



## Synthesis and study of some new tricyclophosphazene containing organo-sulfur and -selenium compounds as fire retardants

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### Abstract

A new series of hexaarylthiocyclophosphazenes and hexaarylselenocyclophosphazenes (*i.e.*  $N_3P_3(E-C_6H_4-R)_6$ , where E= S, R= H(1); E= S, R= OCH<sub>3</sub>(2); E= S, R= CH<sub>3</sub>(3); E= Se, R= H(4); E= Se, R= OCH<sub>3</sub>(5) and E= Se, R= CH<sub>3</sub>(6)) were prepared in good yields by reaction of the corresponding arylthiolate and arylselenolate anions with hexachlorocyclophosphazene under argon atmosphere. The thermal properties of compounds 1-6 were studied by TGA. All prepared compounds showed a good thermal stability. Char yields were between 37-68% at 750°C for compounds 1-6. All compounds were characterized by elemental analysis, FT-IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR and thermal gravimetric techniques.

**Keywords:** Hexachlorocyclophosphazene, Arylthiolate, Arylselenolate, Fire retardants

### Introduction

Phosphazenes, compounds having -P=N- group in their molecules, constitute one of the important class of compounds in the chemistry of phosphorus and nitrogen [1]. The highly reactive P-Cl bonds in hexachlorocyclophosphazene can be easily replaced by reaction with alcohols, amines and organometallic reagents. The halogen replacement reactions are the most important ways to increase the diversity of cyclophosphazenes [1-4]. Chlorocyclophosphazenes have been widely studied because they have excellent flame retardancy and environmental safety. It is worth noting that hexaaryloxyphosphazene and perfluoroaryloxyphosphazene exhibit excellent thermal and chemical stability which can be used to fireproof materials, high temperature lubricants, vacuum pump oils and hard disk surface lubricants [5-7]. Research about the functionality of polyphosphazene is very active and includes flame retardant, special rubber, biomedicine, liquid crystal, photoelectricity materials, and many other uses [8-11].

The aim of this work is to prepare a new series of cyclotriphosphazenes containing organosulfur and organoselenium moieties in hope to use them as fire retardants. To the best of our knowledge, no such compounds have been prepared in the literature.

## 2. 2. Experimental

### 2.1. Synthesis

Phosphorous pentachloride, ammonium chloride and sodium hydride were analytical reagents. All of the materials were purchased from commercial sources and used directly. All of the solvents were analytical grade and distilled before use. Compounds diphenyldiselenide [12], bis(4-methoxyphenyl) diselenide [13], bis(4-methylphenyl) diselenide [14], diphenyldisulphide [15], bis(4-methoxyphenyl) disulphide [16] and bis(4-methylphenyl) disulphide [17] were prepared according to literature methods. Hexachlorocyclotriphosphazene was prepared from the reaction of phosphorus pentachloride and ammonium chloride according to a literature method [18].

#### 2.1.1 Hexa(phenylthio)cyclotriphosphazene (1)

To 0.20 mole of phenyllithium in 100 cm<sup>3</sup> THF was added cautiously 6.41g. (0.20g. atom) of sulfur. The reaction was exothermic; the stirring was continued until all the sulfur had been disappeared. The resulting solution was stirred for additional 1 h at room temperature. The solution was cooled in ice-bath and a solution of hexachlorocyclotriphosphazene (10.43g; 0.03mol) in dry THF (100 cm<sup>3</sup>) was added drop wise to the rapidly stirred solution of PhSLi. After the addition was complete, the reaction mixture was stirred for 24 h at room temperature. The resulting solution was hydrolyzed with distilled water and the extracted with dichloromethane (5 x 50 cm<sup>3</sup>). The organic layer was dried over anhydrous

calcium chloride. Solvent was removed by rotary evaporator, to give a white solid product. Recrystallization of the product from a mixture of ethyl acetate-CH<sub>2</sub>Cl<sub>2</sub> gave compound **1** as a white solid in 56% yield.

#### 2.1.2. Hexakis(*p*-methoxyphenylthio)cyclotriphosphazene (**2**)

This compound was prepared by the same above method using *p*-methoxyphenyl lithium as starting material. Compound **2** was obtained as a white solid in 62% yield.

#### 2.1.3 Hexakis(*p*-methylphenylthio)cyclotriphosphazene (**3**)

Compound **3** was prepared by the same method described above using *p*-methylphenyllithium as starting material. Compound **3** was obtained as a white solid in 52% yield.

#### 2.1.4. Hexa(*phenylseleno*)cyclotriphosphazene (**4**)

This compound was prepared by two methods:

##### Method A

To a solution of bromobenzene (14.13g; 0.09mol) in anhydrous THF (100cm<sup>3</sup>) was added slowly a solution of n-BuLi (1.6 M in hexane, 0.09 mol) at -25°C. The resulting solution was stirred for 30 min under argon atmosphere. When the reaction temperature reached -10°C, selenium powder (7.11g; 0.09 mol) was added all at once. The selenium was completely dissolved, and then hexachlorocyclotriphosphazene (5.22g; 0.015mol) was added to the reaction mixture at -10°C. The reaction mixture was stirred for an additional 30 min at 0°C and an aqueous NH<sub>4</sub>Cl (100cm<sup>3</sup>) was then added. The combined organic extracts were dried over MgSO<sub>4</sub>, filtered and evaporated to afford a crude residue, which was flash chromatographed on hexanes/ethyl acetate (2/1) to afford compound **4** as a white solid in 35% yield.

##### Method B

Sodium borohydride (1.90g; 0.05mol) was added portionwise to a solution of diphenyldiselenide (7.50g, 0.024 mol) in dry THF (30 cm<sup>3</sup>) under argon. The reaction mixture was stirred at room temperature for 30min. The mixture was then treated with a solution of hexachlorocyclotriphosphazene (2.78g, 0.008mol) in THF (25 cm<sup>3</sup>). After stirring for 45 min at room temperature, the reaction mixture is diluted with THF (20 mL), and heated to 60°C with vigorous stirring. After 8h, the mixture is concentrated in vacuo, treated with H<sub>2</sub>O (20 cm<sup>3</sup>) and extracted with diethyl ether (4 x 25cm<sup>3</sup>). The combined organic extracts are dried over MgSO<sub>4</sub>, filtered and evaporated to afford a crude residue, which was flash chromatographed on hexane/ethyl acetate (2/1) to afford compound **4** as white solid in 71 % yield.

#### 2.1.5. Hexakis(*p*-methoxyphenylseleno)cyclotriphosphazene (**5**)

The procedure (method B) is similar to that described for the preparation of **4** except that bis(4-methoxyphenyl) diselenide was used in place of diphenyldiselenide. Compound **5** was obtained in 66% yield as a pale yellow solid.

#### 2.1.6. Hexakis(*p*-methylphenylseleno)cyclotriphosphazene (**6**)

Compound **6** was prepared by method B using bis(4-methylphenyl) diselenide in place of diphenyldiselenide. A pale yellow solid was obtained in 57% yield.

### 2.2. Physical measurements

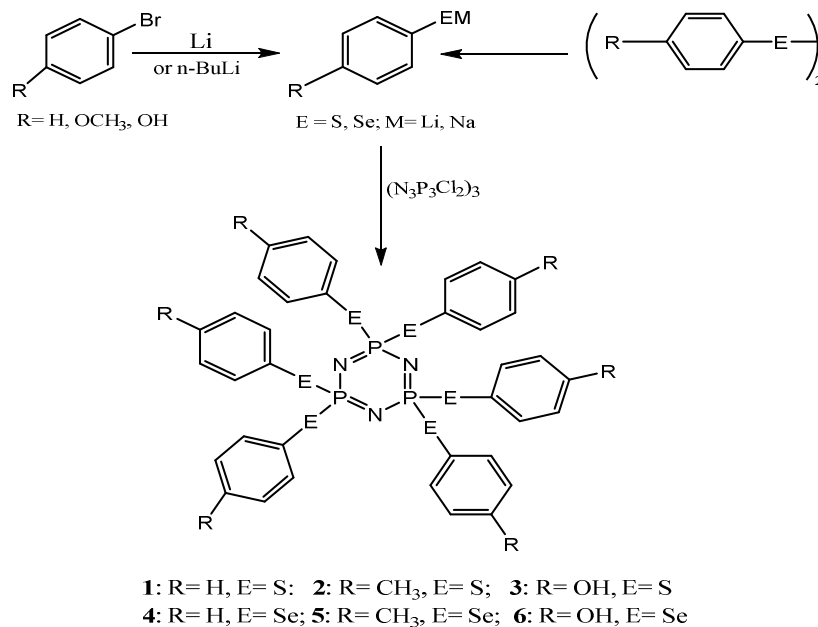
<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a Bruker 300 spectrometer instrument. They were recorded as DMSO-d<sub>6</sub> solutions containing TMS as internal standard. The chemical shifts for all <sup>1</sup>H and <sup>13</sup>C NMR spectra were reported in δ units downfield from the internal reference Me<sub>4</sub>Si. Elemental analyses (C, H, N and S) were performed by Analytical Laboratories of Konstanz University, Germany. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The electronic absorption spectra in the 800–200 nm range were recorded on Sean-80D UV-Vis spectrophotometer, using 1 cm quartz cells. Thermogravimetry (TG) analysis was carried out on a TGA QSO V6.3 Build 189, Universal V4.1 DTAA instrument under argon atmosphere in the temperature range from room temperature to 900°C with 20°C min<sup>-1</sup> heating rate.

## 3. Results and discussion

A series of experiments show that reaction of lithium arylthiolate and sodium arylselenolate are the most suitable reagents for the preparation of these new derivatives. Thus, reaction of aryllithium with sulfur gave the corresponding arylthiolate, which in turn reacted with hexachlorotriphosphazene to give compounds **1**, **2** and **3** in 56%, 62% and 52% yields, respectively. Compounds **4-6** were prepared using two different methods (Scheme 1).

The first one consists of reaction of lithium arylselenolate (prepared from aryl bromide, n-BuLi and selenium powder, method A) with hexachlorocyclotriphosphazene. In the second method, sodium arylselenolate (generated *in situ* from reaction of diaryl diselenide with NaBH<sub>4</sub> (Method B) was reacted with

hexachlorocyclotriphosphazene (Scheme 1). The target products were isolated with good yields (from 57% to 71%) using method B. On the other hand, when using method A, the yield was very low (less than 20%). Method B was also used to prepare compounds **1-3**, but the yields did not exceed more than 15%, Scheme 1. Compounds **1-6** were obtained as white to yellowish-white solids with sharp melting points (Table 1).



**Scheme 1.** Methods of preparation of compounds **1 – 6**.

**Table 1.** Elemental analysis, melting points and yields for compounds **1 – 6**.

Compd.	M.p. °C	Yield (%)	Analysis(%) <sup>a</sup>			
			C	H	N	S
<b>1</b>	112-114	56	54.67(54.74)	3.80(3.83)	5.21(5.32)	24.05(24.35)
<b>2</b>	120-121	62	51.83(52.00)	4.29(4.36)	4.21(4.33)	19.42(19.83)
<b>3</b>	140-143	52	49.01(48.80)	3.33(3.41)	4.67(4.74)	21.35(21.72)
<b>4</b>	119-121	71	40.56(40.36)	2.78(2.82)	3.87(3.92)	
<b>5</b>	103-105	66	40.42(40.31)	3.32(3.38)	3.25(3.36)	
<b>6</b>	136-138	57	36.96(37.04)	2.46(2.59)	3.48(3.60)	

<sup>a</sup> Calculated values are in parentheses.

The characteristic stretching peaks in the IR spectra of the phosphazenes have been assigned. The P=N stretching vibrations, which were observed between 1167 and 1194 cm<sup>-1</sup>, are characteristic of cyclotriphosphazenes [19]. These peaks are shifted to longer wavelengths for **1-6** than in cyclotriphosphazene, which appeared at 1218 cm<sup>-1</sup> [20]. The <sup>1</sup>H and <sup>13</sup>C NMR data also confirm the structures of **1-6**. In the <sup>1</sup>H NMR spectra the CH<sub>3</sub> proton is observed at 2.43 and 2.59 ppm for compounds **3** and **6**, respectively. The methyl protons of methoxy groups for compounds **2** and **5** are observed at 3.23 and 3.64 ppm, respectively. The aromatic protons for all the compounds appear between 6.65 and 7.65 ppm, Table 2.

The detailed <sup>13</sup>C NMR spectral data are given in Table 2. The Se-bound carbon atoms for **4**, **5**, and **6** were observed at 131.7, 122.7 and 126.9 ppm, respectively and agree well with literature values [21]. The methoxycarbons for compounds **3** and **6** were observed at 22.4 and 22.3 ppm, respectively. In general the spectra agree well with the expected structure for each compound, Table 2.

The <sup>31</sup>P NMR spectra of compounds **1-6** exhibit a single peak between 12-15 ppm, indicating that those three phosphorus atoms of the cyclotriphosphazene have the same chemical environment after the hexachlorocyclotriphosphazene is combined with organosulfur or organoselenium compounds, Table 2.

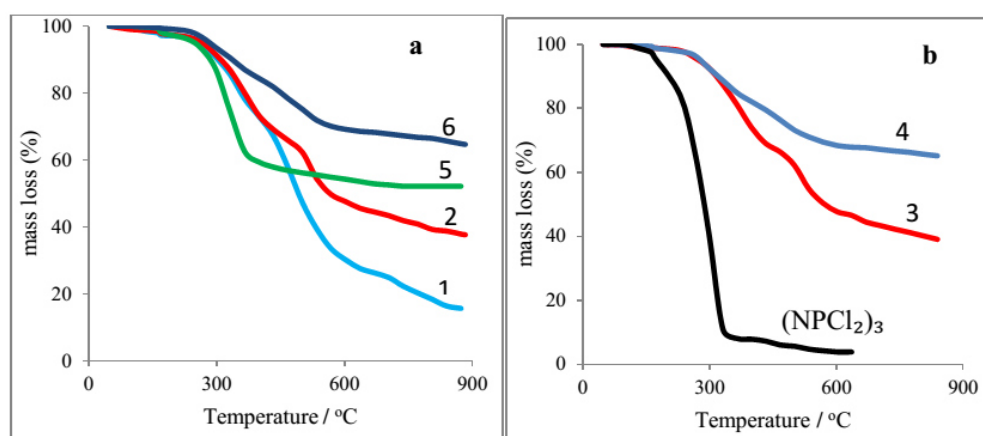
**Table 2:**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of compounds **1-6**.\*

Compd.	$^1\text{H}$ NMR, $\delta$	$^{13}\text{C}$ NMR, $\delta$	$^{31}\text{P}$ NMR, $\delta$
<b>1</b>	7.14(m, 6H, Ar-H); 7.19(m, 12H, Ar-H); 7.31(12H, d, Ar-H);	125.6, 129.0, 129.5, 132.6	12.1
<b>2</b>	3.23(s, 18H, OCH <sub>3</sub> ); 6.68(d, 12H, $J=8.5\text{Hz}$ , Ar-H); 6.85(d, 12H, $J=8.6\text{Hz}$ , Ar-H).	56.6, 114.6, 124.6, 130.4, 157.4.	14.5
<b>3</b>	6.76(d, 12H, $J=8.71\text{Hz}$ , Ar-H); 7.02(d, 12H, $J=8.3\text{Hz}$ , Ar-H); 8.85(sb, 6H, OH).	123.3, 125.1, 130.8, 155.3.	13.6
<b>4</b>	7.02(m, 6H, Ar-H); 7.11(m, 12H, Ar-H); 7.21(d, 12H, $J=7.65\text{Hz}$ , Ar-H).	128.7, 128.6, 130.4, 131.1	15.8
<b>5</b>	3.64(s, 18H, OCH <sub>3</sub> ); 7.04(d, 12H, $J=8.80\text{Hz}$ , Ar-H); 7.82(d, 12H, $J=8.2\text{Hz}$ , Ar-H).	55.8, 114.3, 122.7, 132.1, 160.6.	15.1
<b>6</b>	6.96(d, 12H, $J=7.95\text{Hz}$ , Ar-H); 7.12(d, 12H, $J=8.25\text{Hz}$ , Ar-H); 14.9(sb, 6H, OH).	115.9, 123.0, 132.6, 158.5.	14.3

\*The spectra were recorded in DMSO- $d_6$  at room temperature.  $\delta$  in ppm.

The absorption spectra of the new compounds (*i.e.* **1-6**) were measured in dichloromethane with dilute solutions of  $1 \times 10^{-5} \text{ mol dm}^{-3}$ . Absorption bands were observed for compounds **2** and **3** at 260 and 270 nm, and 230, 260 and 270 nm for compound **6**. Almost the same spectra were observed for compounds **1**, **4** and **5**. No outstanding conclusions could be made from these spectra.

TGA analysis was used to investigate the thermal stabilities of all studied compounds. The thermal degradation of pure hexachlorocyclotriphosphazene begins at about 100°C and is almost complete at 300°C with the mass loss of 96% due to the loss NH<sub>3</sub>, HCl and N<sub>2</sub>, Fig. 1b.



**Figure 1.** TGA curves for compounds **1-6** and  $(\text{NPCl}_2)_3$ .

Thermal degradation of compounds **1-6** was studied up to 900°C and the char yield was found between 37-68% at 750°C, Fig. 1 and Table 3.

**Table 3:** Thermal properties of compounds **1-6**.\*

Compounds	$T_i$	$T_f$	% Char content at 750°C
<b>1</b>	283.8	575.7	41
<b>2</b>	279.7	567.6	37
<b>3</b>	328.4	575.6	38
<b>4</b>	255	551	67
<b>5</b>	236.5	385	52
<b>6</b>	259	551	68

\* $T_i$ = initial temperature,  $T_f$  = final temperature.

In general, the TGA figures show that only compound **5** evaporates firstly, stabilizing at 380°C and exhibiting a higher residue at 800 °C than the corresponding values of the organosulphur compounds **1-3**. Furthermore, compounds **4** and **6** seem to be the most thermal stable compounds, Fig. 1. This is in contrast to the fact that

S-C bond is stronger than Se-C bond [22]. As a result, the high char yields of these compounds make them good flame retardants, based on previously published theory [23]. These results are consistent with previous works [23,24].

## Conclusion

In conclusion, we prepared a new series of cyclotriphosphazene derivatives containing organosulfur and organoselenium moieties. Those compounds show promise for use as fire retardants.

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## References

1. a) Allcock, H. R. *Phosorous-Nitrogen Compounds*, Academic press, New York, (1972).  
b) Allcock H.R. *Chem. Rev.* 72 (1972) 315. c) Allen, C.W. *Chem. Rev.* 91 (1991) 119.
2. Emsley J., Udy, P. B. *J. Chem. Soc. A*, (1972)768.
3. Manners, I. *Coord. Chem. Rev.* 137 (1994) 109.
4. Zhang, J. F., Can, X, Ou, X.M., Fu, W.F. *Chem. Res. Chinese U.* 23 (2007) 679
5. Voznicova, R.K., Taraba, J., Prihoda J., Alberto, M. *Polyhedron.* 27 (2008) 2077.
6. Nader, B.S., Kar, K.K., Morgan, T.A. *Tribol. Trans.* 35 (1992) 37.
7. Zhao, Q., Kang, H. J., Talke, F.E. *Lubri. Eng.* 15 (1999) 16.
8. a) Mate, M., Kasai, P. H., Tyndall, G. W. *IEEE Trans.*,34 (1998) 1744.  
b) El Gouri, M., El Mansouri, A., El Gouri, R., Hadik, N., Cherkaoui, O., Outzourhit, A., El Harfi, A., *J. Mater. Environ. Sci.*, 5 (2014) 400.
9. a) Potin P., Jaeger R. D. *Eur. Polym. J.*, 27 (1991) 341.  
b) El Gouri M., El Bachiri A., Hegazi S. E., Ziraoui R., Rafik M., El Harfi A., *J. Mater. Environ. Sci.*, 2 (2011) 319.  
c) El Gouri M., Cherkaoui, O., Ziraoui, R., El Harfi, A., *J. Mater. Environ. Sci.*, 1 (2010) 157.
10. Chandrasekhar, V. *Inorganic and Organometallic Polymers*, Nova Science Publishers, New York, (2004)
11. Mark J. E., Allcock, H.R.; West, H.R. *Inorganic Polymers*, 2<sup>nd</sup> Ed., Oxford Press, New York, (2005).
12. Reich H.J., Cohen, M.L, Clark. S. *Org. Syn.* 59 (1979) 141; Coll. Vol. 6:533.
13. Shi M., Wang, B.Y., Li, *J.Eur. J. Org. Chem.*, 4 (2005)759 and references therein
14. Shen L., Shin, K., Lee, K.T., Jeong, J. H. *Pharma. Res.*, 27(2004)816.
15. Kesavan K.S., Crusse, B., Bonnet-Delpon, D., Regue, J.P. *Org. Syn.*, 80(2003)184; Coll. Vol. 11(2009)135.
16. Jampilek J., Dolezal M., Dvorak, B. *Chem. Pap.*56(2002)147.
17. Farzaliev V.M., Allakhverdiev M.A., Aliev, Sh.R., Babai, R.M., Rzaeva, I. A., Khalilova, A.Z., Ismailov, E.Z., *Russ. J. Appl. Chem.* 76 (2003) 128.
18. Holleman, A. F., Wiberg, E., *Inorganic Chemistry*. Academic press Diego, (2001) and references therein.
19. Tang, H., Pintauro, P.N., Guo, Q., Oconnor, S. *J. Appl. Polym. Sci.*, 71(1999) 387.
20. Silverstein, R.M., Basseler, G.C., Mari, R. *Spectrometric Identification of Organic Compounds*. John Wiley, New York, 4th ed., Ch. 3 (1981).
21. a) Potapov, V.A., Amosova, S.V., *Rus. J. Org. Chem.*, 39(2003) 1373.  
b) Klayman D. L., Gunther, W.H.H. *Selenium Compounds: Their Chemistry and Biology*”, Wiley, New York, (1973).
22. a) A. Krief and L. Hevesi, " Organoselenium Chemistry 1. Functional Group Transformations", Springer, Berlin ( 1988).  
b) Patai, S., Rappoport, Z, (Eds.). *The Chemistry of Organic Selenium and Tellurium Compounds*. John Wiley and Sons, Chichester, Vol. 1(1988).
23. Van Antwerpen, F., Van Krevelen, D. W.J., *Polym. Sci. Polym. Phys. Ed.* 10 (1972) 2423.
24. a) Liu, Y., Zhao, G., *Chin. J. Chem. Eng.*, 15(2007)429.  
b) Imai, Y., Abe, S., Ueda, M., *J. Polym. Sci. Polym. Chem. Ed.*19(1981)3285.