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THE REACTION OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE WITH BROMONEOPENTYL GLYCOL

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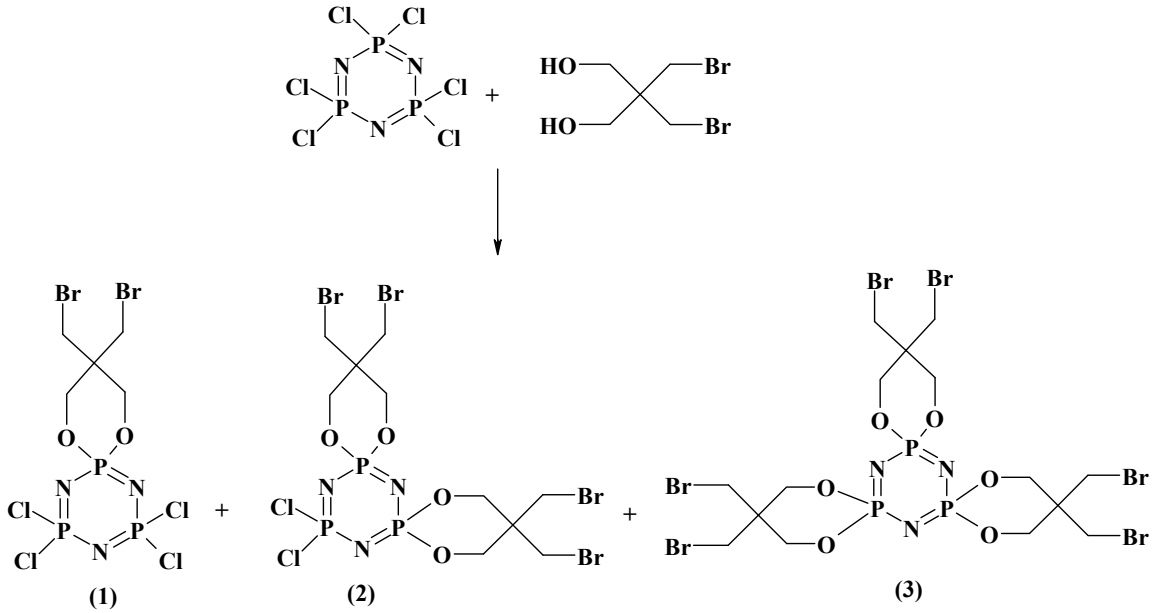
Abstract – In the present work, novel phosphazene derivatives, monospiro- **(1)**, dispiro- **(2)**, and trispiro-2,2-bis(bromomethyl)-1,3-propandioxy **(3)** substituted cyclotriphosphazatrienes were synthesized with the reaction of bromoneopentyl glycol(2,2-bis(bromomethyl)-1,3-propandiol) with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$. The structures of the compounds were determined by elemental analysis, mass spectrometry, ^1H and ^{31}P NMR spectroscopy. The thermal properties of the compounds **(1)**, **(2)** and **(3)** were investigated by DSC and TGA.

INTRODUCTION

Many papers deal with reactions of hexachlorocyclotriphosphazatriene (trimer) with monofunctional alcohols.[1-9] The reactions of phosphazenes with difunctional amines and difunctional alcohols are widely studied.[10-14] Four different structural types which are spiro, ansa, bridged, and open chain are formed with the reactions of cyclophosphazenes with difunctional reagents.[15-17] Reaction of $N_3P_3Cl_6$ with 1,2-ethane-, 1,3-propane- and 1,4-butane-diols (in the presence of pyridine to neutralize the HCl formed) predominantly gave spiro derivatives with 5-, 6-, 7-membered phosphate rings, respectively, whereas ansa derivatives were obtained only in small yields.[13,14,18] The reactions of trimer with 2,2-dimethylpropane-1,3-diol yield monospiro, dispiro, trispiro, ansa, spiro-ansa and doubly-bridged derivatives.[13] The chemical and physical properties of phosphazenes change with the substituted side groups. For example, it is possible to design materials with special properties such as inflammable textile fibers and advanced elastomers,[19] hydraulic fluids and lubricants,[20,21] electrical conductivity.[22] In this study, the reactions of $N_3P_3Cl_6$ with bromoneopentyl glycol, which is an analogue of 1,3-propanediol and is widely used as fire retardent [23] and

anti cancer agent,[24] have been carried out and the compounds **(1)**, **(2)** and **(3)** were obtained. These compounds could be used as precursors in the synthesis of phosphazene polymers, especially in the preparation of flame retardent metarials. Therefore, thermal properties of compounds **(1)**, **(2)** and **(3)** were also investigated with DSC and TGA.



Scheme 1

RESULTS AND DISCUSSION

Hexachlorocyclotriphosphazatriene was reacted with 2, 2-bis(bromomethyl)-1,3-propanediol at 1:1 molar ratio in dry THF in the presence of anhydrous pyridine as hydrogen chloride acceptor for two days at the boiling point of THF under argon atmosphere. At the end of the reaction, the analysis of the reaction mixture by proton decoupled ^{31}P NMR (Figure 1a) shows that the compound **(1)** is the major product and the compounds **(2)** and **(3)** are the minor products. Figure 1a also shows that starting material, $N_3P_3Cl_6$, and trace products which are probably corresponding to ansa and spiro-ansa derivatives exist in the reaction mixture. Formation of the ansa structures in trace amount can be due to the effects of gem-dialkyl groups which is known as Thorpe-Ingold effect.[13,25-29] Therefore, in the substitution reaction of bromoneopentyl glycol with $N_3P_3Cl_6$, gem-CH_2Br groups may result in six membered spiro ring to form, rather than eight membered ansa ring. Based on the area under each peak in the proton decoupled ^{31}P NMR spectrum (Figure 1a), the relative amounts of the compounds **(1)**, **(2)** and **(3)** are calculated as 53.20%, 21.94% and 2.19%, respectively. The yields were 48% for **(1)**, 15 % for **(2)** and 1.90% for **(3)**. Although these results are slightly different to those found by the isolation and purification procedure, the ^{31}P NMR of the reaction mixture is likely to be more representative of the quantitative analysis of the reaction products because the

only separation procedure of the reaction mixture was to filter off the pyridine hydrochloride prior to NMR measurements.

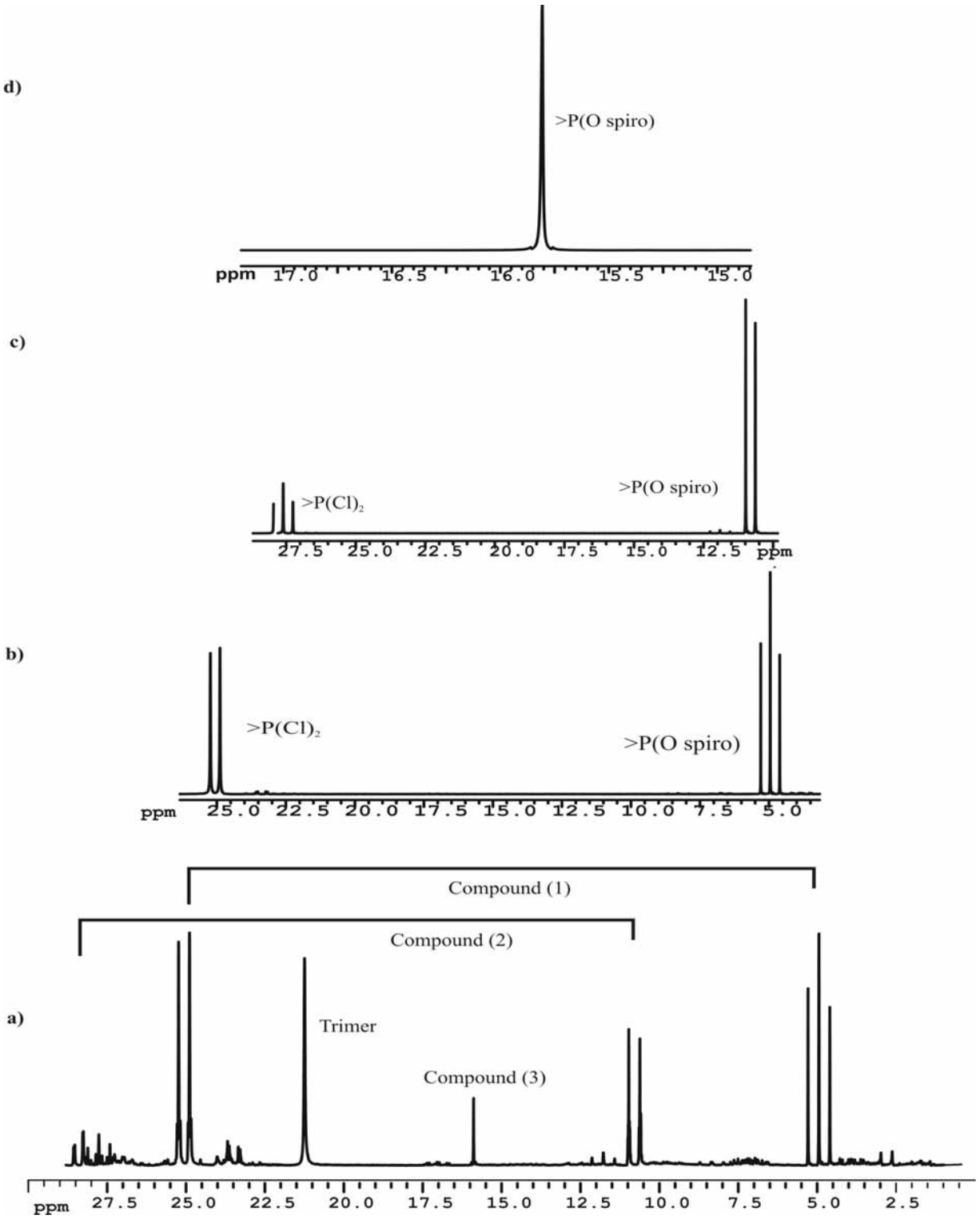


Figure 1. a) Proton decoupled ^{31}P NMR spectrum of the reaction mix. b) Proton decoupled ^{31}P NMR spectrum of compound **(1)** c) Proton decoupled ^{31}P NMR spectrum of compound **(2)** d) Proton decoupled ^{31}P NMR spectrum of compound **(3)** .

The proton decoupled ^{31}P NMR spectrum of the compound **(1)**, 2, 2-(2', 2'-bis(bromomethyl)-1', 3'-propandioxy)-4, 4, 6, 6-tetrachlorocyclophosphazatriene, has A_2X spin system because of two different phosphorus environments within the molecule. It is seen that doublet at δ = 25.06 ppm and triplet at δ = 4.95 ppm are caused by PCl_2 and P(O spiro) groups, respectively ($^2J_{PNP}$ = 69.8 Hz) (Figure 1b). The proton decoupled ^{31}P NMR spectrum of the compound **(2)**, bis(2', 2'-bis(bromomethyl)-1', 3'-propandioxy)-tetracholorocyclotriphosphazene, has AX_2 spin system because of two different phosphorus environments within the molecule. It is seen that doublet at δ = 10.81 ppm and triplet at δ = 27.60 ppm are caused by P(O spiro) and PCl_2 groups, respectively ($^2J_{PNP}$ = 70.4 Hz) (Figure 1c). The proton decoupled ^{31}P NMR spectrum of the compound **(3)**, 2, 2, 4, 4, 6, 6-tris-(2', 2'-bis(bromomethyl)-1', 3'-propandioxy)-cyclophosphazatriene, has A_3 spin system because of all of phosphorus environments are the same within the molecule. It is seen that singlet at δ = 15.8 ppm is caused by P(O spiro) group (Figure 1d).

Furthermore, proton coupled ^{31}P NMR spectra of the compounds **(1-3)** show that the bromoneopentyl glycol replaces two the chlorine atoms in compound **(1)**, four in compound **(2)** and six in compound **(3)**. As an example only the proton coupled ^{31}P NMR spectrum of compound **(1)** is given in Figure 2a which is used to assign the signals at ca. 25 ppm to the PCl_2 groups (no coupling), the signal at ca. 5 ppm corresponds to the P(O spiro)group (expanded signals in Fig. 2b). The three bond-coupling constant of the P(Ospiro) group is calculated as $^3J_{PH}$ = ~13.78 Hz for all three compounds, which is similar to that for 2,2-dimethylpropane-1,3-dioxy substituted cyclophosphazenes ($^3J_{PH}$ = ~ 13.3 Hz).[13]

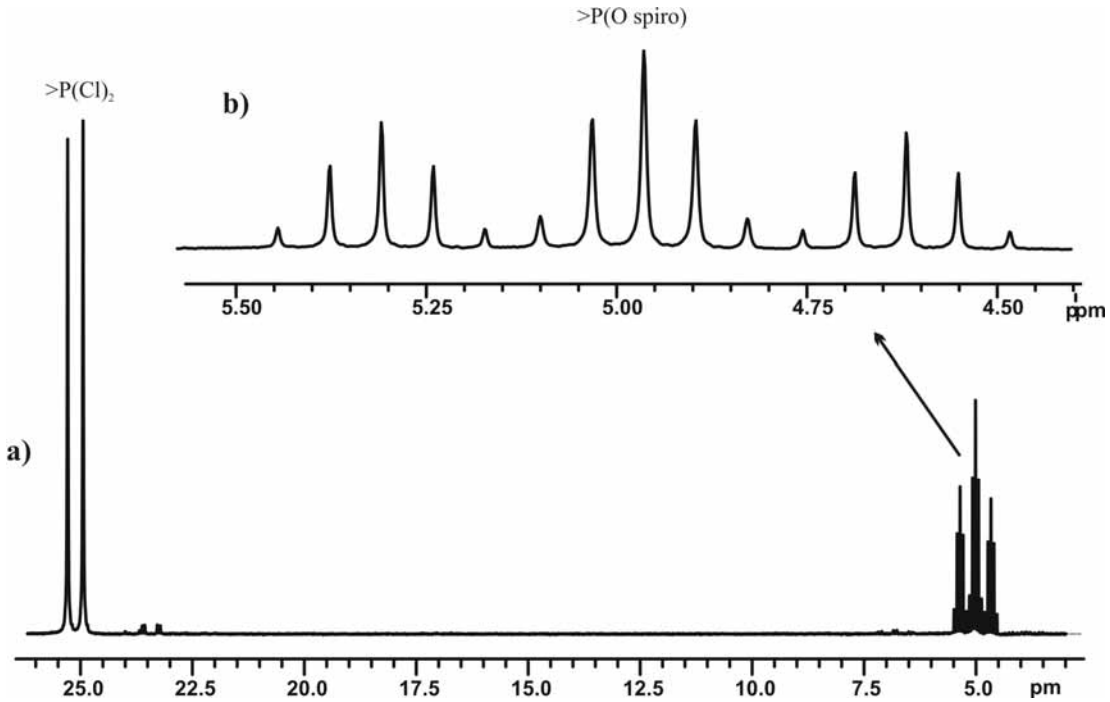


Figure 2. a) Proton coupled ^{31}P NMR spectrum of compound **(1)** b) expansion of signals of the P(O spiro) group.

In general, ^{1}H NMR spectra of the compounds **(1-3)** are essentially identical; the -OCH_2- protons are seen as multiplet ($^{3}J_{H-P}$ = 9.08 Hz, $^{2}J_{H-H}$ = 11.05 Hz, $^{4}J_{H-H}$ = 1.36 and 2.75 Hz) about δ = 4.30-4.50 ppm and -CH_2Br protons are seen as multiplet ($^{4}J_{H-H}$ = 0.94 and 1.38 Hz) at δ = 3.64-3.67 ppm.

Differential Scanning Calorimetry (DSC) was used to determine the thermal transitions of the compounds **(1-3)**. Endothermic peaks corresponding to melting points (*T*m) were generally higher than the *T*m (114 °C) of $N_3P_3Cl_6$. Although the melting points of the new compounds increase with the substitution, compound (**3**) starts to decompose without melting at 314 ºC (Table 1).

Thermogravimetric analysis (TGA) data of bromoneopentyl gylcol, $N_3P_3Cl_6$ and the compounds **(1-3)** are given in Table 1. TGA analyses of compounds showed us the thermal stability of product incerases with the substitution. For instance, while the starting materials, bromonepentyl gylcol and trimer, are exceeding % 99 weight loss at 325 ºC, compounds **(1)**, **(2)**, and **(3)**, respectively, have ~ 46%, 28%, 23% weight loss at this temperature. Furthermore, the new phosphazene derivatives **(1- 3)** gave increasing char yields, which are, respectively, ~ 20%, 32%, and 35% at 700 ºC (Table 1) .

Table 1. DSC and TGA Data for Cyclotriphosphazenes

Compound	DSC *T*m(°C)	TGA (% wt loss)							TGA (% residue)
		175°C	250°C	325°C	400°C	475°C	550°C	625°C	700ºC
Bromoneopenthyl gylcol	112-114	3,8	84,7	99,3	-	-	-	-	0,7
$N_3P_3Cl_6$	114	30,7	99,5	-	-	-	-	-	0,48
(1)	161	0,5	12,7	45,8	68,5	72,2	76,6	78,7	19,9
(2)	187	-	2,5	27,5	55,1	59,3	64,8	66,9	32,2
(3)	314(decomp.)	-	-	23,3	51,3	55,4	61,67	64,7	35,3

EXPERIMENTAL

1. Materials

Hexachlorocyclotriphosphazene (a gift from the Otsuka Chemical Co. Ltd.) was purified by fractional crystallization from *n*-hexane. Bromoneopentyl glycol (Aldrich, 98 %), the following chemicals were obtained from Merck; THF (≥ 99.0 %), *n*-hexane (≥ 99.0 %), pyridine (≥ 99.0 %). All solvents used in this work were purified by conventional methods. THF was distilled over a sodium-potassium alloy under

an atmosphere of dry argon. The deuteriated solvent ($CDCl_3$) for NMR spectroscopy was obtained from Goss Scientific.

2. Methods

Elemental analyses were obtained using a Carlo Erba 1106 Instrument. Mass spectra were an Bruker MicrOTOF LC/MS spectrometer using Electro Spray Ionisation (ESI); ^{35}Cl values were used for calculated masses. Analytical Thin Layer Chromatography (TLC) was performed on silica gel (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 70-230 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). ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^1H NMR and 85 % H_3PO_4 as an external reference for ^{31}P. Thermal data were collected on Mettler Toledo DSC822^e and TGA851 instruments between 25-250 ºC for DSC and 25-700 ºC for TGA using constant 10 ºC/min heating rate with the Star^e Software. Calibration of instruments were made using the standard In/Zn calibration method and spectro grade argon was used as protective and purge gas for all thermal experiments.

3. Synthesis

A solution of $N_3P_3Cl_6$ (3 g, 8,62 mmol) in dry THF (10 mL) was added dropwise to a stirred solution of bromoneopentyl glycol (2,26 g, 8,62 mmol) in dry THF (20 mL) and anhydrous pyridine (1,36 g, 17,24 mmol) in a 100 mL three-necked round-bottomed flask and the reaction mixture was refluxed in oil bath with stirring with magnetic stirrer for 48 h. Then, the reaction mixture was allowed to cool to rt and pyridine hydrochloride was filtered off and the solvent was removed under reduced pressure at 30 °C. $N_3P_3Cl_6$ [Rf = 0.80] and three compounds were detected [Rf = 0.60 (1), 0.42 (2) and 0.16 (3)] by thin-layer chromatography using *n*-hexane-THF (6:1) as mobile phase. These products were separated by column chromatography on silica gel using *n*-hexane-THF (6:1) as eluent. These products are powder and stable on air. Anaytical data of these compounds are given in Table 2.

Table 2. Analytical data of Cyclotriphosphazenes

Comp.	Formula	Anal. Data (%)						MASS	
		Calculated			Found			M^+	$(M)^a$
		N	C	H	N	C	H		
(1)	$C_5H_8Br_2Cl_4N_3O_2P_3$	7,83	11,19	1,50	7,85	11,21	1,52	537	538
(2)	$C_{10}H_{16}Br_4Cl_2N_3O_4P_3$	5,79	16,55	2,22	5,81	16,54	2,22	725	726
(3)	$C_{15}H_{24}Br_6N_3O_6P_3$	4,59	19,70	2,64	4,60	19,71	2,65	915	916

[a] Based on mass of most abundant isotopes

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