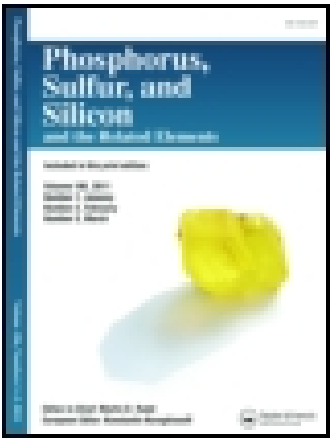

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Synthesis and Characterization of Chloropentaaryloxycyclotriphosphazene Derivatives

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Five chloropentaaryloxycyclotriphosphazene derivatives were synthesized by the reaction of hexachlorocyclotriphosphazene with potassium phenoxide in tetrahydrofuran. A satisfactory yield could be obtained when a 5.1: 1(KOC_6H_4R:$P_3N_3Cl_6$) molar ratio was used. The new compounds were characterized by IR, ^1H NMR, ^{31}P NMR, ^{13}C NMR, and ESI-MS, and for two of them by HR-MS.

Keywords Chloropentaaryloxycyclotriphosphazene derivatives; hexachlorocyclotriphosphazene; phenols; potassium carbonate

INTRODUCTION

Phosphazenes have received increasing interest, not only because of their wide spectrum of chemical and physical properties, but also due to their importance in synthetic chemistry. Different side-group structures affect the chemical and physical properties of ring systems and high polymers based on a phosphazene skeleton.[1–3] Specifically, the properties of phosphazenes can be controlled by the organic groups connected to the phosphazene ring. Accordingly, various phosphazenes

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have been successfully developed in a variety of applications, such as flame retardants, elastomerics, and biomaterials, by controlling the side group.[4–6] In this article, we describe the reaction of hexachlorocyclotriphosphazene with phenols to gain potential intermediates as potential functional materials.

RESULTS AND DISCUSSION

Compound **3** was synthesized according to a modified procedure reported by McBee et al.[7] The dangerous sodium alloy previously used was replaced by potassium carbonate enabling a safer handling and an easier filtration together with a lower cost.

In addition, we found that the reactant ratio had an important effect on the yield of the pentaarylcyclotriphosphazene by following the reaction by ^{31}P NMR tracking, as shown in Figure 1. The yields of $P_3N_3Cl(OC_6H_5)_5$ were, respectively, 52% (4.5:1), 72% (5:1), and 51% (5.5:1). The numbers in parentheses denote the reactant mole ratio ($KOPh:P_3N_3Cl_6$). Consequently, a satisfactory yield of the expected compounds can be obtained when an optimum 5.1:1 $KOPh:P_3N_3Cl_6$ ratio was used. The percentages were measured by ^{31}P NMR.

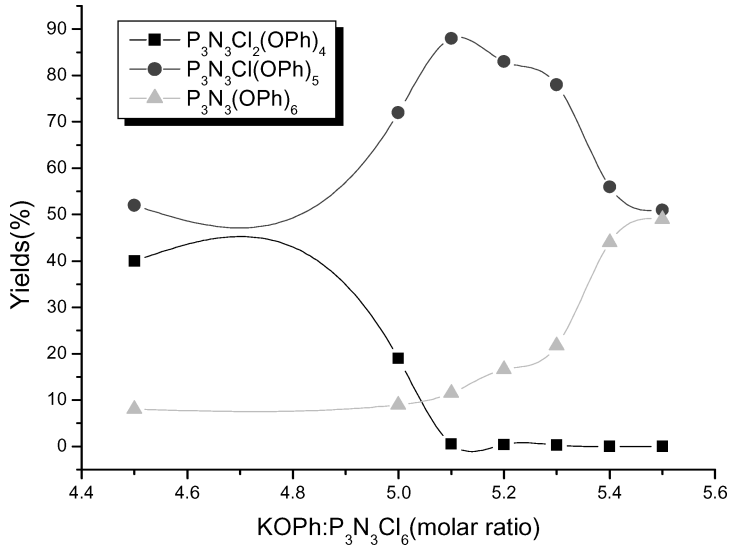


FIGURE 1 Yields of the different substituted phosphazenes vs $KOPh:P_3N_3Cl_6$ ratio (reaction temperature at room temperature).

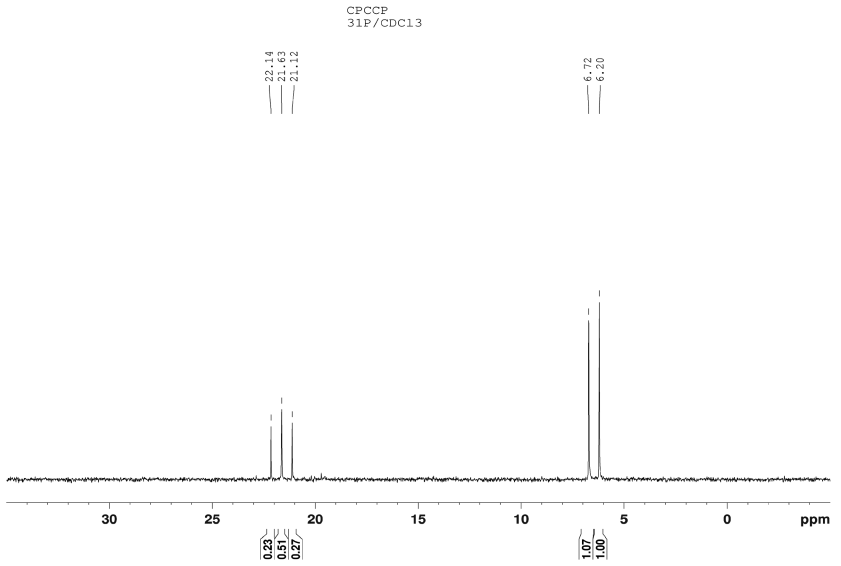


FIGURE 2 ^{31}P NMR spectrum of compound **1** in $CDCl_3$ at room temperature at 162 MHz.

The ^{31}P NMR spectrum of compound **1** is shown in Figure 2. It shows that the two phosphorus nuclei are chemically equivalent, and their chemical shifts are recorded as doublets ($^2J_{PP} = 84.2$ Hz) at high magnetic fields. The only explanation for the absorption is that the two phosphorus nuclei are substituted by four phenoxy groups. It can be concluded that it may have the penta- or 2,2,4,4-tetra-substituted structure (*A* or *B* in Figure 3). Because the coupling constant $^2J_{pp}$ of the 2,2,4,4-tetra-substituted structure (*B* in Figure 3) is at approximately

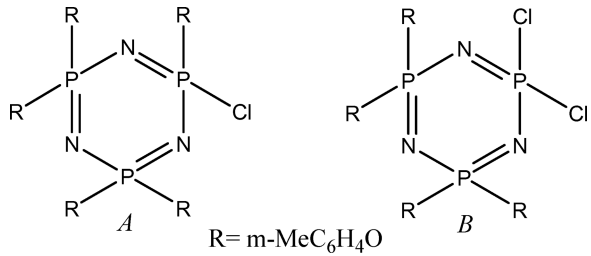


FIGURE 3 Possible structures for ^{31}P NMR spectrum of compound **1**.

60–70 Hz,[8] it clearly supports the proposed *A* in Figure 3, the penta-substituted structure.

CONCLUSION

An economical and safe synthetic route has been developed for the synthesis of chloropentaaryloxycyclotriphosphazenes. The compounds were obtained in good yields when a 5.1:1 KOC_6H_4R:$P_3N_3Cl_6$ ratio was used. The new compounds were characterized by means of IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and mass spectrometry.

EXPERIMENTAL

All chemicals and materials were of analytical grade, and all solutions were freshly dried by standard methods.

^{1}H NMR spectra and ^{13}C NMR spectra were recorded using a Bruker DTX-400 spectrometer. Samples were dissolved in $CDCl_3$ and placed in 5 mm n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference. ^{31}P NMR spectra were recorded using a Bruker DTX-400 spectrometer; 85% H_3PO_4 was used as an external reference. Samples were dissolved in $CDCl_3$ and placed in 5 mm n.m.r. tubes. $CDCl_3$ was used as a "lock" solvent, and chemical shifts were measured relative to TMS (0 ppm).

Mass spectra were acquired in positive ion mode using a Bruker ESQUIRE 3000 ion trap spectrometer equipped with a gas nebulizer probe, capable of analyzing ions up to m/z 6000. Nitrogen was used as drying gas at a flowrate of 4.5 L/min. The nebulizer pressure was 7.5 psi. Measurements and calculations are based on mass of most abundant isotopes.

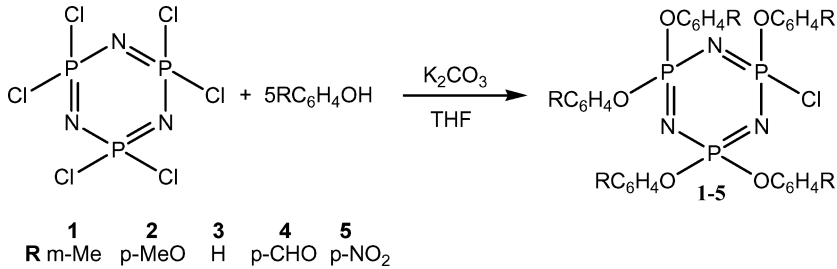
The high-resolution mass spectral data for compounds **2** and **3** were recorded on a Waters Q-Tof micro^{TM}spectrometer by electrospray ionization (ESI) mass spectrometer. The sample was analyzed as a solution in methanol.

Preparation of Hexachlorocyclotriphosphazene

Hexachlorocyclotriphosphazene was prepared by the method described previously.[9] Specifically, a correct quantity of active carbon was added to the reaction system under the reflux for 1 h after the reaction was over. The product was purified by recrystallization from heptane to give hexachlorocyclotriphosphazene as white crystals. Yield: 89%, mp 111–113°C (literature: 111.5–113.5°C), ^{31}P NMR (162 MHz, THF): δ 20.44 ppm (s).

Preparation of Chloropentaaryloxycyclotriphosphazenes

Hexachlorocyclotriphosphazene (1.44 mmol) and tetrahydrofuran (5 mL) were added to a three-neck flask. To this mixture, a solution of potassium aryloxide, which was prepared by the reaction of phenols (7.33 mmol) with potassium carbonate (7.33 mmol) in tetrahydrofuran (20 mL) before the reaction, was added dropwise at room temperature for 1 h. The reaction was kept at this temperature for 1–2 h and then filtered. The solvent was removed by rotary evaporation, and the residue was purified by chromatography on silica gel, for the compounds **1–4** using petroleum ether:ethyl acetate (20:1) as eluent, and for compound **5**, petroleum ether:tetrahydrofuran (4:1) was selected (Scheme 1).



SCHEME 1 Synthetic route of chloropentaaryloxycyclotriphosphazenes.

Data of the title compounds are given below:

Compound **1:** liquid, Yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$)δ ppm 7.15∼6.76 (m, 20H, C_6H_4), 2.27 (s, 15H, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$)δ ppm 21.63 (t, 1P), 6.46 (d, 2P), J(PP) = 84.2 Hz; ^{13}C NMR (100MHz, $CDCl_3$)δ ppm 150.35, 139.61, 129.13, 125.95, 121.76,118.11; IR (KBr) (cm^{-1}): 3033, 1610, 1586 and 1488 (Ar), 2920, 2856 and 1401 (CH_3), 1278, 1210 and 1140 cm^{-1}(P=N), 545P-Cl); ESI-MS: *m/z* 706.1$[M+H]^+$.

Compound **2:** White solid, mp: 78∼80°C, Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$)δ ppm 7.04∼6.70(m, 20H, C_6H_4), 3.78(s, 15H, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$)δ ppm 23.03 (t, 1P), 8.05 (d, 2P), *J*(PP) = 81.0 Hz; ^{13}C NMR (100 MHz, $CDCl_3$)δ ppm 156.77, 143.83, 122.12, 114.37, 55.52; IR (KBr) (cm^{-1}): 3003, 1589 and 1444(Ar), 2958, 2835 and 1400 (CH_3), 1210 and 1164cm^{-1}(P=N), 520 (P–Cl); ESI-MS: *m/z* 786.1$[M+H]^+$. ESI-MS: *m/z* 636.1$[M+H]^+$. HR-MS(ESI): *m/z* calcd. for $C_{35}H_{36}ClN_3O_{10}P_3$ $[M+H]^+$: 786.1297, found 786.1298.

Compound **3:** White solid, mp: 68∼70°C (literature: 69–71°C),[7] Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$)δ ppm 7.26∼6.91(m, 25H, C_6H_5); ^{31}P NMR (162 MHz, $CDCl_3$)δ ppm 22.93 (t, 1P), 7.63 (d, 2P), *J*(PP) = 82.8 Hz; ^{13}C NMR (100 MHz, $CDCl_3$)δ ppm 150.33, 129.52, 125.40,

121.23; IR (KBr) (cm^{-1}): 3060, 1591 and 1487(Ar), 1267, 1178 and 1152 (P=N), 500 (P–Cl); ESI-MS: *m/z* 636.1$[M+H]^+$. HR-MS(ESI): *m/z* calcd. for $C_{30}H_{26}ClN_3O_5P_3$ $[M+H]^+$: 636.0768, found 636.0770.

Compound **4:** White solid, mp: 92∼94°C, Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$)δ ppm 9.97(s, 5H, CHO), 7.83∼7.22 (m, 20H, C_6H_4); ^{31}P NMR (162 MHz, $CDCl_3$)δ ppm 20.71 (t, 1P), 5.17 (d, 2P), *J*(PP) = 85.8 Hz; ^{13}C NMR (100 MHz, $CDCl_3$)δ ppm 190.54, 154.28, 133.97, 131.47, 121.63; IR (KBr) (cm^{-1}): 3105, 1595 and 1499(Ar), 2825, 2741 (O=C–H), 1705 (C=O), 1210, 1179 and 1148 (P=N), 511 (P–Cl); ESI-MS: *m/z* 776.1$[M+H]^+$.

Compound **5:** White solid, mp: 169∼171°C, Yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$)δ ppm 8.22∼7.28(m, 20H, C_6H_4); ^{31}P NMR (162 MHz, $CDCl_3$)δ ppm 21.19 (t, 1P), 4.87 (d, 2P), J(PP) = 87.5 Hz; ^{13}C NMR (100 MHz, $CDCl_3$)δ ppm 153.95, 145.59, 125.71, 121.65; IR (KBr) (cm^{-1}): 3118, 1614, 1589 and 1480 (Ar), 1527 and 1350 (NO_2), 1203, 1183 and 1160 cm^{-1}(P=N), 498 (P–Cl); ESI-MS: *m/z* 861.1 $[M+H]^+$.

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