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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

A NOVEL SYNTHESIS OF HEXASUBSTITUTED CYCLOTRIPHOSPHAZENES

Chengfeng Ye^a, Zefu Zhang^a & Weimin Liu^b

^a State Key Laboratory of Solid Lubrication , Lanzhou Institute of Chemical Physics , Chinese Academy of Sciences , Lanzhou, 730000, P. R. China

^b State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China Published online: 16 Aug 2006.

To cite this article: Chengfeng Ye, Zefu Zhang & Weimin Liu (2002) A NOVEL SYNTHESIS OF HEXASUBSTITUTED CYCLOTRIPHOSPHAZENES, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:2, 203-209, DOI: <u>10.1081/SCC-120002003</u>

To link to this article: http://dx.doi.org/10.1081/SCC-120002003

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SYNTHETIC COMMUNICATIONS, 32(2), 203-209 (2002)

A NOVEL SYNTHESIS OF HEXASUBSTITUTED CYCLOTRIPHOSPHAZENES

Chengfeng Ye, Zefu Zhang, and Weimin Liu*

State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

ABSTRACT

Hexaaryloxyphosphazenes $[N_3P_3(O-C_6H_4-R)_6]$ (R=H, CH₃, OCH₃, C(CH₃)₃, CHO, COCH₃, COOR, C₆H₅, NO₂, 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, ¹H-NMR, ³¹P-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 hexa-aryloxyphosphazenes 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 [N₃P₃Cl₆] 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 HOC₆H₄-R (R=H, Bu^t, OCH₃), the reactions were much slower, lasting 20 h even in the presence of PTC.



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 onepot 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/K₂CO₃ for 3 h or toluene/K₂CO₃ for 16 h, it cannot result in the hexaphenoxycyclotriphosphazene which can be obtained by the reaction in acetonitrile/K₃PO₄ for 3 h with 75% isolated yield.

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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=CH₃, OCH₃) 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/K₃PO₄ 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 CDCl₃ as the solvent for ¹H-NMR as well as $CDCl_3/C_6D_6$ for ³¹P-NMR. The chemical shifts for ³¹P-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); ¹H-NMR: δ 6.85 (d, J=8.8 Hz, 12H), 6.78 (d, J=8.8 Hz, 12H), 2.25 (s, 18H); ³¹P-NMR: δ 8.89; Anal. Calcd for C₄₂H₄₂N₃O₆P₃ 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.¹³100–102°C); IR, v_{max}/cm^{-1} : 1504 (Ph), 1198 (-P=N-), 971 (P-O); ¹H-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	Н	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 ₄ H ₉	10	methanol	65
3j	C_6H_5	3	ethanol	72
3k	NO_2	2	o-dichlorobenzene	78
31	F	3	methanol	78
3m	4-F-3-CF ₃	3	methanol	74
3n	2-COOCH ₃	2.5	ethyl acetate	70
30*	_	0.5	chloroform/hexane	80

*Compound 30 was Hexakis (2-naphthyloxy) cyclotriphosphazene.

3.73 (s, 18H); ³¹P-NMR: δ 9.80; Anal. Calcd for C₄₂H₄₂N₃O₁₂P₃ 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); ¹H-NMR: δ 7.14 (d, J = 8.8 Hz, 12H), 6.88 (d, J = 8.8 Hz, 12H), 1.27 (s, 54H); ³¹P-NMR: δ 8.75; Anal. Calcd for C₆₀H₇₈N₃O₆P₃ 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. $111-112^{\circ}$ C (lit.¹⁴ 110-111°C); IR, ν_{max}/cm⁻¹: 1486 (Ph), 1197 (-P=N-), 952 (P-O); ¹H-NMR: δ 7.18–6.85 (Ar-H); ³¹P-NMR: δ 8.45; Anal. Calcd for C₃₆H₃₀N₃O₁₈P₃ 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, v_{max}/cm^{-1} : 1706 (C=O), 1202 (-P=N-), 968 (P-O); ¹H-NMR: δ 9.93 (s, 6H), 7.68 (d, J=8.8 Hz, 12H), 7.19 (d, J=8.8 Hz, 12H); ³¹P-NMR: δ 6.90; Anal. Calcd for C₄₂H₃₀N₃O₁₂P₃ 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, v_{max}/cm^{-1} : 1681 (C = O), 1501 (Ph), 1205 (-P=N-), 946 (P-O); ¹H-NMR: δ 7.73 (d, J=8.8 Hz, 12H), 7.07 (d, J=8.8 Hz, 12H) 2.57 (s, 18H); ³¹P-NMR: δ 7.37; Anal. Calcd

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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, v_{max}/cm^{-1} : 1725 (C=O), 1208 (-P=N-), 958 (P-O); ¹H-NMR: δ 7.80 (d, J = 8.8 Hz, 12H) 7.04 (d, J = 8.8 Hz, 12H) 3.92 (s, 18H); ³¹P-NMR: δ 6.90; Anal. Calcd for C₄₈H₄₂N₃O₁₈P₃ 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, v_{max}/cm^{-1} : 1717 (C=O), 1217 (-P=N-), 958 (P-O); ¹H-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); ³¹P-NMR: δ 7.46; Anal. Calcd for C₅₄H₅₄N₃O₁₈P₃ 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); ¹H-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); ³¹P-NMR: δ 7.49; Anal. Calcd for C₆₆H₇₈N₃O₁₈P₃ 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, v_{max}/cm^{-1} : 1504 (Ph), 1208 (-P=N-), 954 (P-O); ¹H-NMR: δ 7.33–6.95 (broad, ArH); ³¹P-NMR: δ 9.33; Anal. Calcd for C₇₂H₅₄N₃O₆P₃ 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, v_{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, v_{max}/cm^{-1} : 1504 (Ph), 1215 (-P=N-), 957 (P-O); ¹H-NMR: δ 6.89 (d, J = 3.2 Hz, 12H), 6.81 (d, J = 3.2 Hz, 12H); ³¹P-NMR: δ 8.95; Anal. Calcd for C₃₆H₂₄F₆N₃O₆P₃ 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, v_{max}/cm^{-1} : 1723 (C=O), 1206 (-P=N-), 958 (P-O); ¹H-NMR: δ 7.72 ~ 7.17 (broad, 18H), 3.64 (s, 18H); ¹P-NMR: δ 6.62; Anal. Calcd for C₄₈H₄₂N₃O₁₈P₃ 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, v_{max}/cm^{-1} : 1321 (CF₃), 1263 (C-F), 1221

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(-P=N-), 969 (P-O); ¹H-NMR: δ 7.26–7.06 (broad, ArH); ³¹P-NMR: δ 8.19; Anal. Calcd for C₄₂H₁₈F₂₄N₃O₆P₃ C, 41.71 H, 1.50 N, 3.47. Found C, 41.67 H, 1.37 N, 3.23.

Hexakis(2-naphthyloxy)cyclotriphosphazene (30): 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, v_{max}/cm^{-1} : 1508 (C=O), 1210 (-P=N-), 973 (P-O); ¹H-NMR: δ 7.67–7.02 (ArH); ³¹P-NMR: δ 9.21; Anal. Calcd for C₆₀H₄₂N₃O₆P₃ C, 72.51 H, 4.26 N, 4.23. Found C, 72.46 H, 4.15 N, 4.20.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (grant No. 59825116) and Chinese Academy of Sciences for the financial support.

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Received in the UK December 4, 2000

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