On the Synthesis of Functionalized Cyclic and Polymeric Aryloxyphosphazenes from Phenols

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SYNOPSIS

A very convenient synthetic method is described for the known cyclic aryloxyphosphazenes $[N_3P_3(OC_6H_4\text{-}R)_6]$ (R = Br, CN, CHO, $COCH_3$, COC_6H_5, and NO_2). The method is based on the direct reaction of $[N_3P_3Cl_6]$ with six equivalents of the *para*-substituted phenols HOC_6H_4-R and K_2CO_3 in refluxing acetone and is characterized by very short reaction times and very simple workups, leading directly to the analytically and spectroscopically pure products in very high yields. In the cases where R = H, Bu^t, or OCH_3, the reactions were much slower, but the time could be shortened by using $[Bu_4N]Br$ as the phase-transfer catalyst. Similarly, the polymers $[NP(OC_6H_4\text{-}R)_2]_n$ can be conveniently obtained in ca. 70% and good analytical purity from polydichlorophosphazene $[NPCl_2]_n$ and the *para*-substituted phenols HOC_6H_4-R (R = Br, CN, $COCH_3$, COC_6H_5, and NO_2) in the presence of K_2CO_3 using THF as the solvent.

INTRODUCTION

A variety of hexaaryloxyphosphazenes of the type $[N_3P_3(OR)_6]$ can be prepared by reacting hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ with sodium phenolates or with phenols in the presence of a proton abstractor in an appropriate organic solvent.[1] The reaction times, workups, selectivity, and yields of these reactions vary widely depending on all the variables involved, such as the group R, the solvent, and the reaction conditions. The use of sodium phenolates in refluxing tetrahydrofuran (THF) or dioxane usually requires long reaction times, especially if bulky substituents are present in R.[2] However, it was earlier observed[3] that in the presence of $[Bu_4N]Br$ (TBAB) as the phase-transfer catalyst (PTC) the substitution process is much faster, although it is still slow when steric factors are important.[4] Later, other promoters of the substitution reactions were discovered,[5] such as 4-(alkylamino)pyridines,[5a] tetrabutylphosphonium salts,[5b] or tetrabutylammonium salts in the presence of aliphatic polyethers.[5c]

Many other alternatives have been essayed trying to improve the synthetic procedure, as, e.g., the use of thallium phenolates and TBAB in THF[6] or the direct reaction of $[N_3P_3Cl_6]$ with the corresponding phenol in the presence of $KHCO_3$ in THF[7] or with NaOH in CH_2Cl_2/H_2O in the presence of alkylamonium salts as the PTC.[8,9]

Some recent publications[10] describing the reactions of phenols with haloalkanes and K_2CO_3 in refluxing acetone suggested to us the possibility of applying this technique to the preparation of the aryloxyphosphazenes. Sodium or potassium carbonates or hydrogen carbonates have already been used in the synthesis of phosphazenes,[11,12] especially with biphenols[13] or diamines.[14] Less frequent is the use of acetone as a solvent, although the reaction of $[N_3P_3Cl_6]$ with $NaOC_6H_5$ in acetone at room temperature[15] and with various HOC_6H_4—COR and $KHCO_3$ in 2-butanone[16] has been reported.

Herein, we report the results that we obtained while exploring the preparation of trimeric aryloxyphosphazenes directly from $[N_3P_3Cl_6]$, phenols, and K_2CO_3 in acetone, with and without PTC, and the

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extension of this method to aryloxyphosphazene polymers, aiming to simplify the synthetic procedures leading to those types of compounds, especially to those bearing groups that can be easily functionalized, such as Br, CN, NO_2, CHO, $COCH_3$, COC_6H_5, or OCH_3.

EXPERIMENTAL

The reactions were carried out under nitrogen using the standard Schlenk techniques. The IR spectra were recorded with a Perkin-Elmer FT 1720-X spectrometer. NMR spectra were recorded on Bruker AC-200 and AC-300 instruments, using $CDCl_3$ as the solvent unless otherwise stated. ^1H- and $^{13}C\{^1H\}$-NMR are given in δ relative to TMS. $^{31}P\{^1H\}$-NMR are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H, and N analyses were performed with a Perkin-Elmer 240 microanalyzer. P and Cl analyses were performed by Galbraith Laboratories. For the cyclic phosphazenes, the analytical data given correspond to the reaction products as isolated without purification. GPC were measured with a Perkin-Elmer equipment with a Model LC 250 pump, a Model LC 290 UV, and a Model LC 30 refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through a Perkin-Elmer PLGel (guard, mixed bed 10^4 and 10^3 Å) at 30°C. Approximate molecular weight calibrations were obtained using narrow molecular weight distribution polystyrene standards. T_g were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer.

The K_2CO_3 was dried at 140°C prior to use. The acetone used as the solvent was predistilled from $KMnO_4$ and further distilled from anhydrous $CaSO_4$. Petroleum ether refers to that fraction distilling in the range 60–65°C. Phenol was purified by distillation in a vacuum followed by dissolution in CH_2Cl_2, filtering through Na_2CO_3, and evaporation in a vacuum. The other phenols were used as purchased or recrystallized from CH_2Cl_2/petroleum ether. The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Strem Chemicals) was purified from hot petroleum ether and dried *in vacuo*. TBAB (Aldrich) was used as received.

Synthesis of $[N_3P_3(OC_6H_4\text{-}R)_6]$ (1)

Compound $[N_3P_3(OC_6H_4\text{-}Br)_6]$ (1a)

A mixture of $[N_3P_3Cl_6]$ (2.5 g, 7.18 mmol), HOC_6H_4-Br (7.46 g, 43.1 mmol), and K_2CO_3 (14.3 g, 103 mmol) was refluxed in acetone (200 mL) for 1.5 h. The volatiles were evaporated *in vacuo* and the residue extracted with CH_2Cl_2 (4 × 40 mL). Evaporation of the solvent *in vacuo* gave spectroscopically and analytically pure **1a** as a white solid. Yield: 7.93 g, 95%. The same result was obtained operating under air instead of nitrogen. The CO_2 evolved during the reaction precipitated 0.23 g (1.17 mmol) of $BaCO_3$ from aqueous $Ba(OH)_2$.

^1H-NMR: 6.7 d, 7.3 d (AB system, J_{AB} = 9). $^{31}P\{^1H\}$-NMR: 9.2; (10.3 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 119, 123, 133, 150 br.

ANAL: Calcd for $C_{36}H_{24}O_6Br_6N_3P_3$: C, 37.0%; H, 2.1%; N, 3.6%.
Found: C, 37.0%; H, 2.1%; N, 3.8%.

The same general procedure gave compounds **1b–1e**, with the scale (mmol $[N_3P_3Cl_6]$–mL acetone), reaction times, extraction (if different from for **1a**), yields and, spectroscopic data given below. Note that the CHO derivative **1c** was made using THF as the solvent.

Compound $[N_3P_3(OC_6H_4\text{-}CN)_6]$ (1b)

14.4 mmol–400 mL, 1 h, extraction with CH_2Cl_2 (10 × 40 mL). Yield: 1.08 g, 89%.

^1H-NMR: 7.0 d, 7.5 d (AB system, J_{AB} = 9). $^{31}P\{^1H\}$-NMR: 7.3; (9.0 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 118 (6C, CN); 110, 121, 134, 152 br (36 C, C_6H_4).

ANAL: Calcd for $C_{42}H_{24}O_6N_9P_3$: C, 59.8%; H, 2.9%; N, 14.9%.
Found: C, 59.0%; H, 2.9%; N, 14.7%.

Compound $[N_3P_3(OC_6H_4\text{-}CHO)_6]$ (1c)

1.44 mmol–40 mL THF, 48 h. Yield: 1.13 g, 91%.

^1H-NMR: 7.1 d, 7.7 d (AB system, J_{AB} = 9; 24 H, C_6H_4); 9.9 (s, 6H, CHO). $^{31}P\{^1H\}$-NMR: 7.5; (9.1 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 191 (s, 6C, CHO); 122, 132, 134, 155 (36C; C_6H_4).

ANAL: Calcd for $C_{42}H_{30}O_{12}N_3P_3$: C, 58.5%; H, 3.5%; N, 4.9%.
Found: C, 58.0%; H, 3.6%; N, 4.7%.

Compound $[N_3P_3(OC_6H_4\text{-}COCH_3)_6]$ (1d)

1.44 mmol–40 mL, 1 h. Yield: 1.28 g, 94.1%.

^{1}H-NMR: 7.0 d, 7.8 d (AB system, J_{AB} = 8; 24 H, C_6H_4); 2.6 (s, 18H, $COCH_3$). $^{31}P\{^1H\}$-NMR: 7.9; (9.4 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 27 (6C, CH_3), 197 (6C, CO) 121, 131, 135, 154 (36 C; C_6H_4).

ANAL: Calcd for $C_{48}H_{42}O_{12}N_3P_3$: C, 61.0%; H, 4.5%; N, 4.4%.

Found: C, 61.3%; H, 4.5%; N, 4.5%.

Compound $[N_3P_3(OC_6H_4\text{-}COC_6H_5)_6]$ (1e)

1.44 mmol–40 mL, 0.5 h. Yield: 1.6 g, 84%.

^{1}H-NMR: 7.0–7.6 m (C_6H_5 and C_6H_4). $^{31}P\{^1H\}$-NMR: 8.1; (9.6 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 196 (s, 6C, CO); 121, 129, 130, 132.6, 133.3, 135, 138, 154 (C_6H_5 and C_6H_4).

ANAL: Calcd for $C_{78}H_{54}O_{12}N_3P_3$: C, 71.1%; H, 4.1%; N, 3.2%.

Found: C, 70.7%; H, 4.0%; N, 3.0%.

Synthesis of $[N_3P_3(OC_6H_4\text{-}NO_2)_6]$ (1f)

A mixture of $[N_3P_3Cl_6]$ (2 g, 5.75 mmol), $HOC_6H_4—NO_2$ (4.96 g, 35.7 mmol), and K_2CO_3 (11.9 g, 86.2 mmol) in acetone (100 mL) was refluxed for 1.5 h. The volatiles were evaporated *in vacuo,* and the residue was washed with water at 0°C, then with acetone (15 mL), methanol (20 mL), and diethyl ether (20 mL) and dried *in vacuo* to give **1 f** as a white powder. Yield: 5.05 g, 91%.

^{1}H-NMR (acetone/D_2O): 8.2 d, 7.4 d (AB system, J_{AB} = 9.2). $^{31}P\{^1H\}$-NMR: 7.3; (8.9 in acetone-d_6).

ANAL: Calcd for $C_{36}H_{24}O_{18}N_9P_3$: C, 44.9%; H, 2.5%; N, 13.1%.

Found: C, 44.8%; H, 2.5%; N, 12.8%.

Synthesis of $[N_3P_3(OC_6H_4\text{-}R)_6]$ *R = H(1 g), Bu^t (1 h), OCH_3* (1i)

A mixture of $[N_3P_3Cl_6]$ (1.5 g, 4.3 mmol), HOC_6H_5 (2.47 g, 26.2 mmol), TBAB (6.43 g, 19.4 mmol), and K_2CO_3 (8.9 g, 64.5 mmol) was refluxed in acetone (130 mL) for 3 h. The volatiles were evaporated *in vacuo,* and the residue was extracted with toluene (3 × 15 mL). The solution was washed with water (5 × 50 mL) and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave spectroscopically pure **1g** as white microcrystals. Yield: 2.0 g, 67%.

^{1}H-NMR: 6.7–7.2, m. $^{31}P\{^1H\}$-NMR: 9.2; (10.2 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 122, 125, 130, 151 br.

ANAL: Calcd for $C_{36}H_{30}O_6N_3P_3$: C, 62.3%; H, 4.3%; N, 6.0%.

Found: C, 62.1%; H, 4.3%; N, 5.9%.

Compound **1h** was similarly prepared in 20 h and 71% yield.

^{1}H-NMR: 1.2 (s, 54 H, CH_3), 6.7 d, 7.1 d (AB system, J_{AB} = 9; 24 H, C_6H_4). $^{31}P\{^1H\}$-NMR: 9.5; (10.4 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 32 (18C, CH_3), 35 (6C, $C\{CH_3\}_3$), 121, 127, 149 br, 154 (36C; C_6H_4).

ANAL: Calcd for $C_{60}H_{78}O_6N_3P_3$: C, 69.9%; H, 7.6%; N, 4.1%.

Found: C, 70.3%; H, 7.9%; N, 3.7%.

Compound **1i** was similarly prepared in 20 h and 65% yield. The extraction step required 4 × 40 mL of toluene.

^{1}H-NMR: 3.7 (s, 18 H, CH_3) 6.7 d, 6.8, d (AB system, J_{AB} = 9; 24 H, C_6H_4). $^{31}P\{^1H\}$-NMR: 10.5; (11.4 in acetone/D_2O). $^{13}C\{^1H\}$-NMR: 56 (6C, CH_3), 115, 122, 145 br, 157 (36C; C_6H_4).

ANAL: Calcd for $C_{42}H_{42}O_{12}N_3P_3$: C, 57.7%; H, 4.8%; N, 4.8%.

Found: C, 57.2%; H, 4.8%; N, 4.7%.

Synthesis of the Polymers $[NP(OC_6H_4—R)_2]_n$ (2)

$[NP(OC_6H_4\text{-}CN)_2]_n$ (2b)

A mixture of $[NPCl_2]_n$ (2.43 g, 21.0 mmol), HOC_6H_4-CN (7.5 g, 63 mmol), and K_2CO_3 (11.6 g, 84 mmol) was refluxed in THF (250 mL) for 34 h with vigorous mechanical stirring. The mixture was poured into water (1.5 L) and reprecipitated twice from THF/water and the solid was washed with acetone (4 × 50 mL) and diethyl ether (2 × 50 mL). The white insoluble material was stirred with a 50% mixture of THF/water (25 mL) 48 h and filtered. The residue was dried at 50°C in a vacuum. Yield: 4.3 g, 72%.

$^{31}P\{^1H\}$-NMR (in DMF/D_2O): −17.7.

ANAL: Calcd for $C_{14}H_8O_2N_3P$: C, 59.8%; H, 2.9%; N, 14.9%.

Found: C, 57.9%; H, 2.8%; N, 14.2%. Chlorine content 0.5%.

The other polymers were similarly prepared with the scale (mmol $[NPCl_2]_n$–mL THF, reaction times, and yields given below.

$[NP(OC_6H_4\text{-}Br)_2]_n$ (2a)

13.5 mmol–250 mL, 200 h. It was purified by dissolving in dioxane and precipitating on water. Yield: 3.7 g, 69.7%.

$^{31}P\{^1H\}$-NMR (in THF/D_2O): −18.4.

ANAL: Calcd for $C_{12}H_8O_2NPBr_2$: C, 37.0%; H, 2.1%; N, 3.6%; P, 8.0%.
Found: C, 37.7%; H, 2.2%; N, 3.6%; P, 8.2%.

MW(GPC) = 800,000. M_w/M_n = 2.3.

$[NP(OC_6H_4\text{-}COCH_3)_2]_n$ (2c)

26 mmol–240 mL, 23 h. It was further reprecipitated from dimethylformamide–water. Yield: 5.5 g, 67.3%.

$^{31}P\{^1H\}$-NMR (in DMF/D_2O): −18.6.

ANAL: Calcd for $C_{16}H_{14}O_4NP$: C, 61.0%; H, 4.5%; N, 4.4%.
Found: C, 59.9%; H, 4.2%; N, 4.4%. Chlorine content: 692 ppm.

$[NP(OC_6H_4\text{-}COC_6H_5)_2]_n$ (2d)

17.3 mmol–250 mL, 48 h. It was further reprecipitated from DMF/H_2O. Yield: 5.1 g, 67.1%.

$^{31}P\{^1H\}$-NMR: −20.6 (−18.7 in DMF/D_2O).

ANAL: Calcd for $C_{26}H_{18}O_4NP$: C, 71.1%; H, 4.1%; N, 3.2%.
Found: C, 70.7%; H, 4.0%; N, 3.1%. Chlorine content: 465 ppm. (The material isolated after 13 h reaction time had 0.2% Cl.)

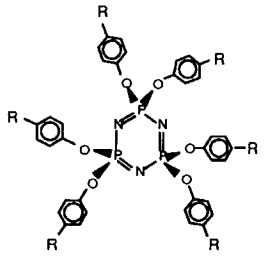
$[NP(OC_6H_4\text{-}NO_2)_2]_n$ (2e)

21 mmol–250 mL, 22 h. Yield: 4.3 g, 64.6%.

ANAL: Calcd for $C_{12}H_8O_6N_3P$: C, 44.9%; H, 2.5%; N, 13.1%.
Found: C, 43.3%; H, 2.4%; N, 12.0%. Chlorine content 0.5%.

RESULTS AND DISCUSSION

Refluxing a mixture of $[N_3P_3Cl_6]$ and six equivalents of the *para*-substituted phenols HOC_6H_4-R (R = Br, CN, CHO, $COCH_3$, COC_6H_5, NO_2) in acetone in the presence of an excess of finely divided K_2CO_3 gave in only 0.5–1.5 h, depending on R and the scale, the known hexaphenoxy derivatives $[N_3P_3(OC_6H_4\text{-}R)_6]$ **1a**–**1f** (see Chart 1). Carried out at room temperature, the reactions took ca. 12 h. The compounds were isolated from the reaction mixture (see Experimental part) spectroscopically and analytically pure without further purification and in high yields. In the case of **1a**, we checked that the same purity and yield can be obtained carrying out the reaction and workup operations under air instead of nitrogen. During the substitution process, the formation of some CO_2 was observed, but



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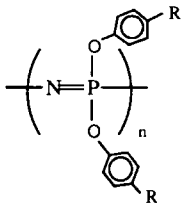
R =	Br	CN	CHO	$COCH_3$	COC_6H_5	NO_2	H	Bu^t	OCH_3	CH_2OH
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**



2

R =	Br	CN	$COCH_3$	COC_6H_5	NO_2
	2a	**2b**	**2c**	**2d**	**2e**

Chart 1

the total amount was insignificant. Thus, in the reaction with HO-C_6H_4-Br, the CO_2 evolved precipitated only 0.027 mol of $BaCO_3$ per mol of phenol. Therefore, it is assumed that the other reaction products are KCl and $KHCO_3$, but not water.

Compound **1a**, which has been recently characterized by X-ray diffraction,[17a] is usually prepared with $NaOC_6H_4$-Br in THF in 168 h[17b] or in 12 h using a twofold excess of the sodium aryloxide followed by purification by chromatography.[17a] The sparingly soluble cyanide derivative **1b** was prepared earlier in 90% yield[12] with Na_2CO_3 in THF in 100 h. This latter observation clearly indicates that in acetone the substitution reaction is much faster than in THF. The origin of this is not clear, but we believe that the higher polarity of the acetone may be important.[18] The products **1d** and **1e** had been prepared using $KHCO_3$ and 2-butanone as the solvent,[16] but the reaction times were much longer (50–70 h) and had to be purified from DMF. The synthesis of **1f** does not require the preparation of the sodium

salt of the phenol, nor the use of $[BuN]_4Br$ as in other methods published earlier.[11,19]

In the case of the phenol HOC_6H_4-CHO, the reaction with K_2CO_3 in refluxing acetone was very fast and was completed in only 20 min to give $[N_3P_3(OC_6H_4\text{-}CHO)_6]$ **1c.** This is also remarkable, because this compound was prepared in 48 h in THF using sodium phenolate.[20] However, the reaction in acetone was accompanied by an unwanted side reaction, probably due to a condensation between the CHO and the acetone in the presence of the basic carbonate. During the short time needed to form **1c,** the collateral process affected only a very small fraction of the terminal CHO groups, but it was very extended when the refluxing was further prolonged. To avoid this effect, we tried the formation of **1c** with K_2CO_3 in THF. The reaction was completed in 6 h at reflux or in 48 h at room temperature, leading to the pure compound in high yield.

As expected, when the reactions of $[N_3P_3Cl_6]$ with the phenols were carried out in the presence of TBAB as PTC, they were much faster.[3] Thus, in adding only 1 mmol of TBAB per 6.5 mmol of $[N_3P_3Cl_6]$, **1a** was formed in 10 min at reflux. The promoter could be easily removed with water and the yield was again very high.

The K_2CO_3–acetone method was also tested with the phenols HOC_6H_4-R for R = H, Bu^t, OCH_3, and CH_2OH to obtain the known hexa-substituted derivatives **1g–1j** (see Chart 1). In those cases, the reactions were much slower (due to the last substitution step), lasting 80 h with the phenol HOC_6H_5 and more than 200 h with the other derivatives, always at the refluxing temperature. However, with PTC, the reaction times could be substantially shortened, although it depended on the amount of the promoter. Thus, with 4.5 mmol of TBAB per mmol of $[N_3P_3Cl_6]$, the reaction times were only 3 h for **1g** (48 h at room temperature) and 8–15 h for the others, depending on the scale. In the resulting preparations, the need for removing the rather large amounts of TBAB decreased the yields, but these were still of the order of 70%. Lower quantities of the promoter resulted in slightly better yields, but much larger reaction times. Taking this into account, the method still has some advantages as compared with the other previously described for **1g, 1h,**[6] and **1i.**[21] However, in the case of the phenol with R = CH_2OH, the K_2CO_3/acetone/TBAB method to give $[N_3P_3(OC_6H_4\text{-}CH_2OH)_6]$ **1j** required longer reaction times (50–60 h) and was accompanied by decomposition. As a result, the preparation was convenient only on a small scale. Therefore, this compound is better obtained by reacting **1c** and $NaBH_4$.[20]

In all cases, and consistently with previous knowledge,[22] the monitoring of the reactions by ^{31}P-NMR revealed that the chlorine/phenoxy substitution sequence follows a mechanism which is preferentially nongeminal and without notable isomeric preferences. Monitoring the reactions by ^{31}P-NMR also showed that with the less reactive phenols (R = H, Bu^t, OCH_3, and CH_2OH), and especially in the presence of the catalyst, an unexpected product could be detected during the first steps of the process. This product has two ^{31}P-NMR signals: a doublet at 20 ppm and a triplet that appears around −5.5 ppm and, therefore, is probably the potassium or TBA salt of the hydroxy derivative $[N_3P_3Cl_5(OH)]$.[23] We checked that a solution of $[N_3P_3Cl_6]$ in acetone remained unaltered for 6 h at reflux or 42 h at room temperature. However, in the presence of K_2CO_3, the product was clearly observed after 1 h at reflux and was formed quantitatively at room temperature in 4 days or in 12 h in the presence of TBAB (no significant reaction was observed between $[N_3P_3Cl_6]$ and the latter after 42 h at room temperature). Taking into account that very little water, if any, is formed in the substitution reactions with the phenols (see above) and that the potassium carbonate used was dried at 140°C, the hydroxy derivative could come from small amounts of water present in the acetone that would react with $[N_3P_3Cl_6]$ only if helped by the carbonate. In any case, its formation, which could not be prevented carrying out the reaction in the presence of anhydrous Na_2SO_4, did not affect the purity of the final hexa-substituted product, although may have some effect on the yields.

A series of experiments showed that the purity of the phenol, the concentration of the reactants, and the efficiency of the stirring are important factors in the reaction time, particularly in scaling up the preparations, which tends to increase it noticeably. All this is reasonable, taking into account that the reacting system is heterogeneous. Therefore, when scaling-up the preparations, it is advisable to check by ^{31}P-NMR that the reactions are actually completed before proceeding to the isolation of the product, especially when using the less reactive phenols.

On the other hand, the data did show a general trend in the substitution rates. In the presence as well as in the absence of the catalyst, the reactions were much faster with the more acidic phenols[24] having electron-withdrawing groups (R = Br, CN,

CHO, $COCH_3$, COC_6H_5, NO_2) than with the less acidic ones having electron-releasing groups (R = Bu^t, OCH_3, CH_2OH). With phenol (R = H), the reaction times were intermediate between those extremes.

Several attempts to extend the K_2CO_3/acetone method to the preparation of phenoxyphosphazene high polymers from $[NPCl_2]_n$ proved that acetone was not convenient as a solvent, leading to insoluble materials. However, refluxing a mixture of polydichlorophosphazene $[NPCl_2]_n$, prepared by thermal polymerization of $[N_3P_3Cl_6]$ in solution,[25] in THF in the presence of K_2CO_3 and an excess of the phenols HOC_6H_4-R (R = Br, CN, $COCH_3$, COC_6H_5, NO_2) gave in ca. 20 h the known polymers $[NP(OC_6H_4\text{-}R)_2]_n$ (**2a–2e**) (see Chart 1). A very simple workup led to the solid products in good yields (ca. 70%), having less than 0.5% chlorine content and with a reasonable analytical purity (only in the case of **2e**, the carbon content was found slightly but significantly lower in all the preparations performed). Prolonging the reflux to 50 h reduced the chlorine content to a few ppm. The polymers with R = CN and NO_2, which are insoluble, were not further purified.

As a comparison, in the published procedures to obtain **2a**,[26] **2c**,[27] **2d**,[28] and **2e**,[27] the yields were of the order of 30–60% with similar or longer reaction times but using TBAB as PTC, and prolonged Soxhlet extractions are required to obtain the pure products. For **2b**,[12] the published procedure is quite similar, using Na_2CO_3 in refluxing benzene, but the yield was 20% and no analytical data were given.

The polymer with R = Br (**2a**) is soluble in THF, and it was possible to measure the average molecular weight by GPC. The value obtained was 800,000 with a polydispersity of 2.3.

In the case of the less reactive phenols (those with R = H or Bu^t), the substitution was much slower, lasting ca. 1000 h, but finally yielded polydiphenoxyphosphazenes having an MW of the order of 800,000 with low polydispersities (ca. 1.5–2).[29]

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