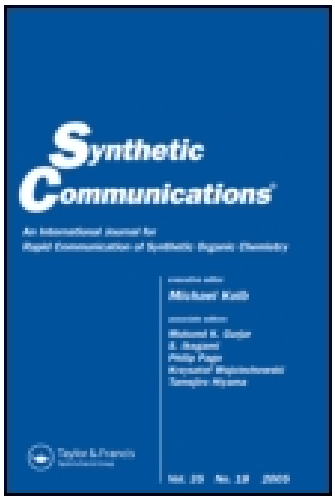

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A NOVEL SYNTHESIS OF HEXASUBSTITUTED CYCLOTRIPHOSPHAZENES

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A NOVEL SYNTHESIS OF HEXASUBSTITUTED CYCLOTRIPHOSPHAZENES

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ABSTRACT

Hexaaryloxyphosphazenes [$N_3P_3(O\text{-}C_6H_4\text{-}R)_6$] (R=H, CH_3, OCH_3, $C(CH_3)_3$, CHO, $COCH_3$, COOR, C_6H_5, NO_2, F, etc) were readily obtained with *ca* 70% isolated yield in refluxing acetonitrile in the presence of anhydrous potassium phosphate. All compounds were characterized by means of elemental analysis, ^{1}H-NMR, ^{31}P-NMR spectroscopy.

In recent years, many efforts were focused on the preparation and characterization of phosphazenes which contain a framework of alternating phosphor and nitrogen atoms with two substituent groups attached to each phosphor atom.[1] It is noticeable that cyclophosphazenes, especially hexaaryloxyphosphazenes and perfluoroaryloxyphosphazenes exhibit excellent thermal and chemical stability which can be used as fireproof materials,

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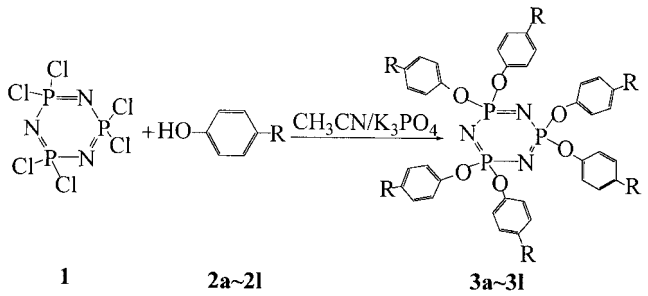
high temperature lubricants, vacuum pump oils and hard disk surface lubricants.[2–4] To meet the need of the both scientific and technological purposes, a wide variety of hexaaryloxyphosphazenes were prepared. The synthetic method usually involved the reaction of hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] with sodium phenolates in an appropriate organic solvent.[5] However, this method required a long time. Therefore several studies have been reported to improve the preparation.[6–8]

Some authors found that phase-transfer catalyst (PTC) can accelerate the substitution reaction.[6–7] However this method some times resulted in the mixture of various substituted phosphazenes. G.A. Carriedo et al.[8] described a very convenient preparation for some known cyclic aryloxyphosphazenes directly from [$N_3P_3Cl_6$], phenols and K_2CO_3 in acetone. But in the case of phenols HOC_6H_4-R (R=H, Bu^t, OCH_3), the reactions were much slower, lasting 20 h even in the presence of PTC.



1 **2a~2l** **3a~3l**

Scheme.

In the present paper, we describe a novel and efficient method of preparation hexaaryloxyphosphazenes that linked either electron-donor or electron-acceptor group. As shown in the scheme, in refluxing acetonitrile, hexasubstituted aryloxycyclotriphosphazenes can be readily synthesized by reaction of $N_3P_3Cl_6$ with phenols in the presence of anhydrous potassium phosphate.

Anhydrous potassium phosphate was reported to be used in the one-pot synthesis of dithiocarbamates.[9–10] A series of experiments show that potassium phosphate is more effective than potassium carbonate in the catalysis of reactions of $N_3P_3Cl_3$ with phenols. While the reaction of $N_3P_3Cl_3$ with phenol (R=H) was performed in acetone/K_2CO_3 for 3 h or toluene/K_2CO_3 for 16 h, it cannot result in the hexaphenoxycyclotriphosphazene which can be obtained by the reaction in acetonitrile/K_3PO_4 for 3 h with 75% isolated yield.

In the case of phenol **2c** (R=Bu^t), the reaction was also very fast. **3c** was prepared in acetone-K_2CO_3 for 20 h in the presence of tetrabutyl ammonium bromide (TBAB)[8] or using thallium 4-*tert*-butyl-phenoxide and TBAB in refluxing THF for 12 h.[11] In contrast, using acetonitrile/K_3PO_4 method without TBAB, the reaction can be completed within 10 h. It is also found that by this method the reaction times of phenols **2a**, **2b** (R=CH_3, OCH_3) could be substantially shortened.

In addition, some other types compounds containing hydroxyl group such as methyl salicylic ester, 4-fluoro-3-trifluoromethyl phenol, 2-naphthalenol also can easily react with $N_3P_3Cl_6$ in acetonitrile/K_3PO_4 to afford corresponding aryloxyphosphazenes, so the long workups and tedious chromatography can be avoided.

EXPERIMENTAL

The FT-IR spectra were recorded with Bio-Rad Win-IR spectrometer. NMR spectra were measured on Varian FT-80A NMR spectrometer, using $CDCl_3$ as the solvent for ^{1}H-NMR as well as $CDCl_3/C_6D_6$ for ^{31}P-NMR. The chemical shifts for ^{31}P-NMR spectra are relative to the external standard of 85% phosphoric acid. C, H, N analyses were performed with a CE-1106 microanalyzer.

Typical Procedure: Hexachlorocyclotriphosphazene (1.0 g, 2.87 mmol), substituted phenol (18.10 mmol), anhydrous potassium phosphate (7.0 g, 32.97 mmol), and 50 mL of acetonitrile were placed in 100 mL flask connected with a drying tube. The mixture was refluxed for 0.5–10 h, and then cooled to room temperature. The solid was filtered and washed twice with 10 mL of acetonitrile. The filtrate and the washings were combined, and the solvent was distilled under reduced pressure. The residue was dissolved in ethyl acetate and washed with 10% NaOH solution for three times and then with water, dried over anhydrous sodium sulfate. After filtration and evaporation, the product was purified by recrystallization from an appropriate solvent (listed in the table).

Hexakis(4-methylphenoxy)cyclotriphosphazene (3a): White solid, m.p. 119–120°C (lit.[12] 116–117°C); IR, ν_{max}/cm^{-1}: 1505 (Ph), 1213 (-P=N-), 968 (P-O); ^{1}H-NMR: δ 6.85 (d, J = 8.8 Hz, 12H), 6.78 (d, J = 8.8 Hz, 12H), 2.25 (s, 18H); ^{31}P-NMR: δ 8.89; Anal. Calcd for $C_{42}H_{42}N_3O_6P_3$ C, 64.86 H, 5.44 N, 5.40. Found C, 64.70 H, 5.31 N, 5.20

Hexakis(4-methyloxyphenoxy)cyclotriphosphazene (3b): White solid, m.p. 100–102°C (lit.[13]100–102°C); IR, ν_{max}/cm^{-1}: 1504 (Ph), 1198 (-P=N-), 971 (P-O); ^{1}H-NMR: δ 6.76 (d, J = 9.6 Hz, 12H), 6.68 (d, J = 9.6 Hz, 12H),

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Table. Reaction Conditions of Phosphazenes

NO	R	Time (h)	Recrystallization Solvent	Yield (%)
3a	CH_3	4	ethanol	70
3b	OCH_3	6	ethanol	67
3c	Bu^t	10	ethanol	70
3d	H	3	ethyl acetate	75
3e	CHO	3	acetonitrile	70
3f	$COCH_3$	2	ethyl acetate	80
3g	$COOCH_3$	2	acetone	76
3h	$COOC_2H_5$	6	methanol	72
3i	$COOC_4H_9$	10	methanol	65
3j	C_6H_5	3	ethanol	72
3k	NO_2	2	*o*-dichlorobenzene	78
3l	F	3	methanol	78
3m	4-F-3-CF_3	3	methanol	74
3n	2-$COOCH_3$	2.5	ethyl acetate	70
3o*	–	0.5	chloroform/hexane	80

*Compound **3o** was Hexakis (2-naphthyloxy) cyclotriphosphazene.

3.73 (s, 18H); ^{31}P-NMR: δ 9.80; Anal. Calcd for $C_{42}H_{42}N_3O_{12}P_3$ C, 57.74 H, 4.85 N, 4.81. Found C, 57.54 H, 4.64 N, 4.70.

Hexakis(4-*tert*-butylphenoxy)cyclotriphosphazene (3c): White solid, m.p. 130–131°C (lit.[13] 132–133°C); IR, ν_{max}/cm^{-1}: 1509 (Ph), 1203 (-P=N-), 956 (P-O); ^{1}H-NMR: δ 7.14 (d, J = 8.8 Hz, 12H), 6.88 (d, J = 8.8 Hz, 12H), 1.27 (s, 54H); ^{31}P-NMR: δ 8.75; Anal. Calcd for $C_{60}H_{78}N_3O_6P_3$ C, 69.95 H, 7.63 N, 4.08. Found C, 69.83 H, 7.58 N, 3.91.

Hexakisphenoxycyclotriphosphazene (3d): White solid, m.p. 111–112°C (lit.[14] 110–111°C); IR, ν_{max}/cm^{-1}: 1486 (Ph), 1197 (-P=N-), 952 (P-O); ^{1}H-NMR: δ 7.18–6.85 (Ar-H); ^{31}P-NMR: δ 8.45; Anal. Calcd for $C_{36}H_{30}N_3O_{18}P_3$ C, 62.34 H, 4.36 N, 6.06. Found C, 62.10 H, 4.25 N, 5.94.

Hexakis(4-formylphenoxy)cyclotriphosphazene (3e): White solid, m.p. 155–158°C (lit.[15] 154–158°C); IR, ν_{max}/cm^{-1}: 1706 (C = O), 1202 (-P=N-), 968 (P-O); ^{1}H-NMR: δ 9.93 (s, 6H), 7.68 (d, J = 8.8 Hz, 12H), 7.19 (d, J = 8.8 Hz, 12H); ^{31}P-NMR: δ 6.90; Anal. Calcd for $C_{42}H_{30}N_3O_{12}P_3$ C, 58.55, H, 3.51 N, 4.88. Found C, 58.34 H, 3.40 N, 4.74.

Hexakis(4-acetophenoxy)cyclotriphosphazene (3f): White solid, m.p. 166–168°C (lit.[7] 167–169°C); IR, ν_{max}/cm^{-1}: 1681 (C = O), 1501 (Ph), 1205 (-P=N-), 946 (P-O); ^{1}H-NMR: δ 7.73 (d, J = 8.8 Hz, 12H), 7.07 (d, J = 8.8 Hz, 12H) 2.57 (s, 18H); ^{31}P-NMR: δ 7.37; Anal. Calcd

for $C_{48}H_{42}N_3O_{12}P_3$ C, 61.02 H, 4.51 N, 4.43. Found C, 61.29 H, 4.67 N, 4.35.

Hexakis(4-(methoxycarbonyl)phenoxy)cyclotriphosphazene (3g): White solid, m.p. 152°C; IR, ν_{max}/cm^{-1}: 1725 (C=O), 1208 (-P=N-), 958 (P-O); ^{1}H-NMR: δ 7.80 (d, J = 8.8 Hz, 12H) 7.04 (d, J = 8.8 Hz, 12H) 3.92 (s, 18H); ^{31}P-NMR: δ 6.90; Anal. Calcd for $C_{48}H_{42}N_3O_{18}P_3$ C, 55.34 H, 4.06 N, 4.03. Found C, 55.23 H, 4.01 N, 3.91.

Hexakis(4-(ethoxycarbonyl)phenoxy)cyclotriphosphazene (3h): White solid, m.p. 87–88°C (lit.[16] 78–80°C); IR, ν_{max}/cm^{-1}: 1717 (C=O), 1217 (-P=N-), 958 (P-O); ^{1}H-NMR: δ 7.83 (d, J = 8.8 Hz, 12H), 7.05 (d, J = 8.8 Hz, 12H), 4.42 (q, J = 7.2 Hz, 12H), 1.40 (t, J = 7.2 Hz, 18H); ^{31}P-NMR: δ 7.46; Anal. Calcd for $C_{54}H_{54}N_3O_{18}P_3$ C, 57.60 H, 4.83 N, 3.73. Found C, 57.48 H, 4.79 N, 3.60.

Hexakis(4-(butoxycarbonyl)phenoxy)cyclotriphosphazene (3i): White solid, m.p. 72–73°C; IR, ν_{max}/cm^{-1}: 1711 (C=O), 1209 (-P=N-), 954 (P-O); ^{1}H-NMR: δ 7.81 (d, J = 8.8 Hz, 12H), 7.04 (d, J = 8.8 Hz, 12H), 4.30 (t, J = 6.4 Hz, 12H), 1.74–1.40 (broad, 24H), 1.04 (t, J = 7.2 Hz, 18H); ^{31}P-NMR: δ 7.49; Anal. Calcd for $C_{66}H_{78}N_3O_{18}P_3$ C, 61.25 H, 6.07 N, 3.25. Found C, 61.18 H, 5.99 N, 3.16.

Hexakis(4-phenylphenoxy)cyclotriphosphazene (3j): White solid, m.p. 199–201°C (lit.[17] 202–203°C); IR, ν_{max}/cm^{-1}: 1504 (Ph), 1208 (-P=N-), 954 (P-O); ^{1}H-NMR: δ 7.33–6.95 (broad, ArH); ^{31}P-NMR: δ 9.33; Anal. Calcd for $C_{72}H_{54}N_3O_6P_3$ C, 75.19; H, 4.73; N, 3.65. Found C, 75.10 H, 4.71 N, 3.59.

Hexakis(4-nitrophenoxy)cyclotriphosphazene (3k): This compound was prepared using typical procedure, crude product washed with acetone then with water, recrystallised from *o*-dichlorobenzene. Yield 78%, m.p. 260–262°C (lit.[18] 260–264°C); IR, ν_{max}/cm^{-1}: 1526 (Ph), 1202 (-P=N-), 943 (P-O); $C_{36}H_{24}N_3O_{12}P_3$ C, 44.89 H, 2.51 N, 13.08 Found C, 44.71 H, 1.37 N, 12.95.

Hexakis(4-fluorophenoxy)cyclotriphosphazene (3l): White solid, m.p. 126–127°C (lit.[4] 127–129°C); IR, ν_{max}/cm^{-1}: 1504 (Ph), 1215 (-P=N-), 957 (P-O); ^{1}H-NMR: δ 6.89 (d, J = 3.2 Hz, 12H), 6.81 (d, J = 3.2 Hz, 12H); ^{31}P-NMR: δ 8.95; Anal. Calcd for $C_{36}H_{24}F_6N_3O_6P_3$ C, 53.95 H, 3.02 N, 5.24. Found C, 53.83 H, 2.86 N, 5.06.

Hexakis(2-(methoxycarbonyl)phenoxy)cyclotriphosphazene (3m): White solid, m.p. 111°C; IR, ν_{max}/cm^{-1}: 1723 (C=O), 1206 (-P=N-), 958 (P-O); ^{1}H-NMR: δ 7.72 ~ 7.17 (broad, 18H), 3.64 (s, 18H); ^{1}P-NMR: δ 6.62; Anal. Calcd for $C_{48}H_{42}N_3O_{18}P_3$ C, 55.34 H, 4.83 N, 3.73. Found C, 57.48 H, 4.79 N, 3.60.

Hexakis(4-fluoro-3-trifluoromethylphenoxy)cyclotriphosphazene (3n): White solid, m.p. 73°C; IR, ν_{max}/cm^{-1}: 1321 (CF_3), 1263 (C-F), 1221

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(-P=N-), 969 (P-O); ^{1}H-NMR: δ 7.26–7.06 (broad, ArH); ^{31}P-NMR: δ 8.19; Anal. Calcd for $C_{42}H_{18}F_{24}N_3O_6P_3$ C, 41.71 H, 1.50 N, 3.47. Found C, 41.67 H, 1.37 N, 3.23.

Hexakis(2-naphthyloxy)cyclotriphosphazene (3o): This compound was prepared using typical procedure, crude product washed with acetone then with water, recrystallized from chloroform/hexane. Yield 80%, m.p. 166–167°C (lit.[19] 168–169°C); IR, ν_{max}/cm^{-1}: 1508 (C=O), 1210 (-P=N-), 973 (P-O); ^{1}H-NMR: δ 7.67–7.02 (ArH); ^{31}P-NMR: δ 9.21; Anal. Calcd for $C_{60}H_{42}N_3O_6P_3$ C, 72.51 H, 4.26 N, 4.23. Found C, 72.46 H, 4.15 N, 4.20.

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