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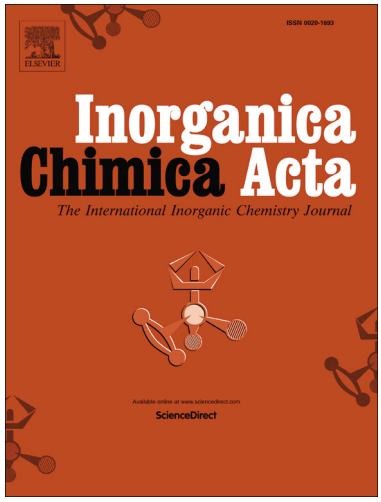

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Faith Aslan, Ali İhsan Öztürk, Mustafa Binici

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Organocyclotriphosphazenes with poly Schiff bases and aldehydes from hexachlorocyclotriposphazene, 5-chloro-salicylaldehyde and 5-bromo-salicylaldehyde under the room conditions without using Ar or N_2 atmosphere

Faith ASLAN[*], Ali İhsan ÖZTÜRK[**], Mustafa BİNİCİ[*]

[*]Harran University, Art&Science Faculty, Department of Chemistry, Şanlıurfa, Turkey.
[**] Osmaniye Korkut Ata University, Art&Science Faculty, Department of Chemistry, Osmaniye, Turkey.
Corresponding author: E-Mail:faslan33@yahoo.com
Adress: Department of Chemistry, Harran University, Şanlıurfa, Turkey

Abstract

In this study, the reactions of hexachlorocyclotriphosphazene with 5-chloro-salicylaldehyde and 5-bromo-salicylaldehyde were separately performed in the presence of K_2CO_3 and trietylamine as a base without using Ar or N_2 atmosphere for the preparation of the organocyclotriphosphazene derivatives bearing six formyl groups (**2** and **3**) again. These reactions were monitored by ^{31}P NMR spectroscopy to determine the formation time of the compounds (**2** and **3**). The result of this analysis showed that the compounds (**2** and **3**) occurred within3 h under the above reaction conditions after the reactions begun. The ^{31}P NMR spectra of the mixtures clearly displayed only singlet signal in the range of 8-9 ppm corresponding to characteristic phosphorus signals of cyclotriphosphazenes. Moreover, these two compounds were obtained in high yields even under such mild reaction conditions. In addition, the compounds (**2** and **3**) were reacted with aniline and some aniline derivatives for the production of new organocyclotriphosphazene derivatives bearing poly Schiff bases (**2a-2k** and **3a-3k**). Although all the primary amines in these reactions were used more than necessary, it was detected that the organocyclotriphosphazene derivative including both formyl and Schiff base moieties (**2k** and **3k**) occurred from only 4-nitro-aniline. Most importantly of all, hydrolysis of hexachlorocyclotriphosphazene in THF solution was also studied. It was determined that hexachlorocyclotriphosphazene did not hydrolysis under these conditions.

Key Words. Cyclotriphosphazene, organophosphazene, salicylaldehyde, Schiff base.

1. Introduction

One from the best known and most studied compounds in the family of phosphazene is also hexachlorocyclotriphosphazene which is the stable and performs nucleophilic substitution reactions very well under the room conditions [1-5]. The derivation of the organocyclotriphosphazenes from hexachlorocyclotriphosphazene begun with famous researchers' works such as Allcock, Shaw and Allen between 1950 and 1960 years [6-8]. Currently, the number of the reported organocyclotriphosphazenes is estimated to be more than 15,000 [9]. Although a lot of hydroxybenzaldehyde and primary amine derivatives are available, the reported organocyclotriphosphazenes bearing aldehyde and imine groups are rather rare among the published studies. The works related to Schiff base without phosphazene which was discovered in 1864 by Hugo Schiff has been still continued to attract attention among chemists [10]. Both Schiff bases and phosphazenes have been known to have a large variety of useful applications.

In the literature, the organocyclotriphosphazene derivatives having formyl groups are produced by using two different methods. First, hexachlorocylotriphsophazene is treated with hydroxybenzaldehyde derivatives in the presence of a base such as K_2CO_3, Cs_2CO_3 or triethylamine in the solvent, generally using K_2CO_3 [11]. These bases, which are used to hold HCl formed in the reaction, are weak bases. In these reactions, all of the reagents are present in the same reaction bubble. In other words, the reaction is performed in one step. Therefore, NaH, one of the strongest bases known, should not be used in such reactions performed in one step. Because, halophosphazene reacts with hydride instead of phenol derivatives. Thus, the desired product could not be obtained. However, NaH can be used in the second reaction method. In addition, such reactions should be carried out under Ar or N_2 gas atmosphere and the solvent used should be used after purification under Ar or N_2 gas atmosphere, too. Second, hexachlorocylotriphsophazene is reacted with sodium salt of hydroxybenzaldehyde derivatives

in the solvent [12]. The salt of phenol derivatives is obtained from the reaction of the phenol derivative with metallic sodium or sodium hydride.

In the recent years, the first method has been preferred more than the second for the synthesis of organocyclotriphosphazene derivatives bearing formyl groups, because the first method is both the easiest and the most economical. The second method must be definitely performed under the airless conditions. This kind of compounds are possible to achieve in good yield with both methods. The effect of the base on the yield of organocyclotriphosphazene derivatives is not known with certainty, according to studies in literature. In fact, we do not come across a study in this field in literature either. As it is known, the synthesis of organocyclotriphosphazene derivatives is generally carried out under Ar or N_2 gas atmosphere. Although the synthesis of organocyclotriphosphazene derivatives was performed without the use of Ar or N_2 gas atmosphere in previous our study, it was determined that the hexasubstituted compounds formed with very good yield [13]. In previous our study, the hydrolysis product of hexachlorocylotriphosphazene from atmospheric moisture and a very small amount water in used solvent were not determined. If the hydrolysis product had occurred, it would be possible to determine spectroscopically or the yield of the prepared products would be significantly less. However, hexachlorocyclotriphosphazene is known to hydrolyze fairly rapidly in water solution [19]. In this study, hydrolysis of hexachlorocyclotriphosphazene in THF solvent was also studied.

Some works have been reported regarding the synthesis of the organocyclotriphosphazene derivatives bearing Schiff base units in the literature. Three different methods for the derivation of such compounds are known [14-16]. Moriya et al. firstly prepared such compounds from the reactions of organocyclotriphsophazene derivatives carrying formyl groups with primary amines [15]. This method has been preferred more than the others to produce such compounds. There is not enough information in the literature about the chemical, physical and biological properties of these compounds. In previously our studies,

it was reported that a great number of new organocyclotriphosphazene derivatives including six imine units were derived from the reactions of hexa(2-formyl-phenoxy)cyclotriphosphazene, hexa(4-formyl-phenoxy)cyclotriphosphazene, hexa(4-formyl-3-metoxy-phenoxy)cyclotriphosphazene, hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene and hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene with aniline, some aniline derivatives and a few aliphatic primary amine derivatives [17-18]. Moreover, we firstly identified to occur some organocyclotriphosphazene derivatives containing both imine and formyl units from some aniline derivatives [13].

In the present study, hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene(**2**) and hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene(**3**) synthesized in our previous study were prepared in the presence of K_2CO_3 and triethylamine in room conditions without using Ar or N_2 atmosphere again. The formation of the compounds **2** and **3** during the reactions were monitored by ^{31}P NMR spectroscopy. According to the result of this analyse, it was understood that the compounds **2** and **3** occurred within 3 hours. When these reactions were continued for 24 hours using K_2CO_3 as a base, the compounds **2** and **3** were definitely not obtained. The reactions of the compounds **2** and **3** with aniline (**a**) and selected aniline derivatives (**b-j**) were also performed to derive the organocyclotriphosphazenes carrying six imine units. However, it was found that such organocyclotriphosphazene derivatives did not occur from all aniline derivatives. In contrast to our previous work, the organocyclotriphosphazene derivatives (**2k** and **3k**) carrying both formyl and Schiff base groups were produced from only 4-nitro-aniline.

2. Experimental section

2.1. Materials

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$), the other chemicals and solvents were procured from Aldrich and Merck. All of the chemicals and solvents were used as received without

further purification. All reactions were carried out under room conditions. N_2 or Ar gas atmosphere was certainly not used in this study.

2.2. Measurements

The NMR (^1H, ^{31}P) spectra were recorded on a Varian VNMRS (400 MHz) spectrometer ($SiMe_4$ as internal and 85% H_3PO_4 as external standards) in $(CD_3)_2SO$, $(CD_3)_2CO$ or $CDCl_3$ solvent. IR spectra were recorded on a Perkin-Elmer spectrum two FTIR spectrometer with ATR. The elemental analyses were performed on a LECO (CHNS-932) elemental analyzer. Melting points were measured on an Electrothermal IA 9200 apparatus in capillary.

2.3. Hydrolysis research experiment of phosphazenes at THF

The solution of the compound 1 in THF solvent was mixed under three room conditions. At the end of this period, NMR spectroscopy analysis of the solution was performed. Furthermore, NMR analysis of the solvent THF was also performed. ^1H NMR (the solution of the compound 1, $CDCl_3$): 3.62 (O-CH_2- of THF), 1.73 (-CH_2- of THF). ^1H NMR (THF, $CDCl_3$): 3.62 (O-CH_2-), 1.73 (-CH_2-). ^{31}P NMR (the solution of the compound 1, $CDCl_3$): 19.84 (a sharp singlet).

2.4. Synthesis

*2.4.1. Synthesis of hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (**2**) in the presence of $(C_2H_5)_3N$*

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (1.00 g, 2.876 mmol), THF (150 mL), $(C_2H_5)_3N$ (4.80 mL, 34.512 mmol) and 5-chloro-salicylaldehyde (5.403 g, 34.512 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 3 h and then, ^{31}P NMR analysis of the mixture was performed. From this analysis, it became clear that the reaction was over. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with produced

$(C_2H_5)_3N.HCl$). The filtered triethylamine hydrochloride [$(C_2H_5)_3N.HCl$] was dried in room conditions and weighed (experimental/calculated: 2.20 g / 2.38 g). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The white powder was collected by filtration. In this way, the compound **2** was achieved as a white solid and pure (81.4% yield, 2.50 g, 3.073 g, mp 115). Anal. Calc. for $N_3P_3C_{42}H_{24}Cl_6O_6$: C, 47.22; H, 2.26; N, 3.93%. Found: C, 47.32; H, 2.39; N, 3.62%. FTIR (υ, cm^{-1}): 1699 and 1678 (HC=O), 1208, 1196, 1176, 1169 and 1155 (P=N), 964, 954 and 944 (P-OAryl).^{1}H NMR (δ, ppm ($(CD_3)_2CO$): 10.0(s, **H**C=O), 7.8-7.4 (Aryl **H**). ^{31}P NMR (δ, ppm): 7.81 (s).

*2.4.2. Synthesis of hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (**2**) in the presence of K_2CO_3*

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (0.25 g, 0,719 mmol), THF (75 mL), K_2CO_3 (1.20 g, 8.629 mmol) and 5-chloro-salicylaldehyde (1.346 g, 8.629 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 3 h and then, ^{31}P NMR analysis of the mixture was performed. From this analysis, it became clear that the reaction was over. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with K_2CO_3, produced KCl and $KHCO_3$). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The white powder was collected by filtration. In this way, the compound **2** was achieved as a white solid and pure (52% yield, 0.40 g, 3.073 g, mp 115). Anal. Calc. for $N_3P_3C_{42}H_{24}Cl_6O_6$: C, 47.22; H, 2.26; N, 3.93%. Found: C, 47.32; H, 2.39; N, 3.62%. FTIR (υ, cm^{-1}): 1699 and 1678 (HC=O), 1208, 1196, 1176, 1169 and 1155 (P=N), 964, 954 and 944 (P-OAryl).^{1}H NMR (δ, ppm ($(CD_3)_2CO$): 10.0(s, **H**C=O), 7.8-7.4 (Aryl **H**). ^{31}P NMR (δ, ppm): 7.81 (s).

*2.4.3. Synthesis of the compound **4** in the presence of K_2CO_3 for 24 h*

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (0.25 g, 0,719 mmol), THF (75 mL), K_2CO_3 (1.20 g, 8.629 mmol) and 5-chloro-salicylaldehyde (1.346 g, 8.629 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 24 h. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with K_2CO_3, produced KCl and $KHCO_3$). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The black powder was collected by filtration. In this way, the compound **4** was achieved as a black solid. FTIR (υ, cm^{-1}): 1688, 1679, 1658 and 1634 (HC=O), 1201, 1179, 1166 and 1146 (P=N), 946 and 932 (P-OAryl).^{1}H NMR (δ, ppm ($(CD_3)_2CO$): 10.20-9.80 (-**H**C=O), 7.6-6.4 (Aryl **H**). ^{31}P NMR (δ, ppm): 10.20 (doublet), -0.55 (triplet).

*2.4.4. Synthesis of hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (**2**) in the presence of $(C_2H_5)_3N$ for 24 h*

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (1.00 g, 2.876 mmol), THF (150 mL), $(C_2H_5)_3N$ (4.80 mL, 34.512 mmol) and 5-chloro-salicylaldehyde (5.403 g, 34.512 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 24 h. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with produced $(C_2H_5)_3N.HCl$). The filtered triethylamine hydrochloride [$(C_2H_5)_3N.HCl$] was dried in room conditions and weighed (experimental/calculated: 2.20 g / 2.38 g). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The white powder was collected by filtration. In this way, the compound **2** was achieved as a white solid and pure (81.4% yield, 2.50 g, 3.073 g, mp 115).

2.4.5. General synthetic procedure for the compounds 2a-2k from the compound 2

In a 100-mL single-necked flat-bottom flask equipped with magnetic mixing, the compound **2** (0.40 g, 0.375 mmol), THF (30 mL), two drops of formic acid and primary amine derivative (4.50 mmol) were added sequentially. The reaction was continued for 24 hours under

room conditions. After the solution was reduced to approximately 5 mL under reduced pressure, the solution was dropped into diethyl ether or alcohol for the removal of free primary amine. The precipitate was filtered off and the color solid was dried under room conditions. The compounds **2a-2k** were obtained from the compound **2.**

*2.4.5.1. Synthesis of hexa[4-chloro-2-(phenyliminomethyl)phenoxy]cyclotriphosphazene (**2a**)*

The compound **2a** occurred from aniline (0.41 mL, 4.50 mmol) as a peach-orange color solid (0.50 g, 87,7%, mp. 185 ºC). Anal. Calc. for $N_9P_3C_{78}H_{54}Cl_6O_6$: C, 61.68; H, 3.58; N, 8.30%. Found: C, 61.71; H, 3.66; N, 8.46%. FTIR (υ, cm^{-1}): 1620 (HC=N), 1187 and 1159 (P=N), 977, 958 and 942 (P-OAryl). ^{1}H NMR (δ, ppm ($CDCl_3$): 8.34 (**H**-C=N), 8.10-6.70 (Aryl **H**). ^{31}P NMR (δ, ppm): 8.13 (s).

*2.4.5.2. Synthesis of hexa[4-chloro-2-(1-naphthyliminomethyl)phenoxy]cyclotriphosphazene (**2b**)*

The compound **2b** occurred from 1-naphthylamine (0.65 g, 4.50 mmol) as a maize color solid (0.65 g, 95,6%, mp 118 ºC). Anal. Calc. for $N_9P_3C_{102}H_{66}Cl_6O_6$: C, 67.34; H, 3.66; N, 6.93%. Found: C, 66.99; H, 3.89; N, 6.96%. FT IR (υ, cm^{-1}: 1620 (HC=N), 1204 and 1161 (υ=N), 958 (P-OAryl). ^{1}H NMR (δ, ppm, $(CD_3)_2CO$): 8.36 (**H**-C=N), 8.20-6.70 (Aryl **H**). ^{31}P NMR (δ, ppm): 8.03 (s).

*3.3.5.3. Synthesis of hexa[4-chloro-2-(3,4-bischloro-pheyliminomethyl)phenoxy] cyclotriphosphazene (**2c**)*

The compound **2c** occurred from 3,4-dichloroaniline (0.73 g, 4.50 mmol) as a peach-orange color solid (0.66g, 91.2%, mp 98 ºC). Anal. Calc. for $N_9P_3C_{78}H_{42}Cl_{18}O_6$: C, 48.48; H, 2.19; N, 6.52%. Found: C, 49.05; H, 2.51; N, 6.47%. FTIR (υ, cm^{-1}): 1620 (HC=N), 1190 and 1162 (P=N), 959 (P-OAryl). ^{1}H NMR (δ, ppm, $(CD_3)_2CO$): 8.35 (H-C=N), 8.00-6.50 (Aryl H). ^{31}P NMR (δ, ppm): 7.87 (s).

*2.4.5.4. Synthesis of hexa[4-chloro-2-(2-mercapto-pheyliminomethyl)phenoxy]cyclotriphosphazene (**2d**)*

The compound **2d** occurred from 2-mercapto-aniline (0.50 mL, 4.50 mmol) as a peach-yellow color solid (0.63 g, 98.3%, mp136 ºC). Anal. Calc. for $N_9P_3C_{78}H_{54}Cl_6O_6S_6$: C, 54.74; H, 3.18; N, 7.37: S, 11.24%. Found: C, 55.18; H, 3.22; N, 7.63: S, 12.29%. FTIR (υ, cm^{-1}): 1614 (HC=N), 1188 and 1163 (P=N), 954 (P-OAryl). ^{1}H NMR (δ, ppm, $(CD_3)_2SO$): 8.25 (**H**C=N), 8.0-6.0 (Aryl H), 5.40 (**H**-S-). ^{31}P NMR (δ, ppm):7.50 (s).

*2.4.5.5. Synthesis of hexa[4-chloro-2-(2-mercapto-benzimidazol-5-yliminomethyl)phenoxy]cyclotriphosphazene (**2e**)*

The compound **2e** occurred from 5-amino-2-mercaptobenzimidazole (0.74g, 4.50 mmol) as a princeton orange color solid (0.62 g, 85%, mp 202 ºC). Anal. Calc. for $N_{21}P_3C_{84}H_{54}Cl_6O_6S_6$: C, 51.70; H, 2.79; N, 15.07: S, 9.86%. Found: C, 49.76; H, 3.62; N, 17.05: S, 12.42%. FTIR (υ, cm^{-1}): 3200 (O-H), 1636 (C=N), 1613 (HC=N), 1186, 1158, 1114 (P=N), 953 (P-O-Aryl). ^{1}H NMR (δ, ppm, $(CD_3)_2SO$): 12.0 and 12.5 (N-H and SH), 8.96 (H-C=N), 8.0-6.4 (Aryl H). ^{31}P NMR (δ, ppm):7.61 (s).

*2.4.5.6. Synthesis of hexa[4-chloro-2-(1H-indazol-6-yl-iminomethyl)phenoxy]cyclotriphosphazene (**2f**)*

The compound **2f** occurred from 6-amino-1H-indazol (0.60 g, 4.50 mmol) as an atomic tangerine color solid (0.53 g, 80.5%, mp 166 ºC). Anal. Calc. for $N_{21}P_3C_{84}H_{54}Cl_6O_6$: C, 57.35; H, 3.09; N, 16.72%. Found: C, 56.14; H, 3.32; N, 17.16: %. FTIR (υ, cm^{-1}): 3272 (O-H), 1631 (HC=N), 1608 (HC=N), 1199, 1159 (P=N), 960, 947 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as (CD3)2CO, CDCl3, DMSO-D.

*2.4.5.7. Synthesis of hexa[4-chloro-2-(fluorine-2-yliminomethyl)phenoxy]cyclotriphosphazene (**2g**)*

The compound **2g** occurred from 2-aminofluorene (0.65 g, 4.50 mmol) as an orange color solid (0.65 g, 84.9%, mp 130 ºC). Anal. Calc. for $N_9P_3C_{120}H_{78}Cl_6O_6$: C, 70.39; H, 3.84; N, 6.16%. Found: C, 65.62; H, 4.03; N, 5.57 %. FTIR (υ, cm^{-1}): 1622 (HC=N), 1194, 1161 (P=N),

959 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as (CD3)2CO, CDCl3, DMSO-D.

*2.4.5.8. Synthesis of hexa[4-chloro-2-(4-mercapto-pheyliminomethyl)phenoxy]cyclotriphosphaze (**2h**)*

The compound **2h** occurred from 4-mercapto-phenyl amine (0.50 mL, 4.50 mmol) as a peach-yellow color solid (0.57 g, 89.0%, mp 185 ºC). Anal. Calc. for $N_9P_3C_{78}H_{54}Cl_6O_6S_6$: C, 54.74; H, 3.18; N, 7.37: S, 11.24%. Found: C, 54.01; H, 3.426; N, 6.955; S, 12.18 %. FTIR (υ, cm^{-1}): 1619 (HC=N), 1188, 1158 (P=N), 957 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as (CD3)2CO, CDCl3, DMSO-D.

*2.4.5.9. Synthesis of hexa[4-chloro-2-(4-cyano-pheyliminomethyl)phenoxy]cyclotriphosphaze (**2i**)*

The compound **2i** occurred from 4-cyano-aniline (0.532 g, 4.50 mmol) as a peach-yellow color solid (0.53 g, 84.8%, mp 167 ºC). Anal. Calc. for $N_{15}P_3C_{84}H_{46}Cl_6O_6$: C, 60.395; H, 2.756; N, 12.582%. Found: C, 59.98; H, 3.341; N, 12.37%. FTIR (υ, cm^{-1}): 2225 (C≡N), 1624 (HC=N), 1192, 1164 (P=N), 958 (P-O-Aryl). ^{1}H NMR (δ, ppm, acetone-D): 9.50 (H-C=O, integral area: 1.0), 8.52 (H-C=N, integral area: 1.13), 8.28 (H-C=N, integral area: 5.44), 8.19-6.61 (Aryl H). ^{31}P NMR (δ, ppm): 8.20-8.05 (weak peaks), 7.97 (severe singlet).

*2.4.5.10. Synthesis of hexa[4-chloro-(2-(4-carboxy-phenyliminomethyl)phenoxy)]-cyclotriphosphazene (**2j**)*

The compounds **2j** occurred from 4-carboxy-aniline (0.617 g, 4.50 mmol) as a peach-yellow color solid (0.56 g, 84.0%, mp 213 ºC). Anal. Calc. for $N_9P_3C_{84}H_{54}Cl_6O_{18}$: C, 56.58; H, 3.05; N, 7.07%. Found: C, 54.26; H, 3.306; N, 6.694%. FTIR (υ, cm^{-1}): 1682 (HCOOH), 1624 (HC=N), 1188, 1160 (P=N), 957 (P-O-Aryl). ^{1}H NMR (δ, ppm, (DMSO): 12.5 (-COOH), 9.72 (H-C=O, integral area: 1.0), 9.63 (H-C=O, integral area: 1.94),8.24 (H-C=N, integral area:3.10), 8.20 (H-C=N, integral area:1.89), 8.00-6.5 (Aryl H). ^{31}P NMR (δ, ppm): 7.60 (triplet), 7.43 (medium singlet) and 7.27 (severe singlet).

2.4.5.11. Synthesis of 2,2,4,4-tetra[4-chloro-(2-(4-nitro-phenyliminomethyl)phenoxy)]-6,6-di[4-

*chcloro-(2-formyl-phenoxy)]-cyclotriphosphazene (**2k**).*

The compound **2k** occurred from 4-nitro-aniline (0.622 g, 4.50 mmol) as a peach-yellow color solid (0.52 g, 89.7%, mp 173 ºC). Anal. Calc. for $N_9P_3C_{60}H_{36}Cl_6O_{15}$: C, 50.400; H, 2.520; N, 8.820%. Found: C, 51.15; H, 3.112; N, 11.98%. FTIR (υ, cm^{-1}): 1694 (HC=O), 1627 (HC=N), 1188, 1162 (P=N), 955 (P-O-Aryl). ^{1}H NMR (δ, ppm, acetone-D): 10.00-9.80 (H-C=O, the integral area: 3.52), 8.60-8.30 (H-C=N, integral area: 3.86), 8.2-6.0 (Aryl H). ^{31}P NMR (δ, ppm): 8.10-7.90 (multiple).

*2.4.6. Synthesis of hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (**3**) in the presence of $(C_2H_5)_3N$*

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (1.00 g, 2.876 mmol), THF (150 mL), $(C_2H_5)_3N$ (4.80 mL, 34.512 mmol) and 5-bromo-salicylaldehyde (6.937 g, 34.512 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 3 h and then, ^{31}P NMR analysis of the mixture was performed. From this analysis, it became clear that the reaction was over. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with produced $(C_2H_5)_3N.HCl$). The filtered triethylamine hydrochloride [$(C_2H_5)_3N.HCl$] was dried under room conditions and weighed (experimental/calculated: 2.20 g / 2.38 g). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The white powder was collected by filtration. In this way, the compound **3** was achieved as a white solid and pure (81.4% yield, 3.10 g, mp 172 ºC). Anal. Calcd for $N_3P_3C_{42}H_{24}Br_6O_6$: C, 37.79; H, 1.81; N, 3.5%. Found: C, 38.60; H, 2.03; N, 3.23%. FTIR (υ, cm^{-1}): 1703 and 1960 (HC=O), 1204, 1190, 1176, 1171 (P=N), 978, 962, 952 (P-O-Aryl). ^{1}H NMR (δ, ppm, $(CD_3)_2CO$): 10.0 (s, **H**C=O), 8.0-7.0 (Aryl **H**). ^{31}P NMR (δ, ppm): 7.58 (s).

*2.4.7. Synthesis of hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (**3**) in the presence of*

K_2CO_3

In a 100-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (0.25 g, 0,719 mmol), THF (75 mL), K_2CO_3 (1.20 g, 8.629 mmol) and 5-bromo-salicylaldehyde (1.734 g, 8.629 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 3 h and then, ^{31}P NMR analysis of the mixture was performed. From this analysis, it became clear that the reaction was over. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off ((with K_2CO_3, produced KCl and $KHCO_3$).). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The white powder was collected by filtration. In this way, the compound **3** was achieved as a white solid and pure (80% yield, 0.77 g, mp 172 ºC). Anal. Calcd for $N_3P_3C_{42}H_{24}Br_6O_6$: C, 37.79; H, 1.81; N, 3.5%. Found: C, 38.60; H, 2.03; N, 3.23%. FTIR (υ, cm^{-1}): 1703 and 1960 (HC=O), 1204, 1190, 1176, 1171 (P=N), 978, 962, 952 (P-O-Aryl). ^1H NMR (δ, ppm, $(CD_3)_2CO$): 10.0 (s, **H**C=O), 8.0-7.0 (Aryl **H**). ^{31}P NMR (δ, ppm): 7.58 (s).

*2.4.8. Synthesis of the compound (**5**) in the presence of K_2CO_3 for 24 h*

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (0.25 g, 0,719 mmol), THF (75 mL), K_2CO_3 (1.20 g, 8.629 mmol) and 5-bromo-salicylaldehyde (1.734 g, 8.629 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 24 h. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with K_2CO_3, produced KCl and $KHCO_3$). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The black powder was collected by filtration. In this way, the compound **5** was achieved as a black solid. FTIR (υ, cm^{-1}): 1689, 1682, 1649, 1632 (HC=O), 1198, 1178, 1166, 1153 (P=N), 957, 943, 925 (P-O-Aryl). ^1H NMR (δ, ppm, $(CD_3)_2CO$): 10.50-9.900 (**H**C=O), 8.0-6.50 (Aryl **H**). ^{31}P NMR (δ, ppm): 10.20 (doublet), -0.50 (triplet).

*2.4.9. Synthesis of hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (**3**) in the presence of*

$(C_2H_5)_3N$ for 24 h

In a 250-mL single-necked flat-bottom flask equipped with magnetic mixing, $N_3P_3Cl_6$ (**1**) (1.00 g, 2.876 mmol), THF (150 mL), $(C_2H_5)_3N$ (4.80 mL, 34.512 mmol) and 5-bromo-salicylaldehyde (6.937 g, 34.512 mmol) were added sequentially. The mixture reaction was maintained at room temperature for 24 h. At the end of the reaction, the insoluble matter of the reaction mixture was filtered off (with produced $(C_2H_5)_3N.HCl$). The filtered triethylamine hydrochloride [$(C_2H_5)_3N.HCl$] was dried under room conditions and weighed (experimental/calculated: 2.20 g / 2.38 g). The solution was concentrated under reduced pressure. Then, the residue was dropped into solvent of ethyl alcohol. The white powder was collected by filtration. In this way, the compound **3** was achieved as a white solid and pure (81.4% yield, 3.10 g, mp 172 ºC).

*2.4.10. General synthetic procedure for the compounds **3a-3k** from the compound **3***

In a 100-mL single-necked flat-bottom flask equipped with magnetic mixing, the compound **2** (0.40 g, 0.375 mmol), THF (30 mL), two drops of formic acid and primary amine derivative (4.50 mmol) were added sequentially. The reaction was continued for 24 hours under room conditions. After the solution was reduced to approximately 5 mL under reduced pressure, the solution was dropped into diethyl ether or alcohol for the removal of free primary amine. The precipitate was filtered off and the color solid was dried under room conditions. The compounds **3a-3k** were obtained from the compound **3.**

*2.4.10.1. Synthesis of hexa[4-bromo-2-(phenyliminomethyl)phenoxy]cyclotriphosphazene (**3a**)*

The compound **3a** occurred from aniline (0.41 mL, 4.50 mmol) as a Peach-orange color solid (0.47 g, 87.9%, mp. 192ºC). Anal. Calc. for $N_9P_3C_{78}H_{54}Br_6O_6$: C, 52.46; H, 3.05; N, 7.06%. Found: C, 52.75; H, 3.44; N, 7.27%. FTIR (υ, cm^{-1}): 1619 (HC=N), 1186, 1161 (P=N), 971, 955, 938 (P-O-Aryl). ^1H NMR (δ, ppm, $(CD_3)_2CO$): 8.34 (**H**-C=N), 8.25-6.70 (Aryl H). ^{31}P NMR (δ, ppm): 7.90 (s).

2.4.10.2. Synthesis of hexa[4-bromo-2-(1-naphthyliminomethyl)phenoxy]cyclotriphosphazene

(3b)

The compound **3b** occurred from 1-naphthylamine (0.65 g, 4.50 mmol) as a maize color solid (0.58 g, 92.8%, mp. 146 ºC). Anal. Calc. for $N_9P_3C_{102}H_{66}Br_6O_6$: C, 58.73; H, 3.19; N, 6.04%. Found: C, 58.76; H, 3.44; N, 6.19%. FTIR (υ, cm^{-1}): 1619 (HC=N), 1201, 1162 (P=N), 957 (P-O-Aryl). ^{1}H NMR (δ, ppm, $(CD_3)_2CO$): 8.35 **(H**-C=N), 8.25-6.60 (Aryl H), 2.84 (strong, $\mathbf{H}_2O$), 2.05 (strong, $(CD_3)_2CO$) .^{31}P NMR (δ, ppm): 8.75 (s).

2.4.10.3. Synthesis of hexa[4-bromo-2-(3,4-bischloro-pheyliminomethyl)phenoxy]

*cyclotriphosphazene (**3c**)*

The compound **3c** occurred from 3,4-dichloroaniline (0.73 g, 4.50 mmol) as a peach-orange color solid (0.56 g, 85.0%, mp. 125 ºC). Anal. Calc. for $N_9P_3C_{78}H_{42}Cl_6Br_6O_6$: C, 42.60; H, 1.93; N, 5.73%. Found: C, 43.00; H, 2.23; N, 5.83%. FTIR (υ, cm^{-1}): 1622 (HC=N), 1188, 1162 (P=N), 957 (P-O-Aryl). ^{1}H NMR (δ, ppm, $(CD_3)_2CO$): 8.33 **(H**-C=N), 8.15-6.90 (Aryl H), 2.84 (strong, $\mathbf{H}_2O$), 2.05 (strong, $(CD_3)_2CO$) .^{31}P NMR (δ, ppm): 7.64 (s).

2.4.10.4. Synthesis of hexa[4-bromo-2-(2-mercapto-pheyliminomethyl)phenoxy]

*cyclotriphosphazene (**3d**)*

The compound **3d** occurred from 2-mercapto-aniline (0.50 mL, 4.50 mmol) as a peach-yellow color solid (0.48 g, 81.0%, mp. 235 ºC). Anal. Calc. for $N_9P_3C_{78}H_{54}S_6Br_6O_6$: C, 47.36; H, 2.75; N, 6.37; S, 9.73%. Found: C, 48.68; H, 3.28; N, 6.68; S, 9.81%. FTIR (υ, cm^{-1}): 1608 (HC=N), 1215, 1167 (P=N), 945 (P-O-Aryl). ^{1}H NMR (δ, ppm, $(CD_3)_2SO$): 7.57 (H-C=N), 7.00-6.30 (Aryl H), 5.36 (**H**-S-), 2.47 ($(CD_3)_2SO$), 3.40 ($\mathbf{H}_2O$). ^{31}P NMR (δ, ppm): 8.96 (s).

2.4.10.5. Synthesis of hexa[4-bromo-2-(2-mercapto-benzimidazol-5-yliminomethyl)phenoxy]

*cyclotriphosphazene (**3e**)*

The compound **3e** occurred from 5-amino-2-mercaptobenzimidazole (0.74g, 4.50 mmol) as a princeton orange color solid (0.60 g, 90.2%, mp. 278 ºC). Anal. Calc. for $N_{21}P_3C_{84}H_{54}S_6Br_6O_6$: C, 45.48; H, 2.45; N, 13.26; S, 8.67%. Found: C, 40.76; H, 3.18; N, 12.44; S, 7.92%. FTIR (υ, cm^{-1}): 3119 (O-H), 1635 (C=N), 1614 (HC=N), 1218, 1202, 1161

(P=N), 974, 959 (P-O-Aryl). ^{1}H NMR (δ, ppm, $(CD_3)_2SO$): 12.5 (N-H ve SH), 8.08 and 7.80 (H-C=N), 7.20-6.50 (Aryl H). ^{31}P NMR (δ, ppm): 7.48 (s).

*2.4.10.6. Synthesis of hexa[4-bromo-2-(1H-indazol-6-yl-iminomethyl)phenoxy] cyclotriphosphazene (**3f**)*

The compound **3f** occurred from 6-amino-1H-indazol (0.60 g, 4.50 mmol) as tangerine color solid (0.53 g, 87.5%, mp. 168 ºC). Anal. Calc. for $N_{21}P_3C_{84}H_{54}Br_6O_6$: C, 49.80; H, 2.69; N, 14.52%. Found: C, 49.66; H, 3.34; N, 15.03%. FTIR (υ, cm^{-1}): 3211 (O-H), 1631 (HC=N), 1608 (HC=N), 1199, 1159 (P=N), 960, 947 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as (CD3)2CO, CDCl3, DMSO-D.

*2.4.10.7. Synthesis of hexa[4-bromo-2-(fluorine-2-yliminomethyl)phenoxy]cyclotriphosphazene (**3g**)*

The compound **3g** occurred from 2-aminofluorene (0.65 g, 4.50 mmol) as an orange color solid (0.61 g, 88.0%, mp. 183 ºC). Anal. Calc. for $N_9P_3C_{120}H_{78}Br_6O_6$: C, 62.28; H, 3.40; N, 5.25%. Found: C, 51.14; H, 3.62; N, 5.08%. FTIR (υ, cm^{-1}): 1622 (HC=N), 1213, 1196, 1161 (P=N), 966, 955, 942 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as (CD3)2CO, CDCl3, DMSO-D.

*2.4.10.8. Synthesis of hexa[4-bromo-2-(4-mercapto-pheyliminomethyl)phenoxy] cyclotriphosphaze (**3h**)*

The compound **3h** occurred from 4-mercapto-phenyl amine (0.50 mL, 4.50 mmol) as a peach-yellow color solid (0.50 g, 84.4%, mp. 238 ºC). Anal. Calc. for $N_9P_3C_{78}H_{54}S_6Br_6O_6$: C, 47.36; H, 2.75; N, 6.37; S, 9.73%. Found: C, 47.45; H, 2.881; N, 6.022; S, 10.24%. FTIR (υ, cm^{-1}): 1619 (HC=N), 1191, 1160 (P=N), 958 (P-O-Aryl). The NMR analysis of the compound was not performed because insoluble in any solvent, such as $(CD_3)_2CO$, $CDCl_3$, DMSO-D.

*2.4.10.9. Synthesis of hexa[4-bromo-2-(4-cyano-pheyliminomethyl)phenoxy]cyclotriphosphaze (**3i**)*

The compound **3i** occurred from 4-cyano-aniline (0.532 g, 4.50 mmol) as a peach-yellow color solid (0.50 g, 86.2%, mp. 164 ºC). Anal. Calc. for $N_{15}P_3C_{84}H_{48}Br_6O_6$: C,52.07; H, 2.480; N, 10.85%. Found: C, 53.32; H, 2.976; N, 12.34%. FTIR (υ, cm^{-1}): 2215 (C≡N), 1612 (HC=N), 1190, 1161 (P=N), 954 (P-O-Aryl). ^{1}H NMR (δ, ppm, acetone-D): 8.53-8.25 (H-C=N), 8.13-6.61 (Aryl H). ^{31}P NMR (δ, ppm): 8.00-7.85 (weak peaks), 7.75 (server singlet).

*2.4.10.10. Synthesis of hexa[4-bromo-(2-(4-carboxy-phenyliminomethyl)phenoxy)] cyclotriphosphazene (**3j**)*

The compound **3j** occurred from 4-carboxy-aniline (0.617 g, 4.50 mmol) as a peach-yellow color solid (0.55 g, 89.6%, mp. 216 ºC). Anal. Calc. for $N_9P_3C_{84}H_{54}Br_6O_{18}$: C, 49.22; H, 2.66; N, 6.15%. Found: C, 48.08; H, 2.915; N, 6.105%. FTIR (υ, cm^{-1}): 1682 (HCOOH), 1624 (HC=N), 1188, 1160 (P=N), 957 (P-O-Aryl). ^{1}H NMR (δ, ppm, DMSO): 12.12 (-COOH), 8.28-82.0 H-C=N, weak multi peaks), 7.7-6.0 (Aryl H). ^{31}P NMR (δ, ppm): 7.50 (weak triplet), 7.26 (medium singlet), 7.11 (server singlet).

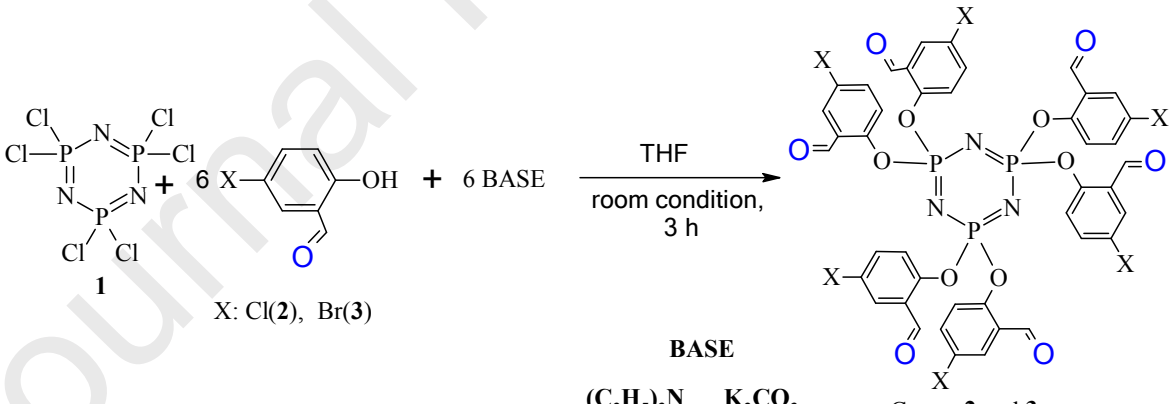
*2.4.10.11. Synthesis of 2,2,4-tri[4-bromo-(2-(4-nitro-phenyliminomethyl)phenoxy)]-4,4,6-tri[4-bromo-(2-formyl-phenoxy)]cyclotriphosphazene (**3k**)*

The compound **3k** occurred from 4-nitro-aniline (0.622 g, 4.50 mmol) as a peach-yellow color solid (0.43 g, 84.3%, mp. 167 ºC). Anal. Calc. for $N_9P_3C_{60}H_{36}Br_6O_{15}$: C, 42.470; H, 2.123; N, 7.432%. Found: C, 44.93; H, 2.884; N, 10.79%. FTIR (υ, cm^{-1}): 1690 (υHC=O), 1624 (HC=N), 1185, 1162 (P=N), 952 (P-O-Aryl). ^{1}H NMR (δ, ppm, acetone-D): 10.00-9.80 (three peaks, H-C=O, the sum of the integral area of peaks: 2.01), 8.60-8.20 (multi-peak, H-C=N, the sum of integral area: 2.57), 8.13-6.00 (Aryl H). ^{31}P NMR (δ, ppm): 8.00-7.70 (multiplet).

3. Results and discussion

3.1. Synthesis

In our previous study, hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (**2**) and hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (**3**) were derived in 59% and 80% yield from the reaction of hexachlorocyclotriphosphazene (**1**) with 5-chloro-2-hydroxy-benzaldehyde in the presence of K_2CO_3 and 5-bromo-2-hydroxy-benzaldehyde in the presence of $(C_2H_5)_3N$ under Ar atmosphere, sequentially [13]. In the present study, the same reactions were carried out separately for the derivation of the compounds **2** and **3** in the presence of both K_2CO_3 and $(C_2H_5)_3N$ without using Ar or N_2 atmosphere. The synthesis reactions of the compounds (**2-5**) were performed as seen in **Schemes 1-3**. All these reactions were followed by ^{31}P NMR spectroscopy to determine the replacement of all the chlorine atoms in the compound **1**. While the reactions were continuing, the first ^{31}P NMR analysis was performed for 3 hours after the reactions begun. The ^{31}PNMR spectra of all the mixtures showed only one signal supporting the hexasubstitution on the cyclotriphosphazene ring. Thus, it was decided that the replacement of all the chlorine atoms in the compound **1** is over and the purification process was started.

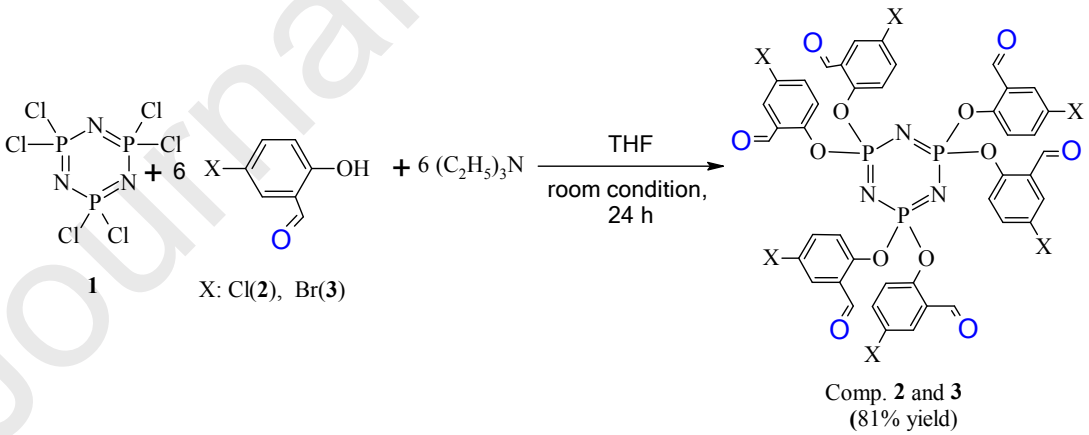


Scheme 1. The Clear Structures and the Synthetic Route of the Compounds 2 and 3 for 3 h in the

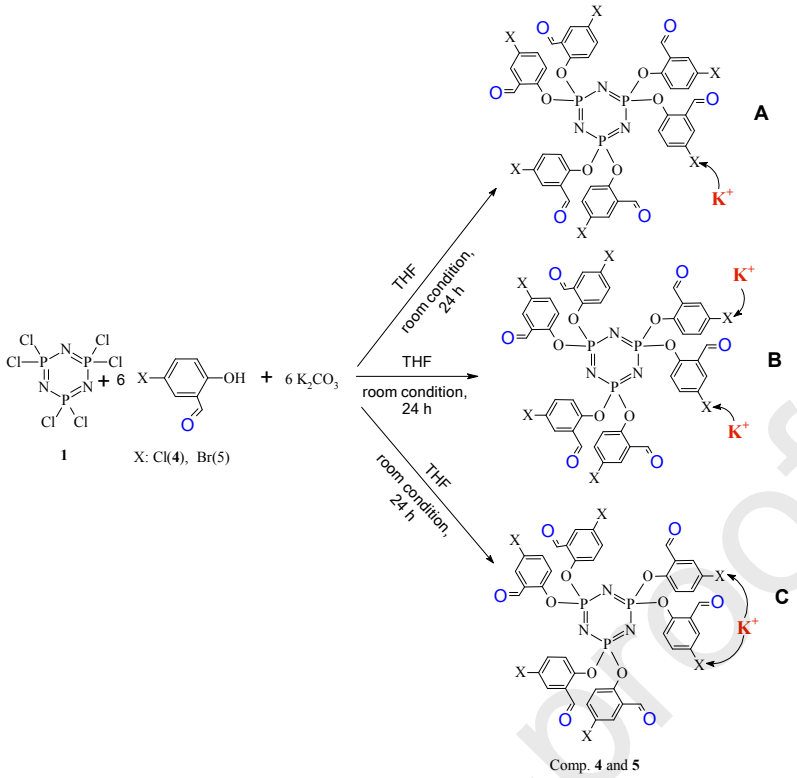
Presence of a Base

Moreover, these reactions were continued for 24 h in the presence of K_2CO_3 and $(C_2H_5)_3N$. While compounds **2** and **3** cannot be obtained in the presence of K_2CO_3 (**Scheme 3**), it is

determined that the compounds **2** and **3** occurred in good yields in the presence of $(C_2H_5)_3N$ (**Scheme 2**). The compounds **4** and **5** are estimated to consist of coordination between compounds 2 and 3 and K_2CO_3 and three different structures (**A**, **B** and **C**) were proposed for the compound **4** and **5**, too (**Scheme 3**). The structures of the obtained compounds 4 and 5 are one of three different structures proposed. The exact structure of the compounds **4** and **5** were not characterized because our goal was to obtain the compounds **2** and **3.** Unlike this study, although the reactions between the compound **1** and some formyl substituted phenol derivatives such as 4-formyl-phenol, 2-formyl-phenol and 4-formyl-2-methoxy-phenol were sustained for 24 hours in the presence of K_2CO_3, the organocyclotriphosphazenes bearing six formyl groups (such as the compounds 2 and 3) were obtained with high yield as pure. [13, 16]. Compared the results of this and similar studies in the literature, it is the right decision to conclude that the proposed coordination for the compounds 4 and 5 occurs between the metal (K^+) and halogen (Cl, Br), which depend on a phosphorus in the cyclotriphosphazene ring. Doublet and triplet peaks in the ^{31}P NMR spectra of the compounds 4 and 5 also support this assessment. This result defined from two studies is quite interesting information for phosphazene chemistry.



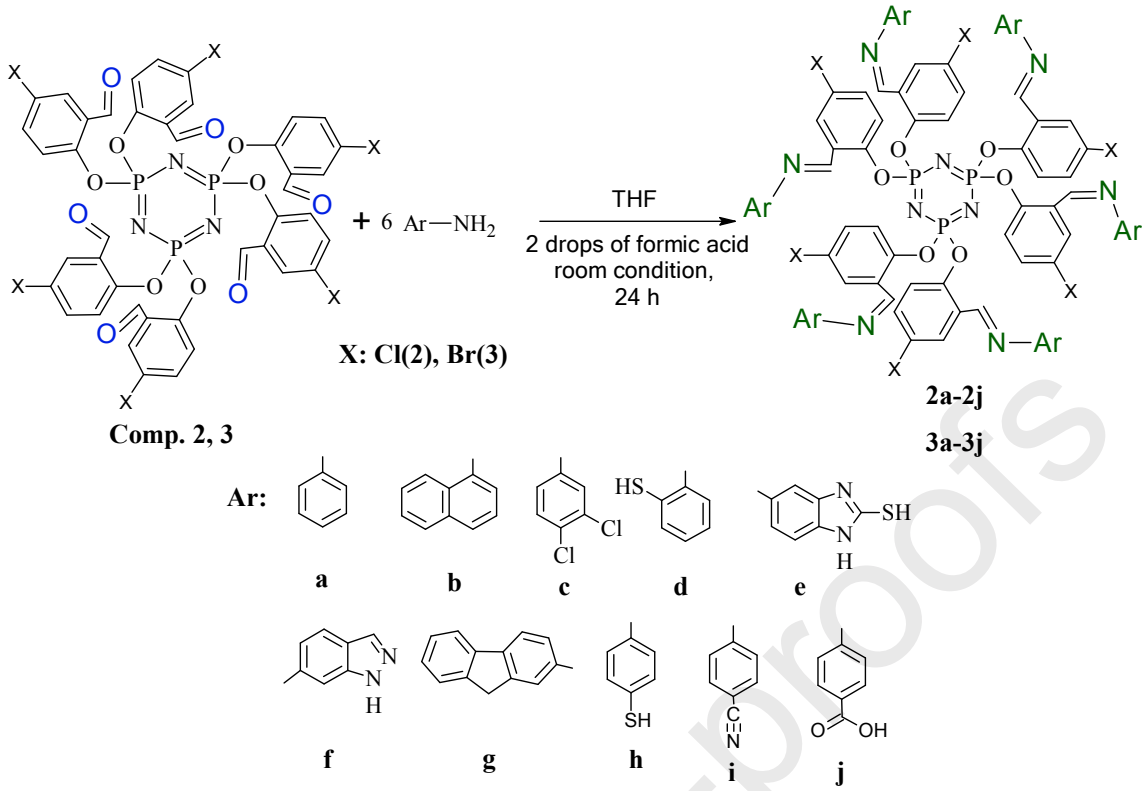
Scheme 2. The clear structures and the synthesis route of the compounds **2** and **3** for 24 h in the presence of $(C_2H_5)_3N$



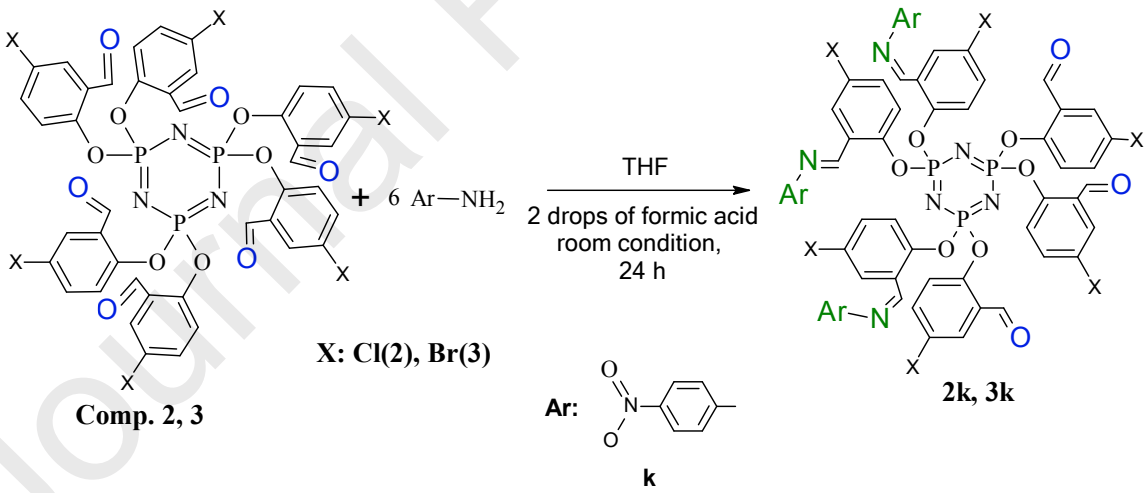
Scheme 3. The Predicted Structures (**A**, **B** and **C**) and the Synthesis Pathway of the Compounds **4** and **5** for 24 h in the Presence of K_2CO_3

To determine whether hexachlorocyclotriphosphazene is hydrolysis at THF, the solution of hexachlorocyclotriphosphazene in THF solvent was stirred with a magnetic mixer for 24 hours under room conditions as we perform the reactions. At the end of this period, ^{1}H and ^{31}P NMR analysis of the mixture and ^{1}H NMR analysis of THF was carried out. Two sharp peaks at 3.62 and 1.73 ppm were detected in the ^{1}H NMR spectrum of the compound 1 solution. These two peaks were determined to belong to $–CH_2-$ protons in THF because these two peaks were also seen in the THF ^{1}H NMR spectrum. That is, the same peaks were seen in both ^{1}H NMR spectra. One sharp peaks at 19.84 ppm were detected in the ^{31}P NMR spectrum of the compound 1 solution. This peak value has the same value as the peak of hexachlorocyclotriphosphazene. As a result of these analyses, it was concluded that there was no hydrolysis of hexachlorocyclotriphosphazene in THF solvent under room conditions.

For the derivation of new organocyclotriphosphazenes containing six imine groups, 1 equiv. of the compounds **2** and **3** were treated with 12 equiv. of aniline (**a**) and some aniline derivatives (**b-k**) in THF in room conditions without using Ar or N_2 atmosphere. Several drops of formic acid were used as a catalyst to make quickly these reactions. Although the excessive amounts of the selected primary amines were used in all the reactions, the organocyclotriphosphazene containing six imine groups did not occur from only 4-nitro-aniline (**k**) (**Scheme 4** and **5**). In previously our study, the organocyclotriphsophazene derivatives containing both formyl and Schiff base groups were firstly identified to occur from the reactions of hexa(4-formyl-pheoxy)cyclotriphosphazene and hexa(4-formyl-2-metoxy-pheoxy)cyclotriphosphazene with 4-cyano-aniline and 4-aminobenzoic acid [13]. 4-nitro-aniline was never used in previously our works and the others works in the literature. Unlike our previous work, the formation of the organocylotriphosphazene derivatives bearing six Schiff base groups from 4-cyano-aniline and 4-amino-benzoic acid in the current study is a very interesting result. The structures of the synthesized organocyclotriphospahzene derivatives were determined using FTIR, NMR (^{1}H, ^{13}C and ^{31}P) and elemental analyses as described in the experimental section. The results obtained in the elemental analyses of all the compounds support the proposed structures.



Scheme 4. The clear structures and the reaction equation for organocyclotriphosphazenes carrying six imine



Scheme 5. The clear structures and the reaction equation for organocyclotriphosphazenes carrying both three imine and three formyl groups

3.2. Characterization

The characteristic P=N, HC=O, P-OAr absorption peaks for the compounds (**2**, **3**, **4** and **5**) were appeared and detected in the FTIR spectra (**Fig 1** and **Fig 2**). These peaks in Fig. **1** ve Fig. **2** spectra are seen as distinct from each other. While HC=O absorption for the compounds **2** and **3** were shown at 1698 -1678 cm^{-1} and 1702-1689 cm^{-1} as the double peaks in the FTIR spectra (**Fig. 1)**, the same peak for the compounds **4** and **5** were observed in the range 1690-1630 cm^{-1} as multi-peaks (**Fig. 2)**. Comparing the FTIR spectra in Fig. 1 and Fig. 2, it was clearly understood that the compounds (**2-3**) and the compounds (**4-5**) differ from their spectra. Hence, it was determined that the compounds (**4-5**) were a phenoxy substituted organophosphazene derivatives bearing formyl groups, but were not pure. The characteristic peak in the region of 3400 cm^{-1} for free Ph-OH was not seen in the spectra of the compounds (**2** and **3**). In the FTIR spectra of the compounds (**2-3**), the characteristic absorption peaks due to P=N and P-O-Ar appeared in the region of 1200-1150 cm^{-1} and 960-940 cm^{-1}, respectively.

While the FTIR spectra of all the compounds (**2a-2j** and **3a-3j**) exhibit characteristic peaks attributed to C=N, P=N and P-OAryl, the characteristic peak in the region of 1700-1680 cm^{-1} for C=O have vanished. The absence of the peak for C=O showed that six formyl groups of the compounds (**2** and **3**) react with primary amines (**a-j**). This result is one of the most important indication for the formation of these organocyclotriphosphazene derivatives containing six imine groups. In the FTIR spectra (**Fig. 3**) of the compounds **2k** and **3k**, in addition to the characteristic C=N, P=N and P-O-Ar stretching vibrations were observed a peak in the range 1700-1680 cm^{-1}. This peak corresponds to the stretching vibrations of the HC=O bond. Therefore, both formyl and imine groups exist in the structures of the compound **2k** and **3k**. The FTIR spectra of all the compounds (**2a-2k** and **3a-3k**) were not observed two bands at around 3300 cm^{-1} for free primary amine due to N-H stretching vibrations.

Both ^{1}H and ^{31}P NMR spectroscopies are the most important methods for verifying the correct structure of the compounds synthesized in this study. From ^{1}H NMR spectra of compounds **2** and **3**, all peaks corresponding to organic groups bound to the phosphazene ring

were identified. Three peaks belonging to all aromatic protons for the compounds **2** and **3** in the spectrum were observed in the range of 8.00−7.00 ppm, which is a typical region for the benzene rings. Additionally, the characteristic proton peak of aldehyde groups (H-C=O) were observed at 10.00 ppm as a singlet. No other proton peaks have been detected in the spectra. In the ^{1}H NMR spectra of the compounds **4** and **5,** the proton peak of the aldehyde groups were observed at around 10.00 ppm as two signals (**Fig. 4**). The results of this analysis showed that the structures of the compounds (**2, 3)** and the compounds **(4**, **5**) synthesized at different periods under the same reaction conditions were different.

The most important information about the structure of the compounds (**2a-2k, 3a-3k**) derived from aniline and aniline derivatives were obtained from ^{1}H NMR spectroscopy, expect 2f-2g and 3f-3g. Since ^{1}H NMR spectra of the compounds (2f-2g and 3f-3g) are not taken, the evaluations are not for these compounds. The signals of all the aromatic protons of these compounds appeared in the region 8.20-6.50 ppm. In their spectra, the signal belonging to the imine and formyl group are the most characteristic peaks. In the ^{1}H NMR spectra of the compounds (**2a-2j, 3a-3j**) bearing six Schiff base groups, the imine proton peak for these compounds were observed in the range 8.30-8.10 ppm as a singlet. However, the proton signal of aldehyde groups was not seen at around 10.00 ppm in the same spectra, expect the compounds 2i, 2j, 3i and 3j. The spectra of four compounds appeared fairly weak proton peak corresponding to aldehyde, according azomethine proton peak. In the ^{1}H NMR spectra of the compounds (**2k** and **3k**), the characteristic peaks belonging to both aldehyde and Schiff base groups were determined at 8.30-8.10 ppm and 10.00-9.50 ppm, respectively. The structure of the compounds (**2k** and **3k**) were also confirmed by obtaining ratios of the integrals of the signals corresponding to the two functional groups. The ratio of the integral area of the proton peaks (HCN/HCO) for the compounds **2k** and **3k** are 3.86/3.52:1.09 and 2.57/2.10:1.27. The –NH_2 protons were not observed between 6.0 and 5.0 ppm in all the spectra of the compounds (**2a-2k, 3a-3k**).

While the proton-decoupled ^{31}P NMR spectra of the compounds **2** and **3** derived for 3 hours in the presence of K_2CO_3 and $(C_2H_5)_3N$ and 24 hours in the presence of $(C_2H_5)_3N$ were observed a singlet peak at 7.81 and 7.58 ppm, the signals were appeared a doublet at 10.0 and a triplet at -1.0 ppm in the ^{31}P NMR spectra of the compounds **4** and **5** derived for 24 hours in the presence of K_2CO_3 (**Fig 6**). The ^{31}P NMR spectra of the compounds **4** and **5** exhibit A2X type spin system due to two different phosphorus environments. The ^{31}P NMR spectra of the compounds (**2a-2j** and **3a-3j**) consist of only a sharp peak between 7.0 and 8.0 ppm for the connection of the same substituents on phosphazene ring. However, the ^{31}P NMR spectra of the compounds (**2k** and **3k**) were appeared multiplet peaks in the region 7.0-8.5 ppm because different phosphorus environments (**Fig. 7**). Since the signals belonging to phosphors in the compounds (**2k** and **3k**) appear in very small chemical shift ranges, it is not possible to suggest the explicit structure of these compounds from these signals. As noted, it is easily determined from these signals that the phosphors in these compounds do not have the same chemical environment.

4. Conclusions

In this study, we identified valuable and very interesting results for phosphazene chemistry. The simplest of these, organocyclotriphosphazenes, which carry six formyl groups from hydroxybenzaldehyde derivatives, were found to form at good yield even under mild conditions without the use of an Ar or N_2 atmosphere. We found the same result in our previous work. The another, it is determined that organocyclotriphosphazene derivatives containing six fromyl groups from 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde occur within 3 h in the presence of both K_2CO_3 and $(C_2H_5)_3N$. If the reaction is to continue for 24 h in the presence of K_2CO_3, it is not possible to obtain organocyclotriphosphazene derivatives containing six formyl groups as pure. When $(C_2H_5)_3N$ was used as a base in this reaction, derivatives of organocyclotriphosphazene containing six formyl groups are obtained, whether the reaction

time is 3 h or 24 h. This second result applies for only 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde. Therefore, if the reactions between hexacholorocylotriphosphazene and organic nucleophiles are monitored by ^{31}P NMR analysis, the waste of time and energy is avoided for the synthesis of organocyclotriphosphazene derivatives.

The organocyclotriphosphazene derivatives derived from 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde were reacted with aniline and selected aniline derivatives for the organocyclotriphosphazene derivatives containing six imine groups. The selected aniline derivatives include some organic structures such as aromatic, heterocyclic, –CN, -COOH, -NO_2, SH and Cl. Although the excess of all the primary amine was used in the reaction, it was determined that it was composed of organophosphazene derivatives which carries both formyl and imine groups from alone 4-nitro-aniline. According to the results determined from this and previous studies, it was determined that both organophosphazene derivatives bearing six formyl groups and primary amine will affect the structure of the organophosphazene derivatives to occur from the reactions between the organophosphazene derivative containing six formyl units and the primary amine. This result is the other most important information that we have identified for phosphazene chemistry in this study.

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References

[1] H. İbişoğlu, E. Erdemir, D. Atilla, Y. Zorlu, E. Şenkuytu, Inorg. Chim. Acta 498 (2019) 119-120.

[2] E. M. Chistyakov, S. N.Filatov, P. A.Yudaev, V. V.Kireev, Tetrahedron Lett. 60 (2019) 444-448.

[3] W. J. Liang, Y. L. Li, P.H. Zhao. G. Z. Zhao, Polyhedron 129 (2017) 30-37.

[4] A. Okumus, G. Elmas, Z. Kilic, N. Ramazanoglu, L. Açık, M. Turk, G. Akca, Turk J. Chem. 41 (2017) 525–547.

[5] A. Uslu, E. Özcan, S. Dural, F. Yüksel, Polyhedron 117 (2016) 394-403.

[6] H. R. Allcock, J. Am. Chem. Soc. 86 (1964) 2591-2595.

[7] C.W. Allen, F.Y. Tsang, T. Moeller, Inorg. Chem, 7 (1968) 2183-2188.

[8] D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw, J. Chem. Soc. A. (1966) 1831-1834.

[9] M. Gleria, R. D. Jaeger, J. Inorg. and Organometallic Polym. 11 (2001) 1-45.

[10] M. Mesbah, T. Douadi, F. Sahli, S. Ssaadi, S. Boukazoula, S. Chafaa, J. Mol. Struc. 1151 (2018) 41-48.

[11] G. A. Carriedo, L. F. Catuxo, F. J. G. Alonso, P. G. Elipe, P. A. Gonzalez, G. Sanchez J. Appl. Polym. Sci. 59 (1996) 1879-1885.

[12] W. Yuan, L. Zhu, X. Huang, S. Zheng, X. Tang, Eur. Poly. J. 41 (2005) 1867-1873.

[13] F. Aslan, A. İ. Öztürk, B. Söylemez, J. Mol. Struc. 1137 (2017) 387-395.

[14] R. Bertani, G. Facchin, Inorg. Chim. Acta 165 (1989) 73-82.

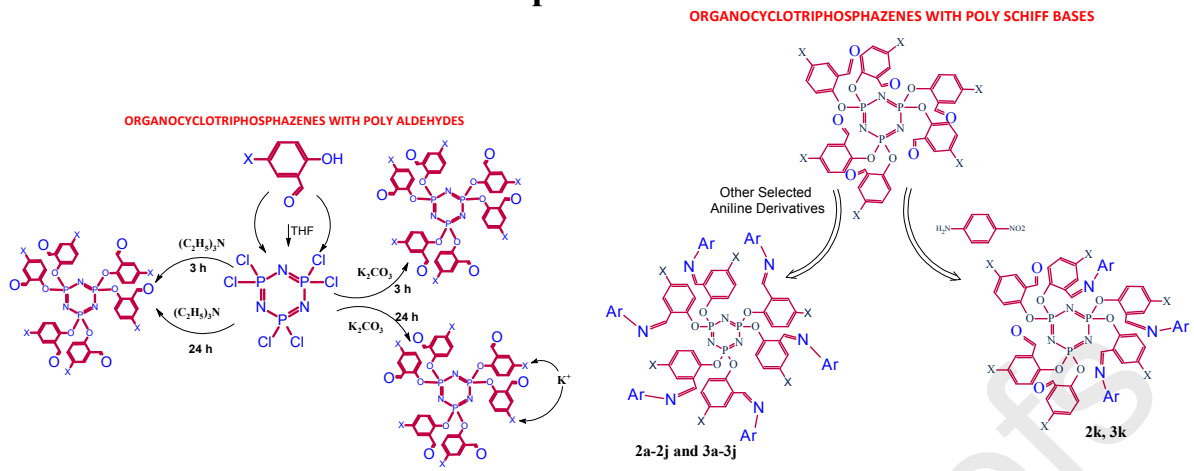
[15] K. Moriya, T. Yamane, T. Suzuki, T. Masuda, H. Mizusaki, S. Yano, M. Kajiwar, Phosphorus, Sulfur, Silicon Relat. Elem. 177 (2002) 1427-1432.

[16] F. Aslan, Z. Demirpence, R. Tatsiz, H. Turkmen, A. I. Ozturk, M. Arslan, Z. Anorg. Allg. Chem. 634 (2008) 1140-1155.

[17] M. Odabasıoglu, G. Turgut, H. Karaer, Phosphorus, Sulfur, Silicon Relat. Elem. 152 (1999) 9-25.

[18] A. I. Öztürk, F.Aslan, Ö. Yılmaz, M. Alğın, M. Arslan, İ. H. Mutlu, Phosphorus, Sulfur, Silicon Relat. Elem. 188 (2013) 585-595.[19] H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press New York and London (1972) 134-135.

Graphical Abstract



Highlights

When the reactions of hexacholorocyclotriphosphazene are also performed under room conditions, expected organocyclotriphosphazene derivatives is obtained with very good efficiency.

There is no need to provide airless media in reactions of hexacholorocyclotriphosphazene with nucleophiles, except for organometallic compounds.

The reactions between hexacholorocyclotriphosphazene and nucleophiles should be monitored by ^{31P} NMR spectroscopy and the reaction should be completed according to the results of this analysis.

The formation of organocyclotriphosphazene derivatives bearing six Schiff base depends on the structures of the aniline derivative and organocyclotriphosphazene derivatives containing six imines.