Wittig Reaction on Carbonyl-containing Cyclotriphosphazenes: the Case of Hexakis(4-formylphenoxy)cyclophosphazene

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(Received October 28, 1987)

Abstract

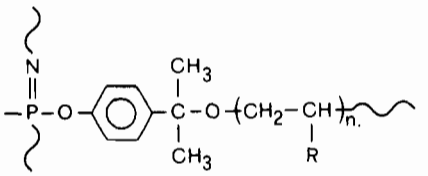
The Wittig reaction between hexakis(4-formylphenoxy)cyclophosphazene $[NP(O\text{-}C_6H_4\text{-}p\text{-}CHO)_2]_3$ (**1**) and several stabilized phosphonium ylides leads to the preparation of double bond-containing cyclophosphazenes. All the characterization data obtained for the synthesized compounds indicated that the cyclophosphazene ring is not involved in this reaction, the only reactive functions being the aldehydic groups in the side substituents of **1**.

These products proved to be promising materials in further functionalization studies and may open interesting perspectives in the case of the corresponding phosphazene high polymers.

Introduction

The increasing interest devoted to poly(organophosphazenes) during the last two decades is basically attributable to the versatility of the synthetic method used for the preparation of these polymers [1], and to the high reactivity of the phosphorus side substituents, which permits the functionalization of the phosphazene materials [2]. Both these facts lead to the synthesis of interesting phosphazene-based macromolecules suitable for use as low temperature elastomers [3], flame-retardant [4] and smoke-suppressant [5] additives, electric conductors [6–8] and photo-conductors [9, 10], biologically important polymers [11, 12], liquid crystals [13, 14], etc.

In recent times, we have carried out research on polyphosphazene synthesis and functionalization, with the aim of preparing new polymers showing improved scientific and technologic characteristics. We focused our attention on the possibility of grafting organic carbon-backboned macromolecules onto polyphosphazene matrices, and we prepared a series



of poly [bis(4-isopropylphenoxy)phosphazene]-g-polystyrene graft copolymers showing improved thermal stability [15] and flame resistance [16], as compared with the same properties of the original polystyrene.

Expanding upon this line we designed successively a new, innovative strategy for grafting vinyl-like polymers onto polyphosphazenes based on the introduction into phosphazene materials of olefinic unsaturated moieties which may act as starting points for the growth of side polymeric organic chains (see Fig. 1).

As a possible synthetic method for reaching this goal we chose the well known Wittig reaction [17]. This important synthetic process consists of a condensation–elimination reaction between a phosphonium ylide and a carbonyl compound to form olefin and phosphorus oxide. Since this reaction is compatible with a wide range of substituent groups on the carbonyl substrate, it constitutes a most valuable method for alkene synthesis.

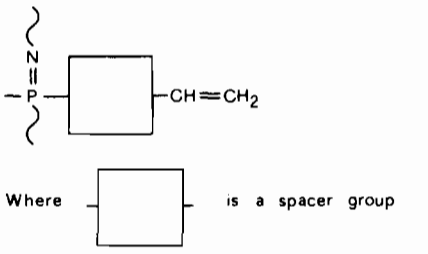


Fig. 1. Strategy for grafting vinyl-like polymers onto polyphosphazenes.

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As suggested elsewhere [18], most of the research on the polymeric phosphazene materials has been anticipated by previous investigations on low molecular weight cyclic oligomers, the cyclophosphazenes, since these trimers are considered good model compounds for the phosphazene high polymers.

Therefore, before studying the Wittig reaction between poly(organophosphazenes) and phosphonium ylides, we developed exploratory syntheses on appropriate cyclophosphazene oligomers, and we considered as a suitable candidate for this work hexakis(4-formylphenoxy)cyclophosphazene [NP-$(OC_6H_4$-*p*-$CHO)_2]_3$ [19].

In this paper we present the reactivity of this molecule with several different phosphonium ylides and the chemical structure of the synthesized cyclophosphazene compounds as determined by elemental analysis, IR, ^1H and ^{31}P NMR spectroscopic investigations.

Experimental

General

Reactions were carried out under a dry nitrogen atmosphere, although manipulation and separation procedures were generally carried out in air.

Tetrahydrofuran (THF) and diethyl ether were dried prior to use over sodium-benzophenone ketyl. Methylene chloride and chloroform were distilled from CaH_2.

IR spectra were taken on a Perkin-Elmer 983 spectrophotometer as Nujol mulls or in CH_2Cl_2 solution. ^1H and ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer.

Elemental analyses were performed by the Analytical Institute of the University of Padua.

Materials

The following phosphonium salts and ylides were prepared according to literature procedures.

Phosphonium salts

(Acetylmethyl)triphenylphosphonium chloride [20], (benzoylmethyl)triphenylphosphonium bromide [20], (carbomethyoxymethyl)triphenylphosphonium bromide [21], (fluorenyl)triphenylphosphonium bromide [22], (cyanomethyl)triphenylphosphonium chloride [23]. [Carbomethoxy(bromo)-methyl]triphenylphosphonium bromide was prepared by the method reported for the corresponding [carboethoxy(bromo)methyl]triphenylphosphonium bromide [24].

[Benzoyl(methyl)methyl]triphenylphosphonium bromide. To a solution of triphenylphosphine (22.81 g, 87.06 mmol) in benzene (80 ml) was added α-bromopropiophenone (10 ml, 14.27 g, 66.97 mmol) and the solution was refluxed with stirring for two days. Then the white precipitate formed was filtered, washed with benzene (2 X 20 ml) and Et_2O (2 X 20 ml) and dried under vacuum. It was recrystallized from $MeOH/Et_2O$ at −20 °C. Yield 29.20 g, 92%; melting point (m.p.) 212–214 °C. *Anal.* Calc. for $C_{27}H_{24}BrOP$ (799.61): C, 81.11; H, 3.03. Found: C, 80.79; H, 3.28%.

Ylides

(Acetylmethylene)triphenylphosphorane [20], (benzoylmethylene)triphenylphosphorane [20], (carbomethoxymethylene)triphenylphosphorane [21], (fluorenyl)triphenylphosphorane [22], (cyanomethylene)triphenylphosphorane [23], [carbomethoxy(bromo)methylene]triphenylphosphorane [24], [benzoyl(cyano)methylene]triphenylphosphorane [25].

[Benzoyl(methyl)methylene]triphenylphosphorane. [Benzoyl(methyl)methyl]triphenylphosphonium bromide (9.48 g, 20 mmol) was dissolved in 100 ml of H_2O and treated with aqueous 2 N NaOH to a phenolphtalein end point. The white solid precipitated was filtered, washed with H_2O (2 X 30 ml), taken up with CH_2Cl_2 (60 ml) and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated to *ca.* 30 ml. Addition of Et_2O (80 ml) gave a white solid which was filtered and dried under vacuum. Yield 6.15 g, 78%; m.p. 157–159 °C.

Hexakis(4-formylphenoxy)cyclophosphazene

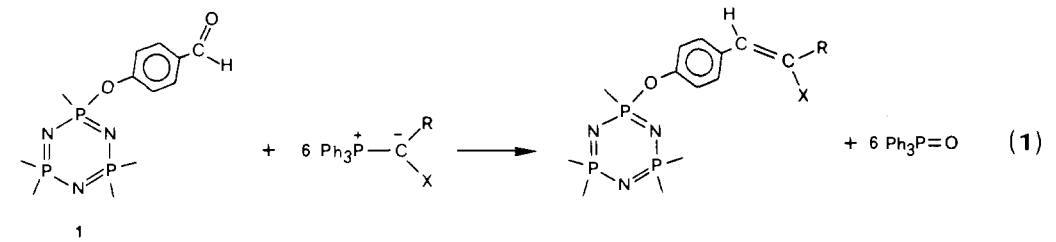
This compound was prepared and purified as reported in the literature [19].

All other chemicals were reagent grade and used without further purification.

Synthesis of Phosphazene Derivatives

Compounds **2**–**8** (Scheme 1) were prepared by the same procedure which is reported below for **2**.

In a 100 ml round-bottomed flask, hexakis(4-formylphenoxy)cyclophosphazene (**1**) (0.43 g, 0.5 mmol) was dissolved in CH_2Cl_2 (40 ml) and (carbomethoxymethylene)triphenylphosphorane (1.10 g, 3.3 mmol) was added to the stirred solution. The mixture was refluxed (except for the preparation of **8** which was carried out at room temperature) for 5 h. The course of the reaction was monitored by IR spectroscopy (in the range 1900–1400 cm^{-1}). The IR spectrum of the starting mixture showed strong bands at 1702 cm^{-1} attributed to the ν(C=O) stretching of the aldehydic group of **1**, and a broad band at 1599 cm^{-1} which includes also the ν(C=O) stretching of the free ylide. During the course of the reaction the growth of new bands located at 1710 [ν(C=O)] and 1630 [ν(C=C)] cm^{-1} was observed



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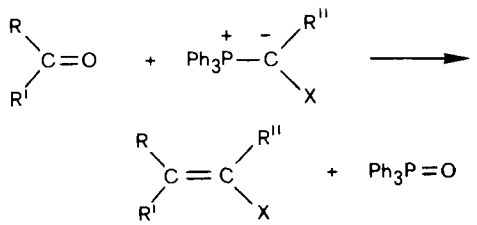
X = H ;	R = $COOCH_3$	a	2
X = H ;	R = $COCH_3$	b	3
X = H ;	R = COC_6H_5	c	4
X = Br ;	R = $COOCH_3$	d	5
X = CH_3 ;	R = COC_6H_5	e	6
XR =		f	7
X = H ;	R = CN	g	8

Scheme 1.

which are typical of an α,β-unsaturated carbonyl system. After completion of the reaction, the solution was cooled to room temperature, concentrated under reduced pressure to about half of the original volume, and precipitated by addition of Et_2O (60 ml). A white cream solid was obtained which was filtered, washed with Et_2O (3 X 20 ml) and purified by chromatography on fluorosil column (2 X 30 cm) using THF as eluant. The final, pale yellow, solution was concentrated under reduced pressure. Addition of Et_2O (50 ml) gave compound **2** as a white product; yield 0.49 g, 82%; m.p. 174–175 °C. **3**: yield 0.43 g, 78%; m.p. 171–172 °C. **4**: yield 0.62g, 84%; m.p. 160–162 °C. **5**: yield 0.66 g, 79%; m.p. 178–180 °C. **6**: yield 0.58 g, 75%; m.p. 154–157 °C. **7**: yield 0.75 g, 86%; m.p. 162–164 °C. **8**: yield 0.37 g, 74%; m.p. 182–185 °C.

Results and Discussion

According to an already well experienced chemistry [17], the Wittig reaction between phosphonium ylides and compounds containing carbonyl functions occurs by nucleophilic attack of the negatively charged ylide carbon on the carbonyl group, leading to the formation of olefin and phosphorus oxide.



It may be noted however that if the same reaction is carried out on carbonyl-containing cyclophosphazenes, two possible sites are susceptible to reaction with the phosphonium ylide, *i.e.* the side substituent in the cyclophosphazene which bears ketonic or aldehydic moieties and the phosphorus atoms in the phosphonitrilic ring. This latter reaction might be expected owing to the marked difference in the electronegativity between the phosphorus and nitrogen atoms in the cycle (see ref. 1, p. 332), and would probably lead to the opening of the inorganic ring and to the formation of low molecular weight degradation products.

In order to exclude this possibility and to ensure the chemical stability of the cyclophosphazene, we limited our attention to the reactions of low basicity ylides **a**–**g** with hexakis(4-formylphenoxy)cyclophosphazene (**1**). These reactions occur according to the general equation reported in Scheme 1 affording, in 74–86% yield, the cyclotriphosphazene compounds **2**–**8**, respectively.

Compounds **2**–**8** are stable both in solution and in the solid state, very soluble in THF, chlorinated and aromatic solvents, but insoluble in alcohol and diethyl ether. They gave satisfactory C, H, and N elemental analyses and were characterized by their IR, ^1H and ^{31}P NMR spectra (Table I).

*Reactions of Keto-stabilized Ylides **a**–**e***

Compounds **2**–**6** are obtained by reacting keto-stabilized ylides **a**–**e** with the formyl-group-containing cyclophosphazene (**1**) as shown in Scheme 1.

Several comments are possible on this reaction.

First of all, it may be observed that the time necessary for driving reaction (1) to completeness

TABLE I. Analytical and Spectral Data for the Cyclophosphazene Derivatives

Compound	Reaction time[a] (h)	Elemental analysis[b]			IR (cm^{-1})		^1H NMR[d]					$^{31}P\{^1H\}$NMR[d] δ(P)
		C	H	N	ν(C=O)	ν(C=C)	δ(H)	^3J(HH)	δ(X)	^3J(HH)	δ(R)	
2	5	59.85 (60.15)	4.54 (4.54)	3.73 (3.51)	1710s	1639m	7.61d	16.1	6.32d	16.1	3.82s	8.14s
3[e]	24	65.71 (65.39)	4.89 (4.94)	3.65 (3.81)	1664s 1686s	1624m 1610m	7.44d	16.4	6.60d	16.4	2.38s	8.05s
4	168	73.68 (73.31)	4.59 (4.51)	2.90 (2.85)	1662s	1609m	[f]		[f]			8.08s
5	6	43.23 (43.12)	2.98 (2.89)	2.54 (2.51)	1724s	1610m	8.12s				3.91s	8.04s
6	480	74.12 (73.98)	5.25 (5.04)	3.12 (2.97)	1640s	[g]	[f]		2.15s			8.20s
7	24	81.95 (82.32)	4.41 (4.49)	2.22 (2.40)		[h]	[f]					8.79s
8	5[i]	64.46 (64.87)	3.61 (3.63)	12.26 (12.61)	[j]	1619m	[f]		5.82d[k] 5.81d[k] 5.51d[l] 5.48d[l]	16.7 16.7 12.3 12.0		7.57–7.79m

[a]In $CHCl_3$ solution under reflux. [b]Calculated values in parentheses. [c]In CH_2Cl_2; s = strong, m = medium. [d]Spectra recorded in $CHCl_3$; δ in ppm, J in Hz; ^1H and $^{31}P\{^1H\}$ NMR chemical shifts were referenced to internal $SiMe_4$ and H_3PO_4 (85%), respectively; s = singlet, d = doublet, m = multiplet. [e]This compound shows in the IR spectrum distinct ν(C=O) and ν(C=C) bands for the s-*cis* and s-*trans* isomers. [f]Obscured by phenyl protons. [g]Obscured by carbonyl band. [h]Obscured by phenyl stretchings. [i]Reaction carried out at 30 °C. [j]$\nu(C\equiv N)$ = 2221 cm^{-1} in CH_2Cl_2. [k]Resonance of the α-proton in the *trans* olefinic configuration. [l]Resonance of the α-proton in the *cis* olefinic configuration.

shows a marked dependence on the electronic properties of the substituents R on the ylide. In fact, for ylides **a**–**c**, where X = H and R = $COOCH_3$, $COCH_3$ and COC_6H_5, respectively, the reaction time increases from 5 h (ylide **a**) to 168 h (ylide **c**). The observed trend is in agreement with the different nucleophilic character of the C-ylide atom in the phosphorane **a**–**c**, as indicated by the pK_a of their conjugated acids which decreases in the order: R = $COOCH_3 > COCH_3 > COC_6H_5$ [26].

Secondly, steric and electronic effects due to the substituents X on the ylide systems seem to play a relevant role on the overall reaction (1). Thus, when the ylidic H atom in the phosphorane **a** is replaced by a Br atom (ylide **d**), no significant changes are observed in the reaction time necessary to complete reaction (1), according to what was found for analogous reactions among the ylide **a** and haloylides with free benzaldehyde [24]. However, in the case of phosphorane **e**, where X is a CH_3 group, the reaction is complete in 20 days, thus indicating a remarkable steric effect of this moiety.

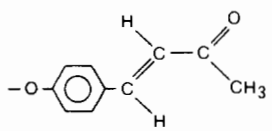
Finally, when reaction (1) was carried out by using [benzoyl(cyano)methylene]triphenylphosphorane as stable ylide, the unsaturated phosphazene derivative is not obtained, further emphasizing the importance of electronic effects of the substituent X on the reactivity of ylides in the Wittig reaction [17].

Interesting conformational features are apparent on the products, which have been evidenced by spectroscopic techniques.

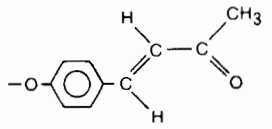
The infrared spectra of derivatives **2**–**6** show ν(C=O) in the range 1724–1664 cm^{-1} and ν(C=C) stretchings in the range 1639–1609 cm^{-1}. These absorptions are diagnostic for a α,β-unsaturated system [27].

Compound **3**, however, shows, both in solution and in the solid state, two distinct bands, either in the ν(C=O) and ν(C=C) region which, on the basis of the relative frequency separation and intensity of the C=O and C=C stretchings [27], may be assigned to the s-*trans* and s-*cis* conformations of the α,β-unsaturated system.

Thus, the bands at 1665 and 1624 cm^{-1} may be assigned to ν(C=O) and ν(C=C) stretchings, respectively, of the s-*trans* isomer, while the other



s-trans



s-cis

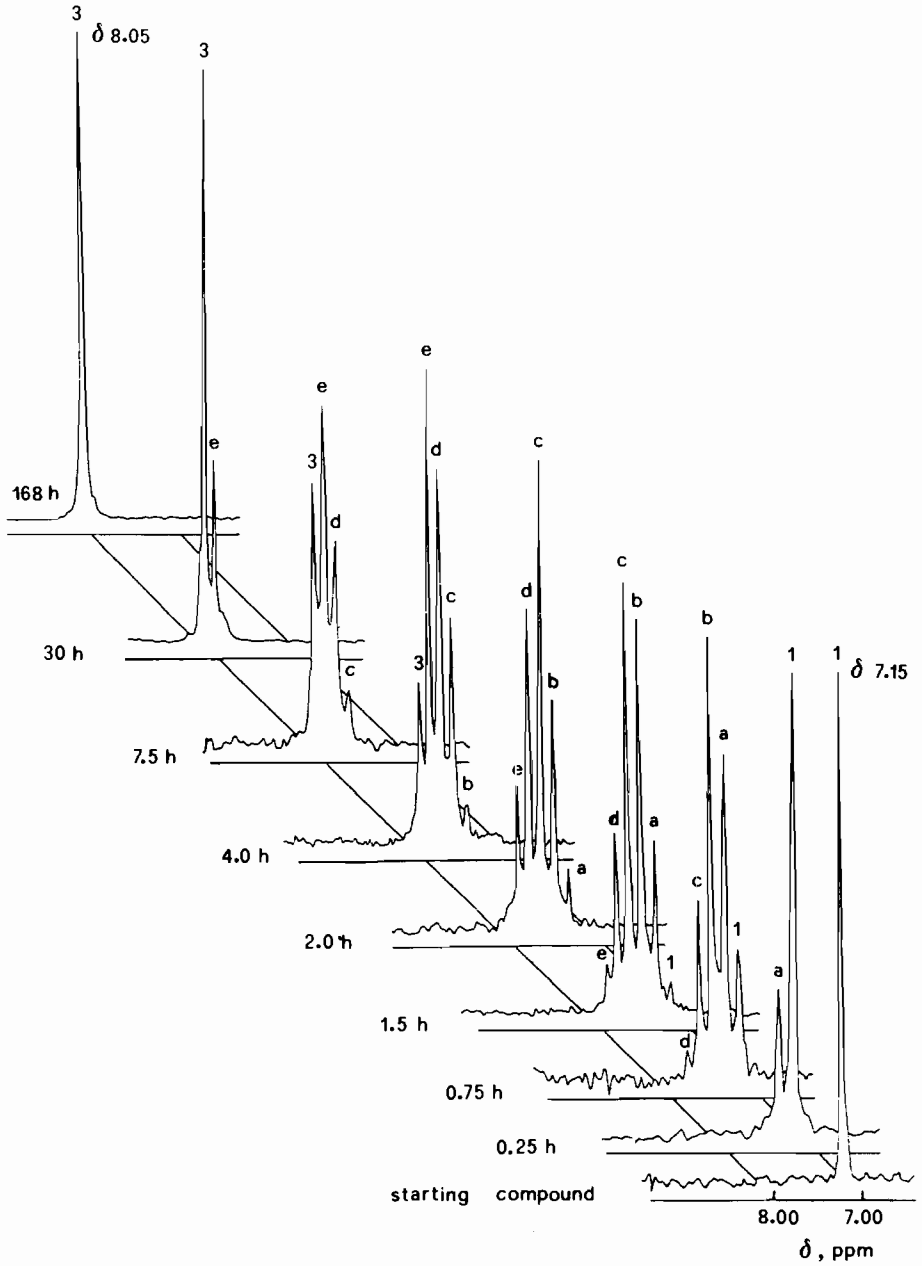


Fig. 2. ^{31}P NMR spectra recorded during reaction (1) between cyclophosphazene **1** and the ylide **b** at 30 °C in $CDCl_3$.

two absorptions ν(C=O) = 1689 cm^{-1} and ν(C=C) = 1610 cm^{-1} may be due to the s-*cis* conformation [27]. Although the IR spectra of the other derivatives **2**, **4**–**6**, do not show a similar behaviour, the broadness of ν(C=O) and ν(C=C) absorptions may suggest the presence, also in these cases, of s-*trans* and s-*cis* conformations.

The ^1H NMR spectra of compounds **2** and **3** display a doublet for each of the olefinic protons with a ^3J(HH) of 16.1 and 16.4 Hz, respectively, indicating a *trans* olefinic configuration for all six unsaturated substituents on the cyclophosphazene matrix [28]. In compound **4** these resonances are obscured by the resonances of the phenyl protons of the COC_6H_5 group. However, a *trans* stereogeometry of the olefinic system for **4** can be reasonably inferred since stabilized ylides react with carbonyl groups to give preferentially *trans*-olefins [17].

^{31}P NMR spectroscopic investigations of the final compounds **2**–**6** are reported in Table I.

All these compounds show in the ^{31}P NMR spectra a unique sharp singlet in the range δ 8.04–8.20 due to symmetrically substituted phosphorus atoms in the cyclophosphazene ring.

However, on treating hexakis(4-formylphenoxy)-cyclophosphazene (**1**) with a slight excess of ylide **b** and following the progress of the reaction by ^{31}P NMR spectroscopy, a very interesting behavior was observed. After the addition of the ylide compound to the cyclophosphazene **1**, the initial peak located at δ 7.15 starts to decrease, while new peaks are growing rapidly (see Fig. 2). A total number of five intermediate peaks located at δ 7.32, 7.49, 7.65, 7.80, and 7.92 are formed at different times, which subsequently disappear to produce, at the end of this process, a new sharp singlet at δ 8.05, corresponding to the final product **3**.

Such behavior is observed to be independent of the nature of the ylide and is not modified by using different experimental conditions. In fact, the same peak sequence at the same chemical shifts is also found when the Wittig reaction on substrate **1** is performed by adding six equivalents of ylide reactants portionwise to the cyclophosphazene **1** and recording the corresponding NMR spectra each time. These spectroscopic results lead us to conclude that the sequence of signals in the ^{31}P NMR spectra reported in Fig. 2 may be attributed to partially reacted cyclophosphazene species containing mono-, bi-, tri-, tetra-, and penta-α,β-unsaturated moieties which are formed during the course of reaction (1).

Reactions of Fluorenyl- (f) and Cyano-stabilized (g) Ylides

In the previously discussed examples, the Wittig reaction reported in Scheme 1 has been carried out using low nucleophilic ylides stabilized by the presence of carbonyl groups. It may be emphasized, however, that the stabilization of ylide compounds can be achieved by other groups with high possibility of delocalizing negative charges.

Two possible examples of these methods have been exploited in this paper, based on the use of fluorenyl ylide **f** stabilized by the presence of the polyaromatic group, and of the cyano ylide **g**.

In the first case, the formyl group-containing cyclophosphazene (**1**) was reacted with (fluorenyl)-triphenylphosphorane (**f**) leading to the derivative **7** in high hield (86%). The analytical and spectroscopic data of the yellow product **7** are reported in Table I. The overall reaction is complete in 24 h. As expected, no degradation products of the cyclophosphazene ring were observed, thus indicating that only aldehydic functions in compound **1** are involved in the process.

In the second example we reacted the cyclotriphosphazene **1** with cyanomethylenetriphenylphosphorane (**g**) at room temperature for 5 h. The product isolated at the end of this process was identified as the phosphazene derivative **8** having six cinnamonitrile groups as substituents on the basis of analytical data, IR, ^{1}H and ^{31}P NMR spectra (see Table I). The ^{1}H NMR spectrum of this product shows for the α-olefinic proton two sets of signals (each formed by two doublets of different intensity) due to the presence of both *cis*- and *trans*-unsaturated isomers and to their random distribution on the phosphazene phosphorus atoms. This arrangement is also confirmed by the ^{31}P NMR spectrum which exhibits four signals in the range δ 7.57–7.79.

Conclusions

In this paper we disclose a new general synthesis for the preparation of double bond-containing cyclophosphazenes, which is based on the use of the Wittig reaction between stabilized phosphonium ylides and phosphazene trimers bearing carbonyl functions.

As suitable material for this study we chose hexakis(4-formylphenoxy)cyclophosphazene (**1**), a trimer which possesses six aldehydic functions on the side substituents.

The trimers **2**–**8** obtained in these syntheses have been characterized by elemental analysis, IR, ^{1}H and ^{31}P NMR spectroscopy. They were identified as fully substituted symmetric trimers containing olefinic moieties in the substituents.

Although valuable in itself, since it allows the preparation of interesting new cyclophosphazenes, this synthetic method has to be considered only as a prelude for the successive extension of already settled synthetic procedures to the corresponding high molecular weight phosphazene macromolecules.

In fact, preliminary experiments performed on phosphazene copolymers containing 4-formylphenoxy and phenoxy moieties in different percentages, $[NP(OC_6H_4\text{-}p\text{-}CHO)_x(OC_6H_5)_{2-x}]_n$ showed that the preparative recipes above described for the cyclophosphazene **1** work equally well when used for these materials.

This work is in progress and will be reported in a forthcoming paper.

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