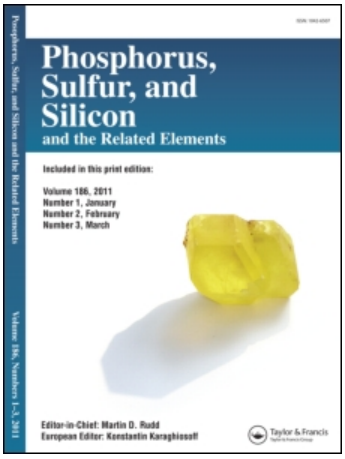

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A. Ihsan Ozturk[a]; Fatih Aslan[a]; Erol Cil[b]; Mustafa Arslan[b]; Adem Kiliç[c]
[a] Harran University, Sanliurfa, Turkey [b] Firat University, Elazig, Turkey [c] Gebze High Technology Institute, Kocaeli, Turkey

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THE SYNTHESIS AND CHARACTERIZATION OF CYCLOALKOXY-LINEAR PHOSPHAZENES

A. Ihsan Ozturk,[a] *Fatih Aslan,*[a] *Erol Cil,*[b] *Mustafa Arslan,*[b] *and Adem Kiliç*[c]
Harran University, Sanliurfa, Turkey;[a] *Firat University, Elazig, Turkey;*[b] *and Gebze High Technology Institute, Kocaeli, Turkey*[c]

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The reactions of N-*dichlorophosphoryl*-P-*trichlorophosphazene,* $Cl_3P{=}N{-}P(O)Cl_2$ *with the sodium salts of cyclopentanol, cyclohexanol, 4-methylcyclohexanol, 3-methylcyclohexanol, 3-methylcyclopentanol are discussed. Pentacycloalkoxy-substituted phosphazenes were obtained from cyclopentanol, 4-methylcyclohexanol, 3-methylcyclohexanol, 3-methylcyclopentanol. Tetrasubstituted derivative also was obtained from cyclohexanol at the same conditions. The structure of products was defined by IR,* ^{1}H, ^{13}C, ^{31}P *NMR, and mass spectroscopy.*

Keywords: Alcoholysis; alkoxyphosphazenes; cycloalkoxyphosphazenes; linear phosphazenes; monophosphazenes

The cyclo- and poly-phosphazenes are probably the best known and most intensively studied phosphorus-nitrogen compounds because they are more stable than monophosphazenes.[1,2] Although there are many publications about cyclo- and polyphosphazenes,[3–26] the number is limited for linear phosphazenes because the short-chain species are generally difficult to synthesize, isolate, and study. However, phosphazenes possess a number of characteristics such as the using of drug components for chemotherapeutic applications and antibacterial activity.[27–29] These compounds are used in the structure of medical implants and drug delivery systems. *N*-di(alkoxy)phosphoryl-*P*-tri(alkoxy)monophosphazene, especially those with different alkyl groups are biologically active compounds.[30]

N-dichlorophosphoryl-*P*-trichlorophosphazene **1**, $Cl_3P{=}N{-}P(O)Cl_2$, which is the short-chain linear phosphazene, is a very sensitive

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Address correspondence to Mustafa Arslan, Firat Universitesi, Fen-Ed. Fak. Kimya Bolumu, Elazig, TR-23169, Turkey.

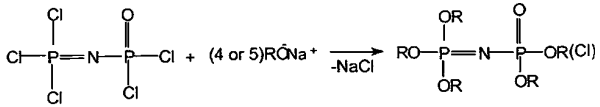
material to air and moisture. It can be obtained by several different reactions.[31–34]

The reactions of compound **1** with amines and alcohols have been reviewed.[35,36] The replacement of one chlorine atom by the allyloxy group and the partial aminolysis of compound **1** with methylamine, *t*-butylamine.[37,38] and diisopyropylamine[39] has been reported. The partial replacement of chlorine atoms has been achieved with *o*-dichloro and *o*-dimethylphenol,[40] 2,4,6-*tert*-butylphenol, and 2,6-di-*tert*-butyl-4-methylphenol.[41] Pentasubstituted derivatives of compound **1** with alcohol such as ethyl, pyropyl, *n*-butyl, *i*-butyl, pentyl alcohol,[42] 4-phenylphenol,[43] benzyl, allyl, tetrahydrofurfuryl alcohol, 2-isopyropyloxyethanol,[44] 2,4,6-trimethylphenol,[45] *o*-methyl- and *p*-methylphenol, α-hydroxynaphthalene,[46] and amines such as pyrrolidine, morpholine, piperidine[47] have been obtained. Trisubstituted derivatives have been obtained from the reaction between **1** and mercaptans such as ethyl, pyropyl and octyl mercaptans.[48] Pentasubstituted organophosphazenes have been obtained from the reaction of **1** with aryllithium or Grignard reagents.[49]

Here, we report the reactions of $Cl_3P{=}N{-}P(O)Cl_2$ with cycloalcohols yielding alkoxymonophosphazenes. Tetrasubstituted phosphazenes have been obtained from the reaction of **1** with cyclohexanol. Pentaalkoxy derivatives were obtained from cyclopentanol, 4-methylcyclohexanol, 3-methylcyclohexanol, and 3-methylcyclopentanol.

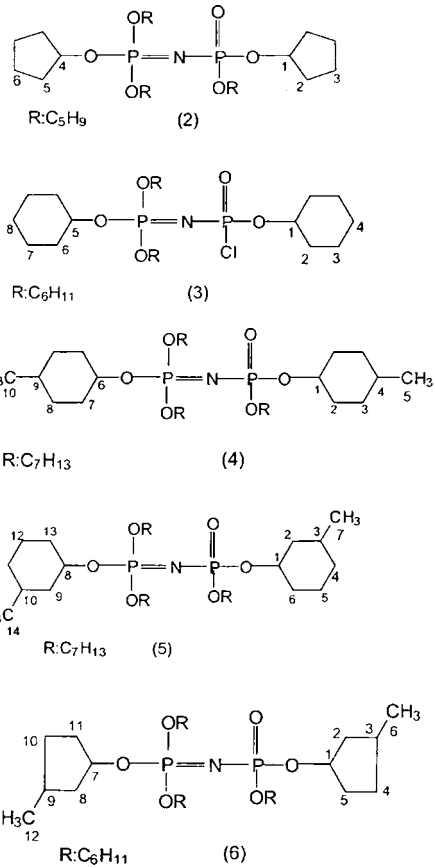
RESULTS AND DISCUSSION

The reaction of **1** with 5 equivalents of sodium cyclopentaoxide, sodium 4-methylcyclohexaoxide, sodium 3-methylcyclohexaoxide, and 3-methylcyclopentaoxide in toluene gave the pentasubstituted compounds as the main products. As the same way, tetrasubstituted compound was obtained from sodium cyclohexaoxide. They were isolated from the reaction mixture by column chromatography and characterized by ^{1}H, ^{13}C, ^{31}P-NMR, mass spectrometry, and FT-IR. Although the starting compound **1** is a very sensitive material to air and moisture, the cycloalkoxysubstituted phosphazenes are stable but fairly hygroscopic.



1 **2-6**

RO^-: $C_5H_9O^-$, $C_6H_{11}O^-$, $C_6H_{10}(4\text{-}CH_3)O^-$, $C_6H_{10}(3\text{-}CH_3)O^-$, $C_5H_8(3\text{-}CH_3)O^-$



SCHEME 1 The structure of compounds **2–6**.

The characteristic stretching peaks in the IR spectra of the phosphazenes have been assigned as in Table I. The P=O and P=N stretching vibrations, 1263–1229 cm^{-1} and 1338–1324 cm^{-1}, respectively, are characteristic of phosphazenes. The nature of the substituents affects the stretching vibrations. Compared to **1** these peaks, especially P=O vibrations are shifted to longer wavelengths for **2–6**.

The NMR data are presented in Table II–IV. Hydrogen and carbon atoms were numbered as shown in Scheme 1. The AB spin pattern in the ^{31}P NMR spectra indicate that the phosphazene skeleton is intact. While phosphorus signals of the $(RO)_3P{=}N-$ unit in the cycloalkoxide-substituted phosphazenes show the least difference from **1**, the signals of the $-P(O)(RO)_2$ unit move to the lower field (Table II).

TABLE I Characteristic IR Vibrations of **1–6** (cm^{-1})

	ν_{C-H}	$\nu_{P=N}$	$\nu_{P=O}$	ν_{P-N}	ν_{P-O-C}	ν_{P-Cl}
1	—	1338	1263	770	—	650
2	2871–2961	1330	1234	720	1008	—
3	2943	1324	1254	717	1020	550
4	2942	1330	1236	768	1008	—
5	2937	1330	1229	717	1020	—
6	2954–2863	1337	1242	722	1017	—

When the phosphorus signals in the substituted phosphazenes are compared to **1**, it is observed that these peaks are shifted to high-field in case of aryloxyphosphazenes,[46] and to downfield in case of arylphosphazenes[49] relative to compound **1**. But there are little differences between cycloalkoxy phosphazenes. For example, in the pentasubstituted *p*-methylphenoxy, *p*-methylphenyl, and 4-methylcyclohexaoxy phosphazenes, the phosphorus signals for PN and PO appear at −13.8, −20.7; 15.4, 13.8; and −2.9, −5.2 ppm respectively. In the aryloxyphosphazenes, the greater shielding may be considered to be a consequence of the resonance and inductive effects. The localization of the electron density on the phosphorus atoms causes a higher magnetic shielding and, thus generates the high field shifts in the position of the resonance of the phosphorus atoms. In the arylphosphazenes, phosphorus atoms may be deshielded by the magnetic anisotropy effect and their peaks will be observed at the lower field.

In the cycloalkoxy-substituted phosphazenes (**2–6**) (Scheme 1) there are essentially two sets of proton groups one in the phosphoryl [—P(O)$(OR)_2$ or —P(O)(OR)Cl] and the other in the phosphazene [$(RO)_3$P=N—] moieties. The two environments can be distinguished in some cases, the latter being more shielded than the former. There are also two sets of carbon atoms. In the ^{1}H NMR spectra, the 2:3 ratio of integral intensities for the two sets of protons is observed for **2**, **4**, **5**, and **6**. There is the 1:3 ratio for **3**. There are also the same ratios between

TABLE II ^{31}P NMR Data of **1–6**

	δ_{PN}	δ_{PO}	J_{PNP}
1	−2.6	−10.6	21.3
2	−3.5	−6.0	64.8
3	−2.8	−6.5	62.6
4	−2.9	−5.2	65.6
5	−3.0	−5.5	65.2
6	−2.2	−5.7	63.0

TABLE III ^{1}H NMR Data of **2–6**

2	1.46–1.79 (H^2, H^3, H^5, H^6), 4.67 (H^1), 4.88 (H^4)
3	1.27 (H^7), 1.50 (H^6), 1.67 (H^4, H^8), 1.84 (H^2, H^3), 4.45 (H^1, H^5)
4	0.85 (H_5, H_{10}), 0.97 (H^8), 1.38 (H^4, H^7, H^9), 1.69 (H^3), 2.07 (H^2), 4.10 (H^1), 4.33 (H^6)
5	0.84 (H^7, H^{14}), 1.20 (H^5, H^{12}), 1.35 (H^3, H^{10}), 1.50 (H^{11}), 1.64 (H^2), 1.87 (H^6), 2.04 (H^9, H^{13}), 3.47 (H^8), 4.10 (H^1)
6	0.80–2.16 (H^6, H^{12}, H^3, H^9, H^4, H^{10}, H^2, H^5, H^8, H^{11}), 3.81 (H^7), 3.88 (H^1)

(For numbering see Scheme 1).

the integral intensities of similar carbons. These observations indicate that cycloalkoxy groups have replaced five or four chlorine atoms in **1**. The nearest protons to the phosphorus atoms are very well characterized by the ^{1}H NMR spectra that show peaks at the lowest downfield. Especially they are clearly observed in **2**, **4**, **5**, and **6** (Table III).

The signals of every carbon atom can be seen in the ^{13}C NMR spectra (Table IV). It is noticed that the nearest carbon atoms to the phosphorus atoms are generally observed at the lowest downfield. In these compounds (**2–6**), the environments of $P(O)(OR)_2$ and $(RO)_3P{=}N$ can be distinguished in some cases. Especially, the nearest carbons to the phosphorus atoms in the $-P(O)(OR)_2$ are deshielded more than that of the $(RO)_3P{=}N-$.

The electron impact MS spectra of **2**, **3**, and **6** showed the parent ions at m/z 519 as M + 2, at 520 as M − 3, and at 587 respectively. The dominant ion is observed at 67 ($C_5H_7^+$, 100%) for **2**. The peaks at m/z values of 43, 57, 69, and 99 correspond to the loss of C_3H_7, C_4H_9, C_5H_9, and $C_6H_{11}O$ for **3**. In addition, the ratio of (M − 3) + 2/M − 3 = 1/3 shows the presence of one chlorine atom in the structure of **3**. Compound **6** gives the dominant ions at m/z 41 ($C_3H_5^+$, 100%), 43

TABLE IV ^{13}C NMR Data of **2–6**

2	23.05 (C^6), 23.23 (C^3), 33.74 (C^5, $^3J_{POCC}$:5.44 Hz), 33.99 (C^2, $^3J_{POCC}$:4.93 Hz), 78.23 (C^1, $^2J_{POC}$:6.15 Hz), 81.63 (C^4, $^2J_{POC}$:7.3 Hz)
3	23.62 (C^8), 24.11 (C^4), 25.64 (C^7), 25.87 (C^3), 33.34 (C^6, $^3J_{POCC}$:4.71 Hz), 33.70 (C^2, $^3J_{POCC}$:4.21 Hz), 77.22 (C^1, $^2J_{POC}$:6.71 Hz), 78.95 (C^5, $^2J_{POC}$:7.5 Hz)
4	22.11 (C^{10}), 22.33 (C^5), 31.80 (C^9), 32.09 (C^4), 33.34 (C^8), 33.61 (C^7, $^3J_{POCC}$: 4.66 Hz), 33.75 (C^3), 34.23 (C^2, $^3J_{POCC}$:4.40 Hz), 75.62 (C^1, $^2J_{POC}$:6.31 Hz), 78.73 (C^6, $^2J_{POC}$:7.0 Hz)
5	22.51 (C^7), 22.68 (C^{14}), 24.53 (C^5), 24.57 (C^{12}), 31.70 (C^4), 31.82 (C^{11}), 34.48 (C^{13}, $^3J_{POCC}$:4.98 Hz), 34.12 (C^2), 34.45 (C^3), 34.53 (C^9), 35.72 (C^{10}), 42.51 (C^6, $^2J_{POC}$:4.5 Hz), 75.37 (C^1, $^2J_{POC}$:6.20 Hz), 78.43 (C^8, $^2J_{POC}$:6.22 Hz)
6	82.6 (C^7, $^2J_{POC}$:7.09 Hz), 14.53–42.29 (C^6, C^{12}, C^4, C^{10}, C^3, C^9, C^2, C^8, C^5, C^{11})

(For numbering see Scheme 1; coupling constants, J, Hz).

($C_3H_7^+$, 100%), 55 ($C_4H_7^+$, 100%), 57 ($C_4H_9^+$, 100%), 67 ($C_5H_7^+$, 100%), 69 ($C_5H_9^+$, 100%), 81 ($C_6H_9^+$, 100%), and 97 ($C_6H_9O^+$, 100%). In the MS spectra of **4** and **5**, the molecular ion peaks are not observed. But the M-62 (62:$C_5H_2^+$), M-96 (96: $C_7H_{12}^+$) peaks which form the degradation products of 4-methylcyclohexaoxy group are observed for **4**. The base ion peak is at *m/z* 177 (100%, probably $C_{13}H_{21}^+$ and/or $C_{11}H_{17}O^+$). The dominant ion peaks are at *m/z* 41 ($C_3H_5^+$, 100%), 52 ($C_4H_4^+$, 100%), 65 ($C_5H_5^+$, 100%), 78 ($C_6H_6^+$, 100%), and 95 ($C_7H_{11}^+$, 100%) for **5**. The peak at *m/z* 177 (97%) is also important. This shows the similar cleavage for **4** and **5**.

EXPERIMENTAL

General

Solvents were dried by conventional methods. All reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates and the separating conditions were determined. The separation of products was carried out by flash column chromatography using Kieselgel 60 (60-230 mesh).

IR spectra were recorded on an ATI Unicam Mattson 1000 FTIR spectrophotometer. ^1H, ^{13}C, ^{31}P-NMR spectra were recorded using a Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63, and 161.98 MHz, respectively. All data were recorded for solutions in $CDCl_3$. The ^1H and ^{13}C chemical shifts were measured using $SiMe_4$ as an internal standard, the ^{31}P chemical shifts, using 85% H_3PO_4 as an external standard. Chemical shifts downfield from the standard are assigned positive δ values. Electron impact mass spectra were obtained by Micromass UK Platform-II spectrometer. Microanalysis was carried out by LECO 932 CHNS-O apparatus. The starting material **1** was prepared by the method of Emsley, Moore and Udy and purified by vacuum distillation.[31]

Synthetic Procedures

The cycloalkoxymonophosphazenes were sythesized as follows:

$(C_5H_9O)_3P{=}N{-}P(O)(C_5H_9O)_2$, **2**: To form the alcoholate, small pieces of metallic sodium (0.644 g, 28 mmol) were slowly added to cyclopentanol (2.41 g, 28 mmol) in 150 ml of toluene by stirring at ambient temperature with argon being passed over the reaction vessel. After the alcoholate reaction was complete, the solution of sodium

cyclopentaoxide was cooled to 0°C. Compound **1** (1.5 g, 5.56 mmol) in 150 ml of toluene was slowly added dropwise to the reaction vessel by stirring during 90 min, and the mixture was allowed to warm to 25°C and the reaction was continued for 36 h at 25°C. The precipitated salt (NaCl) was filtered and the solvent was removed under vacuum. The oily residue was examined by TLC using chloroform/acetone (7:1, $Rf = 0.61$). It was separated by column chromatography. The viscous compound **2** was obtained in 77% yield.

$(C_6H_{11}O)_3P{=}N{-}P(O)Cl(C_6H_{11}O)$, **3**: Conditions as for **2** using 1.06 g (46 mmol) of metallic sodium, 4.60 g (46 mmol) of cyclohexanol, and 2.50 g (9.3 mmol) of compound **1**, eluent chloroform/*n*-hexane (10:1, $Rf = 0.55$). The viscous compound **3** was obtained in 63% yield.

$(4\text{-}CH_3C_6H_{10}O)_3P{=}N{-}P(O)(4\text{-}CH_3C_6H_{10}O)_2$, **4**: Conditions as for **2** using 1.06 g (46 mmol) of metallic sodium, 5.25 g (46 mmol) of 4-methylcyclohexanol, and 2.50 g (9.3 mmol) of compound **1**, eluent chloroform/ethylacetate/*n*-hexane (6:2:1, $Rf = 0.55$). The viscous compound **4** was obtained in 73% yield.

$(3\text{-}CH_3C_6H_{10}O)_3P{=}N{-}P(O)(3\text{-}CH_3C_6H_{10}O)_2$, **5**: Conditions as for **2** using 1.06 g (46 mmol) of metallic sodium, 5.25 g (46 mmol) of 3-methylcyclohexanol, and 2.50 g (9.3 mmol) of compound **1**, eluent chloroform/ethylacetate/*n*-hexane (6:2:1, $Rf = 0.60$). The viscous compound **5** was obtained in 67% yield.

$(3\text{-}CH_3C_5H_8O)_3P{=}N{-}P(O)(3\text{-}CH_3C_5H_8O)_2$, **6**: Conditions as for **2** using 0.46 g (20 mmol) of metallic sodium, 2.00 g (20 mmol) of 3-methylcyclopentanol, and 1.10 g (4.0 mmol) of compound **1**, eluent chloroform/ethylacetate/*n*-hexane (6:3:1, $Rf = 0.66$). The viscous compound **6** was obtained in 46% yield.

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