 1342–1598 cm^{-1}, respectively. The NH-streching frequencies of compounds **7** and **9** were observed at 3433 and 3427 cm^{-1}, respectively. ^{1}H NMR spectra of compounds **6–10** are simple but informative. The pyridinic protons was observed at $\delta = 6.9–8.3$, $\delta = 6.8–8.4$, $\delta = 6.7–7.2$, and $\delta = 6.9–8.2$ as multiplets for compounds **6, 7, 9**, and **10**, respectively. These values are in good agreement with the literature values [24]. The aromatic protons of compound **8** give multiplet at $\delta = 6.9–8.1$. The protons of the methyl groups in compounds **8** and **9** give singlets at $\delta = 2.72$ and 2.51 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. The proton decoupled ^{31}P-NMR spectra of the compounds **6–10** 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 PCl(OAr) = 15.00 and δ PCl_2 = 24.19 in **6**, δ PCl(NHR) = 13.87 and δ PCl_2 = 23.14 in **7**, δ PCl(OAr) = 13.76 and δ PCl_2 = 23.19 in **8**, δ $P(NHR)_2 = -2.71$ and δ PCl_2 = 23.26 in **9**, δ $P(OAr)_2 = -1.51$ and δ $PCl_2 = 26.34$ in **10**. Two band-coupling constants, $^{2}J_{AB}$, of all the compounds, except for **10**, are nearly the same. These values are between 51.0–59.9 Hz and are in good agreement with the literature [17,25,26]. $^{2}J_{AB}$ value of **10** (70 Hz) is higher than others. The ^{31}P NMR spectrum (AB_2) of compounds **9** and **10** reveals the geminal substitution pattern with chemical shifts of P_A −2.71 (t), −1.51(t) and P_B 23.26 (d) , 26.34 (d); J_{AB} 51, 70 Hz, respectively. According to the ^{31}P NMR spectra of compounds **9** and **10**, it is concluded that the only geminal structures are possible.

EXPERIMENTAL

General Remarks

All reactions were performed under an inert atmosphere of N_2 or Ar in predried glassware by using the Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under N_2 or Ar: dioxane (Na), *n*-hexane, ether (Na wire/benzophenone), and THF (Na/benzophenone). Hexachlorocyclotriphosphazatriene (99%) was purchased from Aldrich and purified by recrystallization from *n*−hexane. 2-Hydroxypyridine (97%), 2-amino-6-methylpyridine (98%), 2-aminopyridine, and 2-hydroxy-4-methylquinoline (97%) were purchased from Aldrich and Fluka. Pyridine derivatives were used without further purification as received. All reactions were monitored by using Kieselgel 60 F_{254} (silica gel) precoated TLC plates, and separating conditions were determined. The separation of products was carried out by column chromatography using silica gel (Merck 60,

230–400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length). The purity of compounds **6–10** was checked by TLC and characterized by elemental analyses, ^{1}H-, ^{13}C-, ^{31}P- NMR spectrometry, and FT-IR. Elemental analyses were obtained using a LECO 932 CHNS instrument, and IR spectra were recorded on an ATI Unicam Mattson 1000 FT-IR spectrophotometer as KBr pellets. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Bruker 300 Ultra Shield spectrometer operating at 300.13, 75.46, and 121.49 MHz, respectively. Chemical shifts (δ) are given in ppm relative to TMS. Melting points were measured in open capillary tubes with an Elektrothermal-9200 melting point apparatus and were uncorrected.

Synthesis of **6**. Small pieces of metallic sodium (0.39 g, 17 mmol) were added to **2** (0.82 g, 8.63 mmol) in 25 mL of THF, under Ar atmosphere the solution was stirred till the no hydrogen gas was observed which is an indication of completion of the reaction. Excess sodium was removed by filtration, and the solution of sodium-pyridine-2-oxide was frozen with a liquid nitrogen–acetone mixture. To this solution, **1** (3 g, 8.62 mmol) in THF (20 mL) was slowly added and the resulting mixture was allowed to come at ambient temperature with continued stirring. The reaction mixture was vigorously stirred at room temperature for 48 h and was refluxed for 3 h. The precipitated NaCl was filtered off, and solvent was removed under vacuum. The resulting white solid was subjected to column chromatography using dichloromethane/*n*-hexane (1:3) as eluent and 2,4,4,6,6-pentachloro-2-(2-pyridyloxy)cyclo-2λ^5,4λ^5,6λ^5-triphozphazatriene **6** was obtained with 43% yield. Compound **6** is in white crystalline form, mp = 91–93°C. (R_f = 0.233 dichloromethane/*n*-hexane 1:3). Elemental analysis calcd (%) for $N_3P_3Cl_5OC_5H_4N$ (406.29): C 14.76, H 0.98, N 13.78; Found C 15.57, H 1.173, N 12.96. IR (KBr): ν(CH aryl) 3075, ν(CC aryl) 1598, 1436, ν(P=N) 1205, ν(POC) 956, ν(PCl) 592 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ = 6.9–8.3 [m, 4H, pyridinic H]. ^{13}C, δ = 147, 140, 121, 115 [pyridinic C], 147.6 (s, 1C, C-ipso). ^{31}P; δ (ppm) 15.00 (t, 1P, PCl(O-Ar-Cl), $^{2}J_{AB}$: 59.1 Hz), 24.19 (d, 2P, PCl_2), $^{2}J_{AB}$: 59.1 Hz.

Synthesis of **7**. Compound **3** (0.81 g, 8.62 mmol in 25 mL of ether), Na (0.39 g, 17 mmol), and **1** (3 g, 8.62 mmol in 20 mL of ether) were used in **6**. The reaction mixture was stirred at room temperature for 72 h; solvent was removed in vacuo. The residue was chromatographed (eluent chloroform/*n*-hexane (1:3) and 2,4,4,6,6-pentachloro-2-(2-pyridylamino)cyclo-2λ^5, 4λ^5,6λ^5-triphosphazatriene **7** was obtained with 13% yield. Compound **7** is in white crystalline form, mp = 94–95°C, R_f = 0.256 chloroform/*n*-hexane (1:3). Elemental analysis calcd (%) for $N_3P_3Cl_5C_5H_5N_2$ (405.5): C 14.81, H 1.24, N 17.27; Found: C 15.24, H 1.13, N 13.27. IR (KBr): ν(NH) 3433, ν(CC aryl) 1596, 1442 , ν(P=N) 1226, ν(PCl) 588 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ = 6.81–8.4 [m, 4H, pyridinic H], δ = 1.52 (s, 1H, NH). ^{13}C, δ = 147, 140, 121, 112 [pyridinic C], 158 (s, 1C, C-ipso). ^{31}P: δ (ppm) 13.87 (t, 1P, PCl(NH-Ar), $^{2}J_{AB}$: 59.9 Hz), 24.19 (d, 2P, PCl_2), $^{2}J_{AB}$: 59.9 Hz.

Synthesis of **8**. Compound **5** (1.37 g, 8.62 mmol) in 40 mL dioxane was allowed to react with Na (0.39 g, 17.2 mmol) at 20°C and stirred until the H_2 (g) evolution was completed, **1** (3 g, 8.62 mmol) was added to this mixture, and the same procedure as in the preparation of **6** was followed. The reaction mixture was refluxed for 5 h. The precipitated salt (NaCl) was filtered. The solvent was removed under vacuum and the mixture was chromatographed. Elution with hexane gave unreacted $(NPCl_2)_3$ as identified. The residue was chromatographed (eluent:ethylacetate/*n*-hexane 1:15), and 2,4,4,6,6-pentachloro-2-(4-methyl-2-oxyquinolinyl)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene **8** was obtained (yield: 9%). (R_f = 0.435 ethylacetate: *n*-hexane 1:15). Compound **8** is a white-colored crystal. mp = 124–127°C. Elemental analysis calcd (%) for $N_3P_3Cl_5C_{10}H_8NO$ (470.5) : C 25.51, H 1.70, N 11.90; Found: C 25.91, H 1.79, N 11.28. IR (KBr): ν(CH aryl) 3082, ν(CH aryl) 2982, ν(CC aryl) 1598, 1448, 1342, ν(P=N) 1219, ν(POC) 1008, ν(PCl) 592 cm^{-1}. NMR ($CDCl_3$), ^{1}H, δ 6.94–8.01 [m, 5H, aromatic], δ =2.72 (s, 3H, CH_3). ^{13}C, δ = 156, 150, 144, 130, 128, 126, 124, 122, 112 [aromatic C]. ^{31}P: δ (ppm) 13.76 (t, 1P, PCl(O-Ar), $^{2}J_{AB}$: 59.5 Hz), 23.19 (d, 2P, PCl_2), $^{2}J_{AB}$: 59.5 Hz.

Synthesis of **9**. Compound **4** (1.86 g, 17.24 mmol) was added dropwise at room temperature to a solution of **1** (3 g, 8.62 mmol) in 100 mL THF. The reaction mixture was stirred for 7 days and was then filtered to remove 2-amino-6-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 chloroform gave 4,4,6,6-tetrachloro-2,2-di-(6-methyl-2-pyridylamino)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene **9** which was obtained with 6% yield; R_f = 0.137 (chloroform), mp = 229–230°C. Compound **9** is a white-colored crystal. Elemental analysis calcd (%) for $N_3P_3Cl_4C_{12}H_{14}N_4$ (491): C 29.34, H 2.85, N 19.97;

Found C 29.31, H 2.64, N 18.33. IR (KBr): ν(NH) 3427, ν(CH aryl) 3046, ν(CH al) 2938, 2814, ν(P=N) 1194, ν(CC aryl) 1594, 1461, ν(PCl) 583 cm^{-1}. NMR ($CDCl_3$), ^1H, δ = 6.7–7.28 [m, 6H pyridinic H], δ = 2.51 (s, 3H, CH_3). ^{13}C, δ = 152, 138, 116, 108 [pyridinic C], δ = 29.7 (s, 1C, CH_3). ^{31}P: δ ppm, −2.71 (t, 1P, $P(NH\text{-}Ar)_2$, $^2J_{AB}$: 51 Hz), 23.26 (d, 2P, PCl_2), $^2J_{AB}$: 51 Hz.

Synthesis of **10**. Compound **2** (4.92 g, 51.73 mmol in 30 mL of toluene), Na (2.37 g, 103 mmol), and **1** (3 g, 8.62 mmol in 15 mL toluene) were used as in **6**. The reaction mixture was stirred at room temperature for 24 h and was refluxed for 2 h. After completion of the reaction, the precipitated salt (NaCl) was filtered and the solvent was removed under vacuum. The white solid residue was chromatographed with first ethylacetate after dichloromethane/*n*-hexane (1:1). 4,4,6,6-tetrachloro-2,2-di(2-pyridyloxy)cyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene **10** was obtained with 31% yield; mp = 204–208°C. Elemental analysis calcd (%) for $N_3P_3Cl_4C_{10}N_2O_2$ (457) C 25.81, H 1.72, N 15.05; Found C 25.45, H 1.74, N 14.34. IR (KBr) : ν (CH aryl) 3090, ν(CC aryl) 1594, 1446, ν(P=N) 1213, ν(POC) 935, ν(PCl) 556 cm^{-1}. NMR ($CDCl_3$), ^1H, 6.98–8.23 (m, 8H, pyridinic H), ^{13}C, δ = 147, 140, 120, 113 [pyridinic C], 157.7 (s, 1C, C-ipso). ^{31}P δ (ppm), −1.51 (t, 1P, $P(O\text{-}Ar)_2$, $^2J_{AB}$: 70 Hz), 26.34 (d, 2P, PCl_2), $^2J_{AB}$: 70 Hz.

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