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# THE REACTIONS OF PHENOXY SUBSTITUTED PHOSPHAZENES WITH 1,3-PROPANEDIOL AND 3-AMINO-1-PROPANOL

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**Abstract-** In the present work, two phenoxy substituted phosphazene derivatives, 2-(2,4,6-tri-tert-butylphenoxo)-2,4,4,6,6-pentachlorocyclo-2λ$^5$, 4λ$^5$, 6λ$^5$-triphosphazatriene (**1**) and 2-(2,4,6-tri-methylphenoxo)-2,4,4,6,6-pentachlorocyclo-2λ$^5$, 4λ$^5$, 6λ$^5$-triphosphazatriene, were prepared. The reactions of these derivatives with 3-amino-1-propanol (**3**) and 1,3-propanediol (**4**) were studied. Novel phenoxy- substituted; two mono spiro (**5**, **8**), and two dispiro phosphazene derivatives (**6**, **7**) were synthesized. The structures of the compounds were defined by elemental analysis, IR, $^1$H and $^{31}$P NMR spectroscopy.

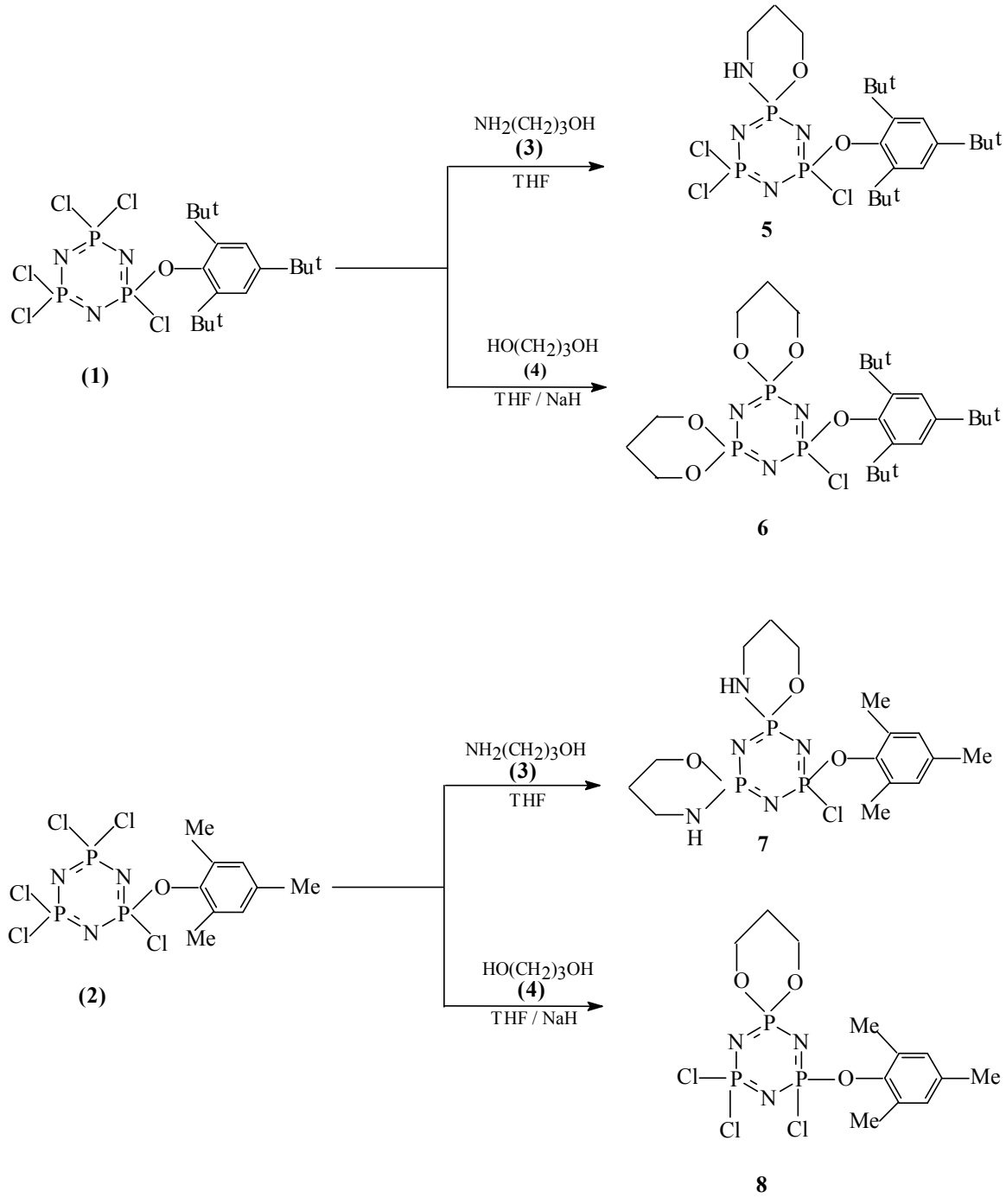
## INTRODUCTION

The cyclophosphazenes probably are the best known and most intensively studied phosphorus-nitrogen compounds. Although a large number of cyclic phosphazenes with monofunctional groups have been prepared and studied,[1] discussion on a substitution with difunctional groups is relatively limited in the literature. There have been several studies of the reactions between halocyclotriphosphazenes and difunctional reagents.[2] There are four structural types for the reactions of difunctional reagent with cyclophosphazenes: spiro, ansa, bridged and open chain.[3] In this article, we report the reactions of phenoxy-substituted phosphazenes (**1** and **2**) with difunctional reagents (**3** and **4**). The novel phenoxy-substituted spiro phosphazene derivatives (**5-8**) have been isolated. White solid compounds, except for **7**, were obtained from these reactions.

## RESULTS AND DISCUSSION

The mono-spiro (**5**) and di-spiro (**7**) products were obtained from treatment of 4 equivalent of 3-amino-1-propanol with compounds (**1** and **2**), respectively. The compounds (**6** and **8**) were obtained from 1,3-

propandiole in presence of sodium hydride with compounds (**1** and **2**), respectively (synthesis of **5-8** are shown in Scheme **1**). Tetrahydrofuran (THF) was used as solvent in these reactions. Thin layer chromatography results showed that reaction mixtures contained more than one product. But, only major products (**5-8**) were isolated from the reaction mixtures by column chromatography.

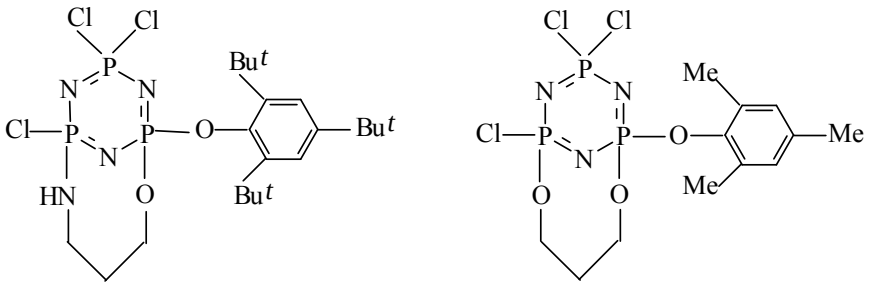



**Scheme 1**

All of the structural proof of compounds (**5-8**) were achieved by IR, $^{1}H$ and $^{31}P$ NMR, mass spectrometer and elemental analyses. All the analytical data are consistent with the proposed structures (**5-8**). These

results are given in the experimental section. Compounds (**5-8**), except for **7**, were synthesized in good yield. Only compound (**7**) was obtained in low yield (27 %). All compounds (**5-8**) are white solids, stable in air and moisture, however compound (**7**) is viscous oil. In the IR spectra of spiro phosphazene derivatives (**5-8**), the characteristic $\nu_{P=N}$ vibrations occur between 1116 and 1257 $cm^{-1}$. The nature of the substituents affects the streching vibrations of P=N. The NH- streching frequencies of compounds (**5** and **7**) were observed at 3389 and 3375 $cm^{-1}$. In the FTIR spectra of the compounds (**5-8**), C-H (aliphatic) and C-C (aryl) streching bands are observed between 2927-2960 and 1369-1477 $cm^{-1}$, respectively. P-Cl streching bands of compounds (**5-8**) are observed at 559, 621, 661, 688 $cm^{-1}$, respectively.

$^1$H NMR spectra of compounds (**5-8**) are relatively simple and show all the protons characteristic of the anticipated structures. The methyl protons resonate at δ = 2.13, 2.39 (4-C*H*$_3$) and δ = 2.31, 2.40 (2-C*H*$_3$) for compounds (**7** and **8**), respectively. The methyl protons resonate at δ = 1.29 (4-Bu$^t$,-C*H*$_3$) and 1.52 (2-Bu$^t$,-C*H*$_3$) in 1:2 ratio for **5**. The methylene protons resonate at δ = 4.41, 3.75 (O-C*H*$_2$-); δ = 3.4 , 3.19 (N-C*H*$_2$) and δ = 1.89 , 1.73 (2-C*H*$_2$) for compounds (**5** and **7**), respectively. These values are in good agreement with the published values (**12, 15**). The methylene protons resonate at δ = 1.78, 2.09 (2-C*H*$_2$), δ 4.3, 4.49 (1,3-C*H*$_2$) for **6** and **8** , respectively. The aromatic ring protons are observed at δ = 7.26-7.30, δ = 7.19-7.23, δ = 6.75-7.08, δ = 6.89-6.91 as multiplets for compounds (**5**, **6**, **7** and **8**), respectively. $^1$H NMR chemical shifts of **5** and **7** compounds are in good agreement with the published values.[5] The proton decoupled $^{31}$P NMR spectra of the compounds (**5** and **8**) have ABX spin system due to three different phosphorus environment within the molecules. Chemical shifts were δ P(spiro) = 11.02, δ PCl(OAr) 12.11 and δ $PCl_2$ = 24.80 in **5**, δ P(spiro) = 6.74, δ PCl(OAr) = 17.79 and δ $PCl_2$ = 28.44 in **8**. These are consistent with the mono-spiro structures as assigned, but also ansa structures (**I**) and (**II**) (**Scheme 2**) may be. But the probability of being ansa structures (**I** and **II**) is less likely due to steric effect of phenols in compounds (**5** and **8**).




**I** **II**

**Scheme 2**

The compound (**7**) may have both *cis* and *trans* isomers. But only one derivative has been seperated by by column chromatography. *Cis* and *trans* derivatives could not be distinguished by spectroscopic data. More

extensive caharacterizations of all compounds might be obtained single crystal X-ray difractions studies but single crystals of sufficiently high quality was not obtained.

According to the $^{31}P$ NMR spectra of compounds (**6** and **7**), it is concluded that the only dispiro structures are possible. Chemical shifts were δ P(spiro) = 12.12 and δ PCl(OAr) = 15.71 in **6**, P (spiro) = 12.42 and δ PCl(OAr) = 23.98 in **7**. The $^{31}P$ NMR spectra of **6** and **7** gave $AB_2$ spin patterns with $^2J_{PNP}$ = 55.1 and 53.9 Hz respectively. These values are in good agreement with the published results.[6] The electron impact MS of **5**, **6, 7** and **8** showed the well defined molecular ions at m/z 580 (100 %), 575 (44 %), 450 (100 %), and (6 %) respectively.

## EXPERIMENTAL

### General Remarks

The compounds (**1** and **2**) were prepared as described elsewhere.[4] All reactions were performed under dry argon atmosphere using standart schlenk techniques. THF was distilled over a sodium-potassium alloy in the presence of benzophenone under dry argon atmosphere. Sodium hydride was used as hydrogen chloride acceptor for synthesis of compounds (**6** and **8**). TLC experiments were performed on silica gel 60 plates (Merck). Column chromatography was done with silica gel (230-400 mesh), product of Merck. Hexachlorocyclotriphoshazene was purchased from Aldrich and purified by recrystallization from *n*-hexane. 2,4,6-trimethylphenol, 2,4,6-tri-*tert*-butylphenol, 1,3-propanediol and 3-amino-1-propanol were purchased from Aldrich and Merck Chem. Co. Sodium hydride, 60% dispersion in mineral oil (Merck); prior to use was removed by washing with dry hexane (Merck) followed by decantation. All reactions were monitored by using Kieselgel 60 $F_{254}$ (silica gel) precoated TLC plates and the separating conditions were determined. The separation of products was carried out by column chromatography, using Kieselgel 60 (230-400 mesh, Merck). The purity of compounds (**5-8**) was checked by TLC and characterized by elemental analyses, $^1H$, $^{31}P$ NMR spectrometry and FT-IR. Elemental analyses were obtained using a LECO 932 CHNS instrument, and IR spectra were recorded on an ATI Unicam Mattson 1000 FT-IR spectrophotometer as KBr pellets. Electron impact mass spectra were obtained by AGILENT 1100 MSD spectrometer. $^1H$ and $^{31}P$ NMR spectra were recorded in $CDCl_3$ solutions on a Bruker 300 Ultra Shield spectrometer operating at 300.13 and 121.49 MHz, respectively. The $^1H$ chemical shifts (δ) were measured using $SiMe_4$ as an internal standard, and the $^{31}P$ chemical shifts were measured using 85% $H_3PO_4$ as an external standard.

### The reaction of 1 with 3-amino-1-propanol to form compound (5)

Compound (**1**) (0.90 g; 1.57 mmol) was dissolved in THF. The solution was frozen with a liquid nitrogen-acetone mixture. To this solution, was slowly added solution of 3-amino-1-propanol (0.47 g; 6.28 mmol) in THF. The reaction mixture was stirred at rt for 48 h. The precipitated amine hydrochloride was

removed by filtration and the solvent was evaporated. The white solid residue was chromatographed with first $CH_2Cl_2$ /*n*-pentane (1:1) after $CH_2Cl_2$ /*n*-pentane (1:3). Compound (**5**) was obtained. (Yield 67 %) ($R_f$ = 0.636 $CH_2Cl_2$ / *n*-hexane 5:1). Compound (**5**) is a white colored crystal, mp 158-160 $^0$C. Anal. Calcd for $C_{21}H_{36}N_4O_2Cl_3P_3$ (575.82) : C 43.75, H 6.25, N 9.72. Found : C 43.78, H 6.12, N 9.20. MS (EI / 150 eV), M(**5**) = 580): m/z 580 ([$M^+$], 100), 526 ($M^+$-$C_4H_6$, 18), 524 ($M^+$-$C_4H_8$, 50), 338 ($M^+$-$C_{18}H_{26}$, 8), 336 ($M^+$-$C_{18}H_{28}$, 25). IR (KBr) : ν(NH) 3389, ν(CH al) 2970, ν(CC aryl) 1477, 1415, 1369, ν(P=N) 1168, ν(POC) 1088, 978, ν(P-Cl) 559 cm$^{-1}$. NMR ($CDCl_3$), $^1$H, δ = 1.29 (m, 9H, 4-Bu$^t$-C*H*$_3$), δ = 1.52 (m, 18 H, 2-Bu$^t$-C*H*$_3$), 7.30 (m, 2H, Ar-*H*), 4.41 (m, NHCH$_2$CH$_2$C*H*$_2$O-), 3.4 (m, NHC*H*$_2$CH$_2$CH$_2$O-), 1.89 (m, NHCH$_2$C*H*$_2$CH$_2$O-). $^{31}$P NMR assigned as ABX pattern, δ 11.02 (A portion of ABX, 1P, PNHO); δ 12.11 (B portion of ABX, 1P, PClOAr,); δ 24.8 (X portion of ABX, 1P, $PCl_2$). Spin system analysed as $^2J_{PP}$ AB = 62, AX = 64, BX = 60 Hz.

**The Reaction of 1 with 1,3-propandiol, to form Compound (6)**

Compound (**1**) (0.61 g; 1.06 mmol)1,3-propanediol (0.32 g; 4.25 mmol) was dissolved in 30 mL of dry THF and cooled in an ice bath and NaH (60% oil suspension, 0.25 g; 6.36 mmol; the oil was removed by washing with dry hexane, followed by decantation) in 20 mL of dry THF was added under an argon atmosphere. The reaction mixture was stirred for 72 h at rt and then it was refluxed for 1 h. After solvent was removed in vacuo. The resulting white solid was dissolved in $CH_2Cl_2$ (30 mL) and precipitated salt (NaCl) was then filtered off, the solvent was removed under reduced pressure and resulting white solid was subjected to column chromatography, using $CH_2Cl_2$/*n*-hexane 5:1 as eluent. Compound (**6**) was obtained in 72 % yield. $R_f$ = 0.381 $CH_2Cl_2$ / *n*-hexane 5:1), mp 187-188 ℃. Compound **6** is a white solid. Anal. Calcd (%) for $C_{24}H_{41}N_3O_5ClP_3$ (580.14) : C 49.64, H 7.06, N 7.23. Found : C 49.69 , H 7.07 , N 6.64. MS (EI / 150 eV), M(**6**) = 575): m/z 575 ([$M^+$], 44), 523 ($M^+$-$C_4H_4$, 26), 521 ($M^+$-$C_4H_6$, 74), 519 ($M^+$-$C_4H_8$, 76), 333 ($M^+$-$C_{18}H_{26}$, 91), 331 ($M^+$-$C_{18}H_{28}$, 100). IR (KBr) : ν(CH al) 2959, ν(P=N) 1247, ν(POC) 1049ν(P-Cl) cm$^{-1}$.NMR ($CDCl_3$), $^1$H, δ = 1.27 (s, 9H, 4-Bu$^t$-C*H*$_3$), δ = 1.44 (s, 18 H, 2-Bu$^t$-C*H*$_3$), 7.19-7.23 (m, 2H, Ar-*H*), 4.3 (s, 4H, 1,3-C*H*$_2$), 1.78 (m, 2H, 2-C*H*$_2$). $^{31}$P $AB_2$ pattern, $\delta_A$ = 15.71 (t, 1P, PClOAr), $J_{AB}$ = 55.1), $\delta_B$ = 12.12 (dd, 2P, 2PClO, $J_{AB}$ = 55.1).

**The reaction of 2 with 3-amino-1-propanol to form compound (7)**

Compound (**2**) (1.00 g; 2.23 mmol in 20 mL of THF) and 3-amino-1-propanol (0.67 g; 8.92 mmol, in 15 mL of THF) were synthesized using the same procedure described for **5**. The reaction mixture vigorously stirred at rt for 72 h. The reaction mixture was filtered to remove the precipitate, the solvent was removed under reduced pressure and resulting colorless oil was subjected to column chromatography, using acetone/*n*-hexane (1:1) as eluent. Compound (**7**) was obtained in 27 % yield. Compound (**7**) was viscous oil. ($R_f$ = 0.472 acetone / *n*-hexane 1:1) Anal. Calcd for $C_{15}H_{25}N_5O_3Cl\ P_3$ (451.75) : C 39.88, H

5.53, N 15.50. Found : C 39.17, H 6.03, N 15.83. MS (EI / 150 eV), M(**7**) = 451): m/z 451 ([$M^+$], 5), 430 ($M^+$-$C_4H_7$, 8), 412 ($M^+$-$C_3H_3$, 4), 351 ($M^+$-$C_6H_7$, 7). IR (KBr) : ν(NH) 3375, ν(CH al) 2962, ν(CC aryl) 1412, ν(P=N) 1257, ν(POC) 1080, 1008, ν(P-Cl) 661 $cm^{-1}$. NMR ($CDCl_3$), $^1H$, δ = 2.13 (s, 3H,4-C*H*$_3$), 2.31 (s, 6H, 2-C*H*$_3$), 6.75 (s, 2H, Ar-*H*), 3.75 (-NHCH$_2$CH$_2$C*H*$_2$OH), 3.19 (-NHC*H*$_2$CH$_2$CH$_2$OH), 1.73 (-NHCH$_2$C*H*$_2$CH$_2$OH).$^{31}$P, $AB_2$ pattern, $\delta_A$ = 23.98 (t, 1P, PClOAr, $J_{AB}$ = 53.9 Hz ), $\delta_B$ = 12.42 (dd, 2P, PNHO, $J_{AB}$ = 53.9 Hz).

**The reaction of 2 with 1,3-propandiol, to form compound (8)**

Compound (**2**) (1 g; 2.23 mmol in 20 mL of THF) and 1,3-propanediol (0.67 g ; 8.92 mmol, in 15 mL of THF) were used as for **7**. The reaction mixture was stirred for 72 h at rt under an atmosphere of argon. Later it was refluxed for 1 h. The reaction mixture was filtered to remove the sodium chloride; the solvent was removed under reduced pressure and resulting white solid was subjected to column cromatography using $CH_2Cl_2$ /*n*-hexane (1:1) as eluent and compound (**8**) was obtained with 55 % yield. Compound (**8**) is white solid, mp = 112-114 $^0$C. ($R_f$ = 0.272 $CH_2Cl_2$ / *n*-hexane 1: 2). Anal. Calcd for $C_{12}H_{17}N_3O_3Cl_3P_3$ (450.26) : C 31.98, H 3.77, N 9.33. Found : C 32.54, H 3.71, N 8.85. MS (EI / 150 eV), M(**8**) = 450): m/z 450 ([$M^+$], 100), 448 ($M^+$-2H, 54), 446 ($M^+$-4H, 81), 414 ($M^+$-Cl, 8). IR (KBr) : ν(CH al) 2927, ν(CC aryl) 1423, ν(P=N) 1243, 1210, 1116, ν(POC) 1057, 979, ν(P-Cl) 688 $cm^{-1}$. NMR ($CDCl_3$), $^1H$, δ = 2.39 (s, 3H, 4-C*H*$_3$), δ = 2.40 (s, 6H, 2-C*H*$_3$), 6.89-6.91(m, 2H, Ar-*H*), 4.49 (m, 4H, 1,3-C*H*$_2$), 2.09 (m, 2H, 2-C*H*$_2$). $^{31}$P ABX pattern, $\delta_A$ = 28.24 (t, 1P, $PCl_2$); $\delta_B$ = 17.79 (t, 1P, PClOAr); $\delta_X$ = 6.74 (t, 1P, P(spiro)). Spin system analysed as $^2J_{PP}$ AB = 65, AX = 66, BX = 71 Hz.

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