Scientific paper

Synthesis and Characterization of Oxime-Phosphazenes Containing 2,2'-Dioxybiphenyl Groups

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Abstract

2,2-Dichloro-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl]cyclotriphosphazene (**2**) was obtained from the reaction of hexachlorocyclotriphosphazene (**1**) with biphenyl-2,2'-diol. 2,2-Bis(4-acetylphenoxy)-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl]cyclotriphosphazene (**3**) was synthesized from the reaction of **2** with 4-hydroxyacetophenone. The novel oxime-cyclophosphazene containing 2,2'-dioxybiphenyl groups **4** was synthesized from the reaction of **3** with hydroxylamine hydrochloride in pyridine. The reactions of this oxime-cyclophosphazene with methyl iodide, benzyl chloride, acetyl chloride, benzoyl chloride, 4-methoxybenzoyl chloride, chloroacetyl chloride, propanoyl chloride, 2-bromoethanol and 2-chlorobenzoyl chloride were studied. Disubstituted compounds were obtained from the reactions of **4** with methyl iodide, benzyl chloride, acetyl chloride, benzoyl chloride and 4-methoxybenzoyl chloride. Pure and defined products could not be obtained from the reaction of **4** with chloroacetyl chloride, propanoyl chloride, 2-bromoethanol and 2-chlorobenzoyl chloride. All products were generally obtained in high yields. The structures of the compounds were proved by elemental analysis, IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.

Keywords: Hexachlorocyclotriphosphazene, phosphazene, oxime derivatives, oxime-phosphazenes.

1. Introduction

Phosphazenes, which are the best known and most intensively studied phosphorus-nitrogen compounds, are materials with interesting properties. For example, they exhibit fire- retardant properties, have high refractive indices, and might find application in non-linear optics, as ferroelectric materials, as liquid crystals or as photoactive materials.[1–7] They also possess a number of characteristics such as biomedical properties and applications due to their strong antitumor activity.[8–12] Their antimicrobial and biological activities on bacterial and yeast cells have been studied.[13–15] Some applications include model compounds for polyphosphazenes, starting materials for the preparation of cyclolinear and/or cyclomatrix phosphazene substrates, commercial polymers with carbon backbones containing pendant cyclophosphazene groups, inorganic hydraulic fluids and lubricants, biologically important substrates such as anticancer agents, insect chemosterilants, pesticides and fertilizers, supports for catalysts, dyes, and crown ether phase transfer catalysts for nucleophilic substitution reactions, core substrates for dendrimers, thermal initiators for anionic polymerization reactions and photosensitive materials.[16]

The literature contains reports on the synthesis of different linear, cyclic or poly phosphazenes.[17–27] The synthesis and different reactions of phosphazenes containing 2,2'-dioxybiphenyl groups were reported.[28,29] There are also a large number of literature reports on reactions of the functional groups on phosphazene substituents.[11,30] Typical of these include coupling reactions of trimeric phosphazene azides with aryloxy, alkoxy and dialkylamino cosubstituents,[31] *N*-vinylic phosphazenes with azodicarboxylic and acetylenic esters,[32] oxime-phosphazene derivatives with alkyl and acyl substituents,[33–36] polymers from 4-formylphenoxy,[37,38] maleic,[39] and 3,4-methylenedioxyphenoxy substituents.[40]

2. Experimental

2. 1. General Remarks

Solvents and other liquids used in the experimental works were dried by conventional methods. Hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] (**1**) was purchased from Aldrich and recrystallized from hexane. Other chemicals were used as purchased. 2,2-Dichloro-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl!?1cyclotriphosphazene (**2**) and 2,2-bis(4-acetylphenoxy)-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl]cyclotriphosphazene (**3**) were prepared as described by Carriedo at al.[29] The reaction of **1** with the biphenyl-2,2'-diol was carried out under dry nitrogen. IR spectra were recorded on an ATI Unicam Mattson 1000 FTIR spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker DPX-300 spectrometer operating at 300.13, 75.46 and 121.49 MHz, respectively. The ^{1}H and ^{13}C NMR chemical shifts were measured using $SiMe_4$ as an internal standard, whereas those for ^{31}P were measured using 85% H_3PO_4 as an external standard. Chemical shifts downfield from the standard were assigned positive δ values.

Synthesis of 2. A mixture of **1** (10.20 g, 29.34 mmol), biphenyl-2,2'-diol (10.70 g, 57.46 mmol), and K_2CO_3 (20.00 g, 144.70 mmol) was stirred in acetone (100 mL) at 0 °C and then reacted at ambient temperature for 24 h. The solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (4 × 75 mL). After the solvent was removed, a white solid **2** formed (15.48 g, 92%). Anal. Calcd. for $C_{24}H_{16}Cl_2N_3O_4P_3$ (574.22): C, 50.20; H, 2.81; N, 7.32. Found: C, 49.80; H, 2.70; N, 7.00%. IR (KBr/cm^{-1}): 3034 and 3071 $\nu_{C-H(ar.)}$, 1194 $\nu_{P=N}$, 942 ν_{P-O-C}. ^{1}H NMR δ 7.68 (4H, d, J = 7.5 Hz, H^5), 7.55 (4H, t, J = 7.6 Hz, H^3), 7.40 (8H, m, H^2, H^4). ^{13}C NMR δ 147.3 (d, $^2J_{POC}$ = 8.9 Hz, C^1), 130.7 (C^5), 130.5 (C^3), 129.0 (C^6), 127.0 (C^4), 122.0 (C^2).

Synthesis of 3. A mixture of **2** (15 g, 26.12 mmol), 4-hydroxyacetophenone (7.70 g, 56.55 mmol), and K_2CO_3 (21.00 g, 151.94 mmol) was stirred in acetone (100 mL) at 0 °C and then refluxed for 4 h. The solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (4 × 75 mL). After the solvent was removed, a white solid **3** formed (18.40 g, 92%). Anal. Calcd. for $C_{40}H_{30}N_3O_8P_3$ (773.60): C, 62.10; H, 3.91; N, 5.43. Found: C, 61.98; H, 4.00; N, 5.45%. IR (KBr/cm^{-1}): 1684 $\nu_{C=O}$, 1175 $\nu_{P=N}$, 955 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 25.1 (2P, d, P($O_2C_{12}H_8$)), 9.4 (1P, dd, P($OC_6H_4COCH_3$)$_2$) (AB_2 system, J_{AB} = 94 Hz). ^{1}H NMR δ 8.17 (4H, d, J = 8.8 Hz, H^9), 7.62 (4H, d, J = 7.6 Hz, H^5), 7.55 (4H, d, J = 7.5 Hz, H^8), 7.51 (4H, t, J = 6.5 Hz, H^3), 7.44 (4H, t, J = 7.4 Hz, H^4), 7.22 (4H, d, J = 8.0 Hz, H^2), 2.62 (6H, s, H^{12}). ^{13}C–NMR δ 197.1 (C^{11}), 153.5 (d, $^2J_{POC}$ = 3.0 Hz, C^7), 147.3 (d, $^2J_{POC}$ = 2.9 Hz, C^1), 134.7 (d, $^5J_{POCCCC}$ = 1.5 Hz, C^{10}), 130.9 (C^9), 130.6 (C^5), 130.2 (C^3), 128.0 (C^6), 127.0 (C^4), 121.9 (C^2), 121.2 (d, $^3J_{POCC}$ = 7.1 Hz, C^8), 27.0 (C^{12}).

Synthesis of 4. A mixture of **3** (12.00 g, 15.52 mmol) and hydroxylamine hydrochloride (2.5 g, 35.14 mmol) was refluxed in pyridine (15 mL) for 3.5 h. After the reaction was complete, the mixture was allowed to cool and was slowly poured into water (100 mL) and reprecipitated twice from water. The white solid **4** was washed with alcohol and dried at 50 °C in a vacuum. Yield: 78% (9.77 g). Anal. Calcd. for $C_{40}H_{32}N_5O_8P_3$ (803.63): C, 59.78; H, 4.01; N, 8.71. Found: C, 60.00; H, 4.27; N, 8.59%. IR (KBr/cm^{-1}): 3376 ν_{OH}, 1636 $\nu_{C=N}$, 1170 $\nu_{P=N}$, 973 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 25.4 (2P, d, P($O_2C_{12}H_8$)), 10.0 (1P, dd, P($OC_6H_4C(CH3)NOH)_2$) (AB_2 system, J_{AB} = 94 Hz). ^{1}H NMR δ 11.33 (2H, s, H^{13}), 7.82 (4H, d, J = 7.9 Hz, H^9), 7.68 (4H, d, J = 7.3 Hz, H^5), 7.53 (4H, t, J = 8.3 Hz, H^3), 7.51 (8H, m, H^8, H^4), 7.18 (4H, d, J = 7.9 Hz, H^2), 2.20 (6H, s, H^{12}). ^{13}C NMR δ 152.7 (C^7), 150.7 ($^2J_{POC}$ = 7.18 Hz, C^1), 149.7 (C^{11}), 147.6 (C^9), 135.1 (C^5), 130.6 (C^{10}), 128.8 (C^3), 127.7 (C^6), 127.2 (C^4), 122.1 (C^2), 121.3 (d, $^3J_{POCC}$ = 7.2 Hz, C^8), 12.1 (C^{12}).

Reaction of 4 with Methyl Iodide; Synthesis of 5. A solution of 1.00 mL (2.28 g, 16.06 mmol) methyl iodide in acetone (10 mL) was slowly added dropwise to a stirred and cooled (0–5 °C) mixture of **4** (0.70 g, 0.87 mmol) and K_2CO_3 (1.00 g, 7.24 mmol) in acetone (30 mL). The reaction was carried out at room temperature for 3 h and then refluxed for 12 h. After the reaction was complete, the precipitate was filtered off and the solvent was removed. The product was dissolved in a very little amount of acetone and precipitated with water several times. The white solid **5** was washed with alcohol and dried at 50 °C in a vacuum. Yield: 70% (0.51 g). Anal. Calcd. for $C_{42}H_{36}N_5O_8P_3$ (831.68): C, 60.65; H, 4.36; N, 8.42. Found: C, 60.39; H, 4.65; N, 8.18%. IR (KBr/cm^{-1}): 1601 $\nu_{C=N}$, 1179 $\nu_{P=N}$, 941 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 25.3 (2P, d, P($O_2C_{12}H_8$)), 10.0 (1P, dd, P($OC_6H_4C(CH_3)NOCH_3)_2$) (AB_2 system, J_{AB} = 92 Hz). ^{1}H NMR δ 7.83 (4H, d, J = 8.5 Hz, H^9), 7.67 (4H, d, J = 7.5 Hz, H^5), 7.52 (4H, t, J = 7.5 Hz, H^3), 7.45 (4H, d, J = 7.4 Hz, H^8), 7.38 (4H, t, J = 7.6 Hz, H^4), 7.16 (4H, d, J = 7.7 Hz, H^2), 3.40 (6H, s, H^{13}), 2.19 (6H, s, H^{12}). ^{13}C NMR δ 153.6 (C^{11}), 152.7 (d, $^2J_{POC}$ = 2.9 Hz, C^7), 150.7 (d, $^2J_{POC}$ = 3.0 Hz, C^1), 147.6 (d, $^5J_{POCCCC}$ = 0.9 Hz, C^{10}), 135.1 (C^9), 130.6 (C^5), 128.3 (C^3), 127.8 (C^6), 127.2 (C^4), 122.1 (C^2), 121.3 (d, $^3J_{POCC}$ = 6.5 Hz, C^8), 62.1 (C^{13}), 12.1 (C^{12}).

Reaction of 4 with Benzyl Chloride; Synthesis of 6. A solution of 1.00 mL (1.10 g, 8.69 mmol) benzyl chloride in acetone (10 mL) was slowly added dropwise to a stirred and cooled (0–5 °C) mixture of **4** (0.70 g, 0.87 mmol) and K_2CO_3 (1.00 g, 7.24 mmol) in acetone (30 mL). The reaction was carried out at room temperature for 24 h. After the reaction was complete, the precipitate was filtered off and the solvent was removed. The product was dissolved in a very little amount of acetone and was precipitated with alcohol several times. The white solid **6** formed (0.60 g,

70%). Anal. Calcd. for $C_{54}H_{44}N_5O_8P_3$ (983.87): C, 65.92; H, 4.51; N, 7.12. Found: C, 66.23; H, 4.74; N, 6.95%. IR (KBr/cm^{-1}): 1600 $\nu_{C=N}$, 1173 $\nu_{P=N}$, 947 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 25.3 (2P, d, P($O_2C_{12}H_8$)), 10.0 (1P, dd, P($OC_6H_4C(CH_3)NOC_7H_7)_2$) ($AB_2$ system, J_{AB} = 93 Hz). ^{1}H NMR δ 7.82 (4H, d, J = 8.3 Hz, H^9), 7.68 (4H, d, J = 7.3 Hz, H^5), 7.53 (4H, d, J = 7.3 Hz, H^8), 7.47 (4H, d, J = 7.3 Hz, H^{15}), 7.38 (10H, m, H^3, H^{16}, H^{17}), 7.22 (4H, d, J = 8.1 Hz, H^2), 7.16 (4H, t, J = 6.2 Hz, H^4), 5.22 (4H, s, H^{13}), 2.19 (6H, s, H^{12}). ^{13}C NMR δ 154.3 (C^{11}), 152.7 (d, $^2J_{POC}$ = 3.5 Hz, C^7), 147.6 (d, $^2J_{POC}$ = 3.3 Hz, C^1), 138.4 (C^{14}), 133.9 (C^9), 131.1 (C^3), 130.7 (C^5), 130.4 (C^6), 128.8 (C^{17}), 128.5 (C^{15}), 128.2 (C^6), 127.8 (d, $^5J_{POCCCC}$ = 1.2 Hz, C^{10}), 127.2 (C^4), 122.1 (C^2), 122.3 (d, $^3J_{POCC}$ = 6.7 Hz, C^8), 75.9 (C^{13}), 12.1 (C^{12}).

Reaction of 4 with Acetyl Chloride; Synthesis of 7. A solution of 1.00 mL (1.20 g, 15.28 mmol) acetyl chloride in acetone (10 mL) was slowly added dropwise to a stirred and cooled (0–5 °C) mixture of **4** (0.70 g, 0.87 mmol) and K_2CO_3 (1.00 g, 7.24 mmol) in acetone (30 mL). The reaction was carried out at room temperature for 24 h. After the reaction was complete, the precipitate was filtered off and the solvent was removed. The product was dissolved in a very little amount of acetone and precipitated with alcohol several times. The white solid **7** formed (0.69 g, 90%). Anal. Calcd. for $C_{44}H_{36}N_5O_{10}P_3$ (887.70): C, 59.53; H, 4.09; N, 7.89. Found: C, 59.75; H, 4.38; N, 8.13%. IR (KBr/cm^{-1}): 1601 $\nu_{C=O}$, 1601 $\nu_{C=N}$, 1178 $\nu_{P=N}$, 937 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 25.3 (2P, d, P($O_2C_{12}H_8$)), 9.8 (1P, dd, P($OC_6H_4C(CH_3)NOCOH_3)_2$) (AB_2 system, J_{AB} = 94 Hz). ^{1}H NMR δ 8.15 (4H, d, J = 7.3 Hz, H^9), 7.82 (4H, d, J = 7.3 Hz, H^5), 7.65 (4H, d, J = 7.4 Hz, H^8), 7.45 (8H, m, H^3, H^4), 7.18 (4H, d, J = 7.9 Hz, H^2), 2.61 (6H, s, H^{12}), 2.19 (6H, s, H^{14}). ^{13}C NMR δ 153.7 (C^{13}), 150.4 (C^{11}), 147.4 (d, $^3J_{POC}$ = 2.7 Hz, C^7), 134.8 (d, $^3J_{POC}$ = 3.2 Hz, C^1), 130.9 (d, $^5J_{POCCCC}$ = 1.0 Hz, C^{10}), 130.5 (C^9), 130.2 (C^5), 128.1 (C^3), 127.5 (C^6), 127.0 (C^4), 121.9 (C^2), 121.1 (d, $^3J_{POCC}$ = 7.5 Hz, C^8), 27.0 (C^{14}), 11.9 (C^{12}).

Reaction of 4 with Benzoyl Chloride; Synthesis of 8. A solution of 1.00 mL (1.20 g, 8.60 mmol) benzoyl chloride in acetone (10 mL) was slowly added dropwise to a stirred and cooled (0–5 °C) mixture of **4** (0.70 g, 0.87 mmol) and K_2CO_3 (1.00 g, 7.24 mmol) in acetone (30 mL). The reaction was carried out at room temperature for 24 h. After the reaction was complete, the precipitate was filtered off and the solvent removed. The product was dissolved in a very little amount of acetone and precipitated with alcohol several times. The white solid **8** formed (0.60 g, 68%). Anal. Calcd. for $C_{54}H_{40}N_5O_{10}P_3$ (1011.84): C, 64.10; H, 3.98; N, 6.92. Found: C, 64.35; H, 4.08; N, 7.13%. IR (KBr/cm^{-1}): 1747 $\nu_{C=O}$, 1599 $\nu_{C=N}$, 1173 $\nu_{P=N}$, 974 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 24.1 (2P, d, P($O_2C_{12}H_8$)), 9.6 (1P, dd, P($OC_6H_4C(CH_3)NOC_7H_5O)_2$) ($AB_2$ system, J_{AB} = 94 Hz). ^{1}H NMR δ 8.14 (4H, d, J = 7.4 Hz, H^{15}), 8.11 (4H, d, J = 7.3 Hz, H^5), 8.09 (4H, d, J = 8.6 Hz, H^9), 7.68 (4H, d, J = 7.6 Hz, H^8), 7.60 (4H, d, J = 7.7 Hz, H^2), 7.50 (10H, m, H^3, H^{16}, H^{17}), 7.22 (4H, t, J = 4.5 Hz, H^4), 2.61 (6H, s, H^{12}). ^{13}C NMR δ 163.4 (C^{13}), 147.6 (C^{11}), 131.2 (d, $^2J_{POC}$ = 3.3 Hz, C^7), 131.8 (d, $^2J_{POC}$ = 2.9 Hz, C^1), 130.4 (C^{17}), 129.8 (d, $^5J_{POCCCC}$ = 1.3 Hz, C^{10}), 129.5 (C^9), 129.2 (C1^5), 129.0 (C^6), 128.9 (C^{14}), 128.3 (C^5), 127.8 (C^3), 127.2 (C^6), 122.1 (C^4), 121.6 (C^2), 121.4 (d, $^3J_{POCC}$ = 7.0 Hz, C^8), 12.1 (C^{12}).

Reaction of 4 with 4-Methoxybenzoyl Chloride; Synthesis of 9. A solution of 0.5 g (2.92 mmol) 4-methoxybenzoyl chloride in acetone (10 mL) was slowly added dropwise to a stirred and cooled (0–5 °C) mixture of **4** (0.70 g, 0.87 mmol) and K_2CO_3 (1.00 g, 7.24 mmol) in acetone (30 mL). The reaction was carried out at room temperature for 24 h. After the reaction was complete, the precipitate was filtered off and the solvent removed. The product was dissolved in a very little amount of acetone and precipitated with alcohol several times. The white solid **9** formed (0.73 g, 68%). Anal. Calcd. for $C_{56}H_{44}N_5O_{12}P_3$ (1071.89): C, 62.75; H, 4.14; N, 6.53. Found: C, 63.00; H, 4.38; N, 6.30%. IR (KBr/cm^{-1}): 1739 $\nu_{C=O}$, 1604 $\nu_{C=N}$, 1167 $\nu_{P=N}$, 938 ν_{P-O-C}. ^{31}P NMR (DMSO-d_6) δ 25.3 (2P, d, P($O_2C_{12}H_8$)), 9.9 (1P, dd, P($OC_6H_4C(CH_3)$ $NOC_8H_7O_2)_2$) (AB_2 system, J_{AB} = 92 Hz). ^{1}H NMR δ 8.04 (8H, m, H^{15}, H^9), 7.66 (4H, d, J = 7.6 Hz, H^5), 7.47 (12H, m, H^3, H^{16}, H^4), 7.21 (4H, d, J = 8.0 Hz, H^8), 7.11 (4H, d, J = 8.9 Hz, H^2), 3.84 (6H, s, H^{18}), 2.53 (6H, s, H^{12}). ^{13}C NMR δ 164.0 (C^{13}), 163.2 (C^{17}), 152.2 (C^{11}), 152.1 (d, $^2J_{POC}$ = 3.0 Hz, C^7), 147.6 (d, $^2J_{POC}$ = 3.2 Hz, C^1), 132.7 (d, $^5J_{POCCCC}$ = 1.0 Hz, C^{10}), 132.0 (C^{15}), 130.8 (C^9), 130.4 (C^5), 129.5 (C^3), 128.3 (C^6), 127.2 (C^4), 122.1 (C^2), 121.6 (d, $^3J_{POCC}$ = 7.2 Hz, C^8), 120.9 (C^{14}), 114.8 (C^{16}), 56.0 (C^{18}), 14.9 (C^{12}).

3. Results and Discussion

The reaction of **2** with 2 equiv. of 4-hydroxyacetophenon in the presence of K_2CO_3 in acetone gave 2,2-bis(4-acetylphenoxy)-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl]cyclo triphosphazene (**3**). Oxime compound 2,2-bis(4-[(1)-*N*-hydroxyethanimidoyl]phenoxy)-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl]cyclotriphosphazene (**4**) was synthesized from the reaction of **3** with hydroxylamine hydrochloride in pyridine.

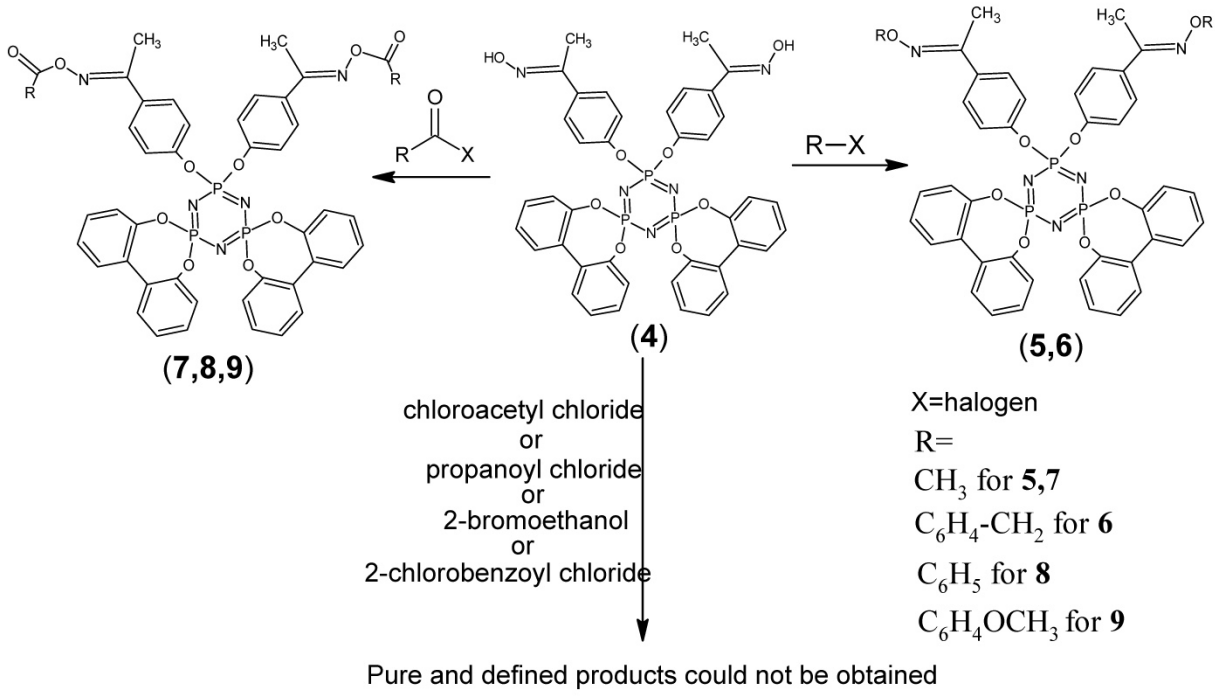
Disubstituted compounds were obtained from the reactions of **4** with methyl iodide, benzyl chloride, acetyl chloride, benzoyl chloride and 4-methoxybenzoyl chloride in acetone in the presence of K_2CO_3 via replacement of all the oxime protons with alkyl and acyl groups. Pure and defined products could not be obtained from the reaction of **4** with chloroacetyl chloride, propanoyl chloride, 2-bromoethanol and 2-chlorobenzoyl chloride.

The structures of the compounds were elucidated by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as by

elemental analyses. General presentation of the reactions is shown in Scheme **1** and structures of the compounds **2**–**9** are shown in Scheme **2**. All products were generally obtained in high yields.

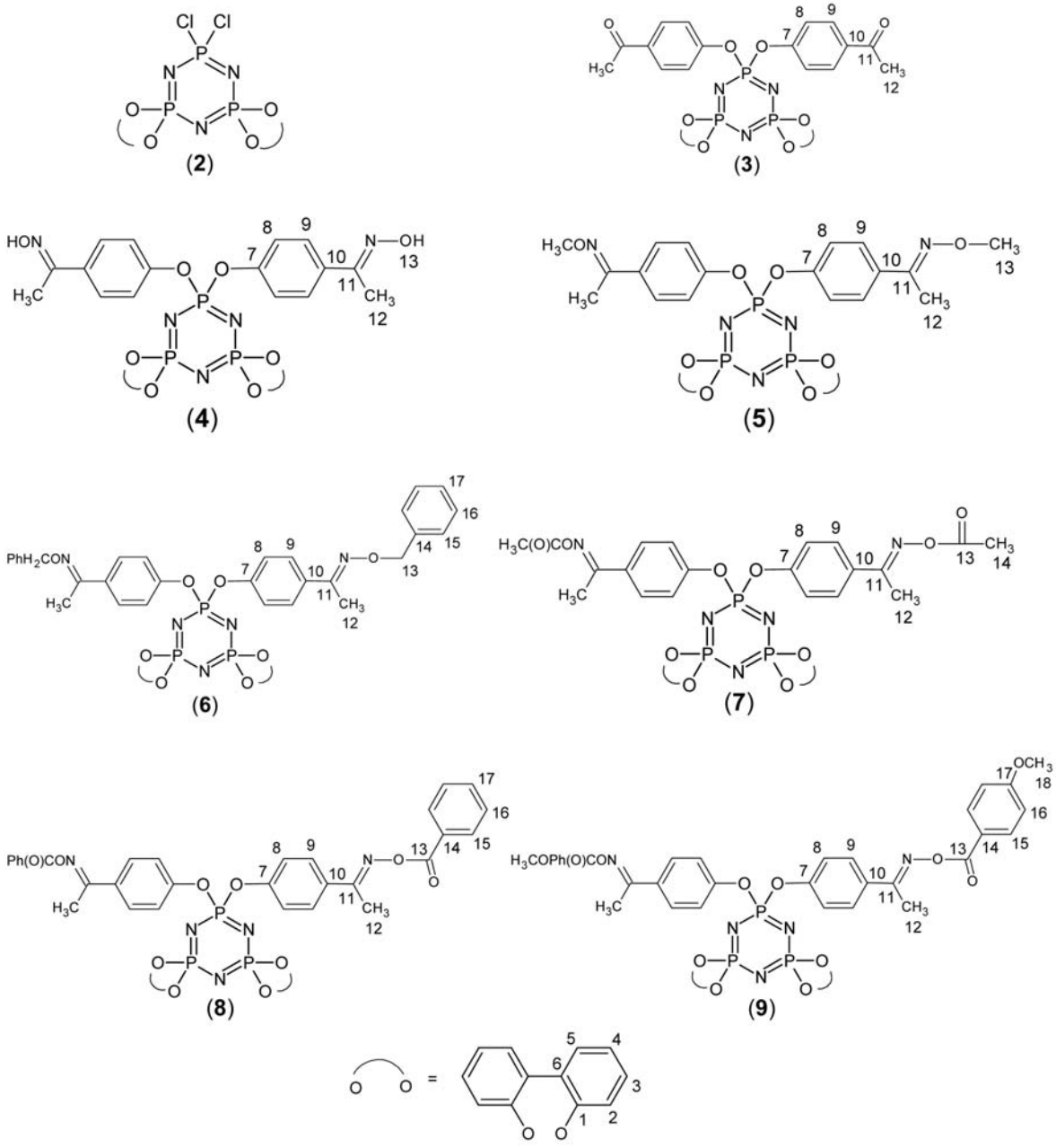
The characteristic stretching peaks in the IR spectra of the phosphazenes have been assigned as in experimental section. The P=N stretching vibrations, which are observed between 1167 and 1194 cm^{-1}, are characteristic of cyclophosphazenes. These peaks are shifted to longer wavelengths for **2**–**9** than in **1**, which appeared at 1218 cm^{-1}. The OH stretching vibration in the IR spectra of **4** indicates the oxime compound. The absence of the OH stretching vibration in the IR spectra of **5**–**9** indicates that all hydrogen atoms of the OH groups have been replaced by the alkyl and acyl substituents.

The ^{31}P NMR data for **2**–**9** are given in experimental section. The ^{31}P NMR spectra did not show the expected AB_2 pattern. Further splitting was observed, which indicates that the two phosphorus atoms attached to the dioxybiphenyl ring are not magnetically equivalent. This non-equivalence of the two phosphorus atoms could be due to the difference in the angle of twist of the two phenyl groups of the biphenyl moieties and their twist in a different direction. The reason for this reversal twist/distortion could be due to the advantageous thermodynamically stable seven-membered dioxybiphenyl ring conformation by imparting reduced 6,6' hydrogen-hydrogen contacts without broadening the O–P–O angle. The observation of dd due to the two phosphorus atoms attached to the dioxybiphenyl groups indicates that such a conformation possibly exists in the solution. This may be due to the fact that in solution either averaging of the conformational possibilities is not complete or the twisted biphenyls of the dioxybiphenyl seven-membered spiro rings attend kinetically-stable conformations due to the intrinsic nature of the substitution groups. The ^{31}P NMR shifts of **2**–**9** vary between 9.4 and 25.4 ppm with similar J values (AB_2 system). There are two peaks in the ^{31}P NMR spectra of **2**–**9**. This data demonstrates that compounds **2**–**9** have one isomer. However, in our similar published studies, we also observed weak peaks due to the *syn* and *anti* isomerism of the –C=N groups, so we obtained compounds that are mixtures of *syn* and *anti* isomers from the reactions of hexakis(4-[(hydroxyimino)methyl]phenoxy) cyclotriphophazene and hexakis(4-[(1)-*N*-hydroxyethanimidoyl]phenoxy)cyclotriphophazene with different alkyl and acyl halogens.[33–36]



Scheme 1. General presentation of the reactions.

The ^{1}H and ^{13}C NMR data also confirm the structures of **2**–**9** (Scheme 2). In the ^{1}H NMR spectra the OH proton is observed at 11.13 ppm for **4**. It is understood from the integral intensities that there are two OH protons in **4**, which is the original oxime-phosphazene containing 2,2'-dioxybiphenyl groups. The methyl protons, which have attached carbon atoms of –C=N– groups for **4**–**9** are observed between 2.2 and 2.6 ppm. The aromatic protons for all the compounds appear between 7.16 and 8.17 ppm.



Scheme 2. The structures of the compounds **2**–**9**.

The detailed ^{13}C NMR spectral data are given in experimental section. The ketone carbon atom for **3** is observed at 153.7 ppm. The methyl carbons, which have attached carbon atoms of –C=N– groups for **4**–**9** are observed between 11.9 and 14. 9 ppm.

4. Conclusion

In this paper we report on the preparation of oxime-cyclophosphazene containing 2,2'-dioxybiphenyl groups from 2,2-bis(4-acetylphenoxy)-4,4,6,6-bis[spiro(2',2''-dioxy-1',1''-biphenylyl]cyclotriphosphazene, and studies on its rections with methyl iodide, benzyl chloride, acetyl chloride, benzoyl chloride, 4-methoxybenzoyl chloride, chloroacetyl chloride, propanoyl chloride, 2-bromoethanol and 2-chlorobenzoyl chloride.

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Povzetek

2,2-Dikloro-4,4,6,6-bis[spiro(2',2''-dioksi-1',1''-bifenilil]ciklotrifosfazen (**2**) je bil pripravljen z reakcijo med heksaklorociklotrifosfazenom (**1**) in bifenil-2,2'-diolom. 2,2-Bis(4-acetilfenoksi)-4,4,6,6-bis[spiro(2',2''-dioksi-1',1''-bifenilil]ciklotrifosfazen (**3**) je bil sintetiziran z reakcijo med **2** in 4-hidroksiacetofenonom. Novi oksim-ciklofosfazen **4**, ki vsebuje 2,2'-dioksibifenilne skupine, je bil pripravljen z reakcijo med **3** s hidroksilamin hidrokloridom v piridinu. Raziskane so bile reakcija tega oksim-ciklofosfazena z metil jodidom, benzil kloridom, acetil kloridom, benzoil kloridom, 4-metoksibenzoil kloridom, kloroacetil kloridom, propanoil kloridom, 2-bromoetanolom in 2-klorobenzoil kloridom. Disubstituirane spojine so nastale pri reakciji med **4** in metil jodidom, benzil kloridom, acetil kloridom, benzoil kloridom in 4-metoksibenzoil kloridom. Definirani in čisti produkti pri reakciji med **4** in kloroacetil kloridom, propanoil kloridom, 2-bromoetanolom in 2-klorobenzoil kloridom niso nastali. Vsi produkti so nastali z večinoma visokimi izkoristki. Strukture spojin smo dokazali z elementno analizo, IR, ^{1}H, ^{13}C in ^{31}P NMR spektroskopijo.