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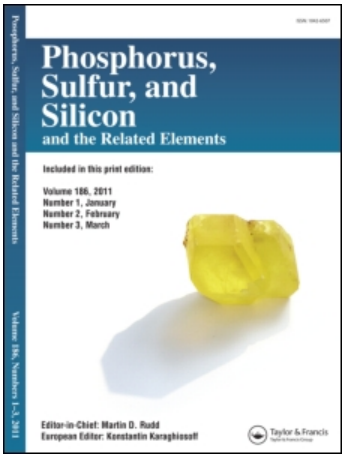

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Organo Phosphazenes: Preparation and Structure Determination of Some Reactive Difunctton-Terminated Tetra(Phenoxy)Cyclotriphosphazenes

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ORGANO PHOSPHAZENES: PREPARATION AND STRUCTURE DETERMINATION OF SOME REACTIVE DIFUNCTION-TERMINATED TETRA(PHENOXY)CYCLOTRIPHOSPHAZENES

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Abstract In this study, the reactive nongeminal difunction-terminated tetra(phenoxy)cyclotriphosphazenes $N_3P_3(O\phi)_4(OY)_2$, where OY=OϕCHO-*p*, OϕCH$_2$OH-*p*, and OCH$_2$-C≡CH, were synthesized as potential precursors for incorporating the phosphazene ring onto the traditional organic polymers. The structures of the compounds were determined. The applications of these compounds will be discussed in the meeting.

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INTRODUCTION

It is well known that reactive functional cyclotriphosphazenes are valuable precursors for synthesizing a wide range of organophosphazene-contained polymers.[1-5] In this study, we wish to report the synthesis and characterization of the nongeminal reactive difunction-terminated tetra(phenoxy)-cyclotriphosphazenes, $N_3P_3(O\phi)_4(OY)_2$, where Oϕ represents OC_6H_5 and OY represents OϕCHO-*p*, OϕCH$_2$OH-*p*, and OCH$_2$C≡CH. The phenoxide ion was chosen as one of the nucleophiles due to its reactivity and thermal stability. The preparation routes and the yields of the compounds are discussed, and the structures of the compounds are determined.

RESULTS AND DISCUSSION

As shown in the following scheme, there are two routes to synthesize the target compounds, nongeminal $P_3N_3(O\phi)_4(OY)_2$, using hexachlorocyclotriphosphazene, $P_3N_3Cl_6$, as a substrate for substitution by the sodium salt of proper alcohols.

$$N_3P_3Cl_6 + 4\ NaO\phi \xrightarrow{-4NaCl} N_3P_3(O\phi)_4Cl_2 \quad (I)$$

$$N_3P_3(O\phi)_4Cl_2 \xrightarrow[-2NaCl]{+2NaOY} N_3P_3(O\phi)_4(OY)_2 \quad \text{Route 1}$$

$$N_3P_3Cl_6 + 2\ NaOY \xrightarrow{-2NaCl} N_3P_3(OY)_2Cl_4 \quad (I)$$

$$N_3P_3(OY)_2Cl_4 \xrightarrow[-4NaCl]{+4NaOC_6H_5} N_3P_3(O\phi)_4(OY)_2 \quad \text{Route 2}$$

In this study, compound II, $N_3P_3(O\phi)_4(O\phi CHO\text{-}p)_2$, was prepared according to Route 1. An attempt to follow Route 2 was unsuccessful due to the displacement of 4-fomylphenoxide by phenoxde. However, Route 2 was followed for compound III, $N_3P_3(O\phi)_4(OCH_2C{\equiv}CH)_2$ to obtain higher yield. The hydroxy-terminated phosphazene compound IV, $N_3P_3(O\phi)_4(O\phi CH_2OH\text{-}p)_2$ was synthesized by reduction of compound II according to the following reaction:

$$N_3P_3(O\phi)_4(O\phi CHO\text{-}p)_2 \xrightarrow[2.3N\ HCl]{1.NaBH_4} N_3P_3(O\phi)_4(O\phi CH_2OH\text{-}p)_2$$

Table I. Yield and Elemental Analysis data.

cpd	yield %[a]	Elemental Analysis % found C	H	N	% calcd C	H	N
II	62	61.00	4.03	5.58	60.88	4.01	5.61
III	42	58.45	4.19	6.61	58.35	4.21	6.81
IV	50	60.63	4.55	5.55	60.56	4.52	5.57

a: the yield was calculated from the starting compound $N_3P_3Cl_6$.

As listed in Table I, the compounds produced were in good yields and the Elemental Analysis data found were in consistant with the calculated values. The Mass data of the compouds all showed the molecular ion peaks. The fragmentation pathway observed mainly involved the loss of $-O\phi$, $-O\phi CHO\text{-}p$

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for compound II, -Oϕ, -$OCH_2C{\equiv}CH$for compound III, and -Oϕ, -OϕCH_2OH for compound IV, respectively. The retention of the cyclic trimeric ring was shown by the presence of the strong absorption at 1100-1300 cm^{-1} in the IR spectra. The characteristic absorptions for the phenoxy, aldehyde and propargyloxy groups were also observed for the individual case and listed in Table II.

Table II. IR data of the compounds (cm^{-1}).

cpd	PN	P-O-C	C=C(Ar)	C=O	O-H	C≡C	≡C-H
II	1140	1050	1600,1500,1470	1700	-	-	-
III	1225	1000	1600,1495,1455	-	-	2100	3300
IV	1140	1050	1600,1500,1470	-	3600-3200	-	-

The NMR(^1H, ^{13}C, ^{31}P) data for the compounds are listed in Table III. The spectra were all in accord with the assigned

Table III. NMR data of the compounds (ppm)[b].

cpd		^{31}P		^1H	^{13}C
II	P(OϕCHO-*p*)(Oϕ)	8.9	-CHO	9.98(s)	190.3
	$P(O\phi)_2$	8.9	-Oϕ	6.8-7.7(m)	120.7-154.7
			-Oϕ	6.8-7.7(m)	120.7-154.7
III	$P(OCH_2C{\equiv}CH)(O\phi)$	12.9	≡C-H	3.25(t)	75.5
	$P(O\phi)_2$	9.3	$-CH_2$	4.65(m),4.07(m)	54.0
			-C≡	-	77.4
	J_{AB}	89.7	-Oϕ	6.8-7.5(m)	121.3-150.4
IV	P(OϕCH_2OH-*p*)(Oϕ)	8.5	$-CH_2$	4.74(s)	63.2
	$P(O\phi)_2$	8.5	-OH	3.00(s)	-
			-Oϕ	7.0-7.5(m)	120.1-154.9

b: the ^1H and ^{13}C chemical shifts are given in ppm relative to TMS, ^{31}P data are relative to 85% H_3PO_4, and the coupling constants are in Hz.

structures. Of particular interest were the ^{31}P NMR spectra. For compound II, the singlet and sharp resonance at 8.9 ppm revealed that the aldehyde group was far from the skeletal

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phosphorus atoms that seperated chemical shifts were not detected for P(OΦ)(OΦCHO-*p*) and P(OΦ)$_2$ environments. Similarly, for compound IV, the chemical shift of P(OΦ)(OΦ-CH_2OH) was overlapped with that of P(OΦ)$_2$ at 8.5 ppm. Since tetra(phenoxy)dichlorocyclotriphosphazene isolated in the first step of Route 1 was exlusively nongeminal isomer, compounds II and IV were also exclusively nongeminal isomers. On the other hand, two sets of AB_2 patterns seperated by about 0.3 ppm and a trace of AX_2 pattern indicated that compound III were predominantly *cis* and *trans* nongeminal isomers with trace amount of geminal isomer.
For application, we further used compound III and compound IV as precursors and successfully prepared cyclotriphosphazene-contained polydiacetylene and cyclotriphosphazene-contained polyurethane. Details about this will be published elsewhere.

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CONCLUSION

In all, we prepared three nongeminal difunction-terminated cyclotriphophazene compounds and showed good yields. These newly reported difunctional cyclotriphosphazenes represent examples of organofunctional phosphazenes and will exhibit interesting monomer and polymer chemistry.

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