Chinese Chemical Letters Vol. 12, No. 4, pp. 301 – 304, 2001

A Novel Synthesis of Some Hexasubstituted Cyclotriphosphazenes

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Abstract: Some known and new hexaaryloxyphosphazene $N_3P_3(O\text{-}C_6H_4\text{-}R)_6]$ (R=H, CH_3, OCH_3, $C(CH_3)_3$, CHO, F, C_6H_5COOR, *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.

Keywords: Phosphazene, cyclotriphosphazene, phenols, potassium phosphate.

In recent years, many efforts were focused on the preparation and characterization of phosphazene which contained a framework of alternating phosphorous and nitrogen atoms with two substituent groups attached to each phosphorous atom[1]. It is noticeable that cyclophosphazene, especially hexaaryloxyphosphazene and perfluoroaryloxyphosphazene exhibit excellent thermal and chemical stability which can be used as fireproof materials, 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 hexaaryloxyphosphazene 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]. G.A. Carriedo *et al*[8] described a very convenient preparation for the known cyclic aryloxyphospha-zene$[N_3P_3(OC_6H_4\text{-}R)_6]$ (R = Br, CN, CHO, $COCH_3$, COC_6H_5, NO_2, H, Bu^t, OCH_3) directly from $[N_3P_3Cl_6]$, phenols, and K_2CO_3 in acetone. But in the case of phenols $HOC_6H_4\text{-}R$ (R = Bu^t, OCH_3), the reactions were much slower, lasting 20 h even in the presence of PTC.

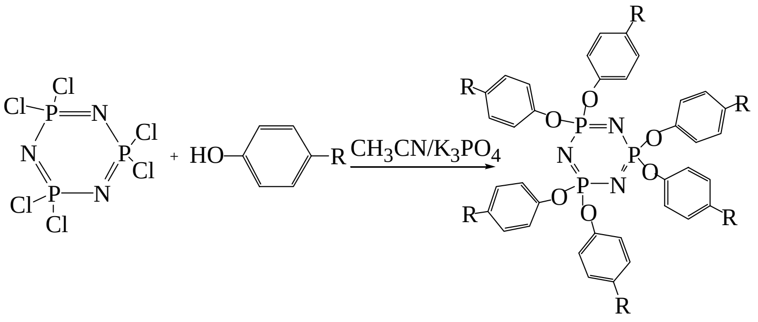
In this work, we found that in refluxing acetonitrile, hexasubstituted cyclotriphosphazene can be readily synthesized by reaction of $N_3P_3Cl_6$ with phenols in the presence of anhydrous potassium phosphate.

Hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ was prepared from the reaction of phosphorus pentachloride and ammonium chloride. The crude product was sublimed at 140°C *in vacuo* and then recrystallized twice from heptane, mp 113℃. ^{31}P-NMR

($CDCl_3$): 18.95 (singlet). All the phenols were recrystallized from methane dichloride/petroleum ether before utilization. Anhydrous potassium phosphate was obtained from the dehydration of potassium phosphate trihydrate at 110°C under 0.1 torr pressure in the presence of diphosphorous pentaoxide followed by being finely powdered. Acetonitrile was distilled from P_2O_5 prior to use.

Typical procedure: Hexachlorocyclotriphosphazene (1.0 g, 2.87 mmol), substituted phenol (18.10 mmol), anhydrous potassium phosphate (7.0 g, 32.97 mmol), 50 mL of acetonitrile were placed in 100 mL flask connected with a drying tube. The mixture was refluxed for 0.5~10 hours, 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 (showed in **scheme 1**).

Scheme 1



R=	CH_3	OCH_3	Bu^t	H	CHO	$COOCH_3$	$COOC_2H_5$	$COOC_4H_9$	C_6H_5	F	4-F-3-CF_3	NO_2
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**	**1l**

All compounds were characterized by means of elemental analysis, ^{31}P-NMR, ^{1}H-NMR[9], the results were listed in **Table 1**.

In the literatures, the substitution reactions of $N_3P_3Cl_3$ were carried out in the solvent of tetrahydrofuran (THF), acetone or dioxane. Considering that high temperature can lead the reaction rate to be fast, we choose acetonitrile as the solvent instead of acetone or THF. Anhydrous potassium phosphate was reported to be used in the one-pot synthesis of dithiocarbamates[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 can not 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 **1c** (R = Bu^t), the reaction was also very fast. **1c** 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 **1a**, **1b** (R = CH_3, OCH_3) could be shortened than that of the conventional procedure.

The acetonitrile / K_3PO_4 method was also applied to the phenols **1e-1i** (R = CHO, $COOCH_3$, $COOC_2H_5$, $COOC_4H_9$). H. R. Allcock and co-workers[12] have described the synthesis of compound **1i** by the reaction of ethyl *p*-hydroxybenzoate sodium salt with $N_3P_3Cl_3$ in dioxane in the presence of TBAB for 72 h followed by column chromatograph. But in our case the reaction time was greatly shortened, and the tedious chromatography was avoided.

Table 1 Characterization of aryloxyphosphazenes

Compound	Elemental analysis /Found (Calcd)			^{31}P-NMR	Mp (℃)	Yield (%)
	C	H	N			
1a	64.70 (64.86)	5.31 (5.44)	5.20 (5.40)	8.89 (s)	119-120	70
1b	57.57 (57.74)	4.64 (4.85)	4.70 (4.81)	9.80 (s)	100-102	67
1c	69.83 (69.95)	7.58 (7.63)	3.91 (4.08)	8.88 (s)	130-131	70
1d	62.10 (62.34)	4.25 (4.36)	5.94 (6.06)	8.45 (s)	111-112	75
1e	58.34 (58.55)	3.40 (3.51)	4.74 (4.88)	6.90 (s)	155-156	70
1f	55.23 (55.34)	4.01 (4.06)	3.91 (4.03)	6.90 (s)	152	76
1g	57.48 (57.60)	4.79 (4.83)	3.60 (3.73)	7.46 (s)	87-88	70
1h	61.18 (61.25)	5.99 (6.07)	3.16 (3.25)	7.49 (s)	72-73	65
1i	75.10 (75.19)	4.71 (4.73)	3.59 (3.65)	9.33 (s)	198-199	72
1j	53.83 (53.95)	2.86 (3.02)	5.06 (5.24)	8.95 (s)	126-127	78
1k	41.67 (41.71)	1.37 (1.50)	3.23 (3.47)	8.19 (s)	73	72
1l*	44.71 (44.89)	2.34 (2.51)	12.95 (13.08)	----	260-262	78

*Compound **1l** can not dissolved in $CDCl_3$, ethyl acetate.

Aryloxyphosphazenes containing fluorine which are potential lubricants also can be readily afforded by this method, so the long reaction time and high temperature conditions[13] can be averted.

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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9. ^{1}H-NMR (80 MHz, CDCl$_3$, δ ppm, J Hz) spectroscopy of the phosphazenes: **1a**: 6.85 (d, 12H, J = 8.8,), 6.78 (d, 12H, J = 8.8,), 2.25 (s, 18H); **1b**: 6.76 (d, 12H, J = 9.6,), 6.68 (d, 12H, J = 9.6,), 3.73 (s, 18H); **1c**: 6.88 (d, 12H, J = 8.8,), 6.81 (d, 12H, J = 8.8,), 1.09 (s, 54H); **1d**: 7.18-6.85 (ArH); **1e**: 9.93 (s, 6H), 7.68 (d, 12H, J = 8.8,), 7.19 (d, 12H, J = 8.8,); **1f**: 7.80 (d, 12H, J = 8.8,), 7.04 (d, 12H, J = 8.8,), 3.92 (s, 18H); **1g**: 7.83 (d, 12H ,J = 8.8,), 7.05 (d, 12H, J = 8.8,), 4.42 (q, 12H, J = 7.2,), 1.40 (t, 18H, J = 7.2,); **1h**: 7.81 (d, 12H, J = 8.8,), 7.04 (d, 12H, J = 8.8,), 4.30 (t, 12H, J = 6.4,), 1.74 -1.40 (broad, 24H), 1.04 (t, 18H, J = 7.2,); **1i**: 7.33-6.95 (ArH); **1j**: 6.89 (d, 12H, J = 3.2,), 6.81 (d, 12H, J = 3.2,); **1k**: 7.26-7.06 (ArH).
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Received 30 September, 2000