(Vinyloxy)fluorocyclotriphosphazenes

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Abstract

The reactions of the lithium enolate of acetaldehyde, $LiOCHCH_2$, with hexafluorocyclotriphosphazene, $N_3P_3F_6$, lead to the series of (vinyloxy)-fluorocyclotriphosphazene, $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ (n = 2–5). The ^1H NMR data show that throughout the entire series, the substituent is bound through the oxygen end of the ambidentate enolate. The reaction shows a reluctance to go past the trisubstituted stage and the fluorine atom in $N_3P_3F(OCH{=}CH_2)_5$ can not be removed even under forcing conditions. Evidence from the ^1H, ^{19}F and ^{31}P NMR spectra shows that a non-geminal pathway is exclusively followed. Differences in the reaction patterns with enolate anions followed by $N_3P_3F_6$ and $N_3P_3Cl_6$ are discussed.

Introduction

The reactions of enolate anions with halocyclotriphosphazenes occur exclusively at the oxygen end of the ambidentate nucleophile giving rise to (alkenoxy)-phosphazenes [1]. One of these materials, the mono-(vinyloxy)pentachlorotriphosphazene, $N_3P_3Cl_5OCH{=}CH_2$, has proven to be a valuable monomer for the synthesis of organofunctional phosphazene polymers [2]. Extensions of the enolate anion reaction have allowed for the preparation of a variety of derivatives of the type $N_3P_3Cl_4(X)OCR{=}CH_2$ (X = Cl; R = H, CH_3, C_6H_5; X = CH_3, R = H, CH_3, C_6H_5) [3]. The stereochemical course of the reaction of the enolate anion of acetaldehyde with $N_3P_3Cl_6$ has been investigated [4]. All possible positional and stereoisomers in the series $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1–6) have been detected by ^{31}P NMR spectroscopy. Although all the geminal isomers were detected, a predominantly non-geminal reaction pathway was observed. The non-geminal pattern is also observed in the reaction of aryloxides [5], alkoxides [6] and aryloxy steroid salts [7] with $N_3P_3Cl_6$. The corresponding fluorophosphazene reactions have received much less attention. Derivatives of $N_3P_3F_6$ include $N_3P_3F_5OR$ (R = CH_3, C_2H_5) [8], $N_3P_3F_5OCR{=}CH_2$ (R = H, C_6H_5) [1], $N_3P_3F_5OC(=CH_2)(CH_2)_4$ [1] and 2,4,6-$N_3P_3F_3(OCH_2C_3F_7)_3$ [9]. The reactions of $N_3P_3X_5N{=}P(C_6H_5)_3$ (X = Cl, F) with the methoxide anion have recently been investigated [10]. In this paper, we present the synthesis of the series of (vinyloxy)-fluorocyclotriphosphazenes, $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ (n = 2–5). The purpose for undertaking this investigation was to compare the reaction pathway followed by a specific oxygen base with $N_3P_3F_6$ and $N_3P_3Cl_6$ and to expand the range of available organofunctional phosphazenes.

Experimental

Hexachlorocyclotriphosphazene (Firestone Corp.) was converted to hexafluorocyclotriphosphazene ($N_3P_3F_6$) by a previously reported procedure [11]. n-Butyl lithium (1.6 M solution in hexane) was obtained from Aldrich. Tetrahydrofuran (THF) (Aldrich) was distilled from sodium-benzophenone ketyl. Hexanes (35–55 °C) and benzene** (Fisher) were distilled by standard procedures. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 MHz (^1H), 235.2 (^{19}F) and 101.2 MHz (^{31}P). Tetramethylsilane, Me_4Si (for ^1H NMR) and fluorotrichloromethane, $CFCl_3$ (for ^{19}F NMR) were used as internal references. For ^{31}P NMR, 85% H_3PO_4 was used as an external standard. Chemical shifts upfield to the reference are assigned a negative sign. ^{31}P NMR spectra were recorded under conditions of broad band decoupling. Mass spectra were determined on a Finnegan 4610 spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories.

Preparation of $N_3P_3F_4(OCH{=}CH_2)_2$

A solution of 40 ml (0.064 mol) of n-butyllithium was added to 80 ml of tetrahydrofuran in an apparatus

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**Benzene is a suspected carcinogen, use only in a well-ventilated hood.

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described elsewhere [12]. The resulting mixture was stirred for 16 hours at room temperature to allow for complete formation of the lithium enolate, $LiOCH=CH_2$, which was then added directly to 8.00 g (0.032 mol) of $N_3P_3F_6$ in 100 ml of THF at 0 °C. The reaction mixture was heated to reflux. After removal of solvent, the resulting oil was distilled (bp 45–48 °C at 0.10 mmHg) to yield 2.75 of crude product. A 2.00 g sample of this material was subject to flash chromatography using benzene/hexanes (1/4) as an eluent. A 1.38 g (20.0% of theory) sample of a water-white liquid was obtained. Attempts at chromatographic separation of isomers failed. *Anal.* Calcd. for $N_3P_3F_4O_2C_4H_6$: C, 16.17; H, 2.02; mol wt. 297. Found: C, 16.67; H, 1.94; mol. wt. 297 (mass spectrum).

Preparation of $N_3P_3F_3(OCH=CH_2)_3$ and $N_3P_3F_2(OCH=CH_2)_4$

The lithium enolate, prepared from 100 ml of n-butyllithium (0.160 mol), was added to 10.0 g of $N_3P_3F_6$ (0.04 mol) as described above. After removal of the solvent, the resulting oil was distilled (35–42 °C at 0.02 mmHg) to give 4.65 g of crude material. A 3.00 g sample of this oil was subject to flash chromatography, as described above, resulting in the isolation of two products: 1.06 g (12.8% of theory) of a water-white liquid which was identified as $N_3P_3F_3(OCH=CH_2)_3$ was obtained first. *Anal.* Calcd. for $N_3P_3F_3O_3C_6H_9$: C, 22.43; H, 2.80; mol. wt. 321. Found: C, 23.14; H, 2.68; mol. wt. 321 (mass spectrum). A second fraction containing 0.98 g (11.0% of theory) of a water-white liquid, which was identified as $N_3P_3F_2(OCH=CH_2)_4$, was also obtained. *Anal.* Calcd. for $N_3P_3F_2O_4C_8H_{12}$: C, 27.83; H, 3.48; mol. wt. 345. Found: C, 28.54; H, 3.52; mol. wt. 345 (mass spectrum). Attempts at chromatographic separation of isomers for the tris and tetrakis derivatives failed.

Preparation of $N_3P_3F(OCH=CH_2)_5$

The lithium enolate, prepared from 100 ml of n-butyllithium (0.16 mol), was added to 6.00 g (0.024 mol) of $N_3P_3F_6$ as described above. The oil remaining after removal of the solvent was distilled (bp 45–50 °C at 0.02 mmHg) to give 0.94 g of crude product. Chromatographic separation, as described above, gave primarily the tri- and tetrasubstituted materials $N_3P_3F_{6-n}(OCH=CH_2)_n$ (n = 3, 4) along with 0.24 g (2.7% of theory) of a water-white liquid which was identified as $N_3P_3F(OCH=CH_2)_5$. *Anal.* Calcd. for $N_3P_3FO_5C_{10}H_{15}$: mol. wt. 369. Found: Mol. wt. 369 (mass spectrum).

Attempted Preparation of $N_3P_3(OCH=CH_2)_6$ from $N_3P_3F_6$

Several reactions were carried out with up to 10 molar equivalents of the enolate anion and reaction times of up to 120 hours. The major product obtained with these reactions was the tetrakis derivative along with small amounts of the tris and pentakis derivatives.

Results and Discussion

Previous studies have shown that attack on the phosphorus atom in formation of the monosubstituted derivatives of $N_3P_3X_6$ (X = F [1], Cl [1, 3] and the entire series of $N_3P_3Cl_6$ [4] derivatives occurs at the oxygen end of the ambidentate enolate anion. These chemical precedents along with the close similarity of the ^1H NMR spectra of the series $N_3P_3F_{6-n}(OCH=CH_2)_n$ (n = 2–5) (Table I) to the previously reported [1] spectrum of $N_3P_3F_5(OCH=CH_2)$ indicates that the new materials reported in this study are (vinyloxy)fluorocyclotriphosphazenes.

TABLE I. ^1H NMR Chemical Shift Data for $N_3P_3F_{6-n}(OCH=CH_2)_n$ (n = 1–5).[a]

Compound	δ_{Ha}[b]	δ_{Hb}[b]	δ_{Hx}[b]
$N_3P_3F_5OCH=CH_2$[c]	5.13	4.85	6.48
$N_3P_3F_4(OCH=CH_2)_2$	5.09	4.80	6.48
$N_3P_3F_3(OCH=CH_2)_3$	5.06	4.77	6.49
$N_3P_3F_2(OCH=CH_2)_4$	5.06	4.73	6.51
	5.00	4.70	6.48
$N_3P_3F(OCH=CH_2)_5$	5.09	4.70	6.52
	4.97	4.65	6.48

[a] Chemical shifts in ppm from TMS. [b] Assignments are as follows: ≡POC=C(Ha)(Hx)(Hb). [c] Taken from ref. 1.

The ^{31}P NMR spectrum (Table II), of the products obtained at the stage of disubstitution, $N_3P_3F_4(OCH=CH_2)_2$, shows a large complex triplet, attributed to the $\equiv PF_2$ center, and a complex doublet, corresponding to the $\equiv PF(OCH=CH_2)$ centers. If a geminal isomer were present, a signal corresponding to a $\equiv P(OCH=CH_2)_2$ center would be observed in the high field region of the spectrum and would not possess a large, one bond phosphorus–fluorine coupling constant. No such signal was observed in the spectrum, thus, at the stage of distribution, the reaction proceeds exclusively by a non-geminal pathway. The ^{19}F NMR spectrum (Table II) shows two complex doublets corresponding to the $\equiv PF_2$ and $\equiv PF(OCH=CH_2)$ centers. The relative amounts of *cis* and *trans* isomers in $N_3P_3F_4(OCH=CH_2)_2$ is unclear. The triplet in the ^{31}P NMR spectrum is indicative of either a *trans* isomer or an equivalence of the $^1J_{PF}$ coupling constants in the $\equiv PF_2$ center since the two fluorine atoms in the $\equiv PF_2$ center are inequivalent

TABLE II. ^{31}P and ^{19}F NMR Data for $N_3P_3F_{6-n}(OCH{=}CH_2)_n$.[a]

Compound	$\equiv PF_2$ Centers			$\equiv PF(OCH{=}CH_2)$			$\equiv P(OCH{=}CH_2)_2$
	$\delta_{^{19}F}$	$\delta_{^{31}P}$	$^1J_{PF}$[b]	$\delta_{^{19}F}$	$\delta_{^{31}P}$	$^1J_{PF}$[b]	$\delta_{^{31}P}$
$N_3P_3F_5OCH{=}CH_2$[c]	−69.5	11.0	910.0	−65.6	11.2	887.7	
$N_3P_3F_4(OCH{=}CH_2)_2$	−69.9	10.3	919.8	−66.1	10.6	895.8	
$N_3P_3F_3(OCH{=}CH_2)_3$				−65.7	11.0	871.5	
$N_3P_3F_2(OCH{=}CH_2)_4$				−65.5	12.3	903.0	11.1
$N_3P_3F(OCH{=}CH_2)_5$				−65.2	12.2	916.6	11.1

[a]Chemical shifts in ppm; coupling constants in Hz. [b]Approximate values from complex spectra. [c]^{31}P data taken from ref. 1.

in the *cis* isomer. The Hx signals in the ^1H NMR spectrum show a doubling of lines over what is observed in $N_3P_3F_5OCH{=}CH_2$. This observation combined with the fact that nearly equal amounts of *cis* and *trans*-$N_3P_3Cl_4(OCH{=}CH_2)_2$ are obtained in the corresponding reaction with $N_3P_3Cl_6$ [4] suggests a *cis/trans*-$N_3P_3F_4(OCH{=}CH_2)_2$ mixture. The exclusive formation of non-geminal products in the $N_3P_3F_6$ reaction is in contrast to the $N_3P_3Cl_6$ reaction where a small amount of the geminal isomer is also observed [4].

In the trisubstituted derivative, $N_3P_3F_3(OCH{=}CH_2)_3$, the ^{31}P NMR spectrum (Table II) shows a complex doublet, which can be assigned to the $\equiv PF(OCH{=}CH_2)$ centers. No resonance is observed for either a $\equiv PF_2$ or a $\equiv P(OCH{=}CH_2)_2$ center, which would arise from a geminal (2,2,4-) substitution pattern. The ^{19}F spectrum (Table II) allows for verification of this observation, and shows only a complex fluorine resonance in the $\equiv PF(OCH{=}CH_2)$ region. For a geminal isomer to be present, a signal would be present in the $\equiv PF_2$ region of the spectrum. Thus, at the stage of trisubstitution, only the formation of the non-geminal isomers is observed. This is in contrast to the observation of the formation of both the geminal and non-geminal isomers in the corresponding reaction of $N_3P_3Cl_6$ leading to the trisubstituted derivative $N_3P_3Cl_3(OCH{=}CH_2)_3$ [4]. The complexity of the ^1H, ^{19}F and ^{31}P spectra suggest the existence of both *cis* and *trans*-$N_3P_3F_3(OCH{=}CH_2)_3$.

The ^{31}P spectrum (Table II) of the tetrakis derivative, $N_3P_3F_2(OCH{=}CH_2)_4$, shows two resonances, a complex doublet and complex smaller multiplet. The doublet arises from the $\equiv PF(OCH{=}CH_2)$ centers, while the small multiplet can be assigned to the $\equiv P(OCH{-}CH_2)_2$ center. If the geminal tetrakis isomer were present, a signal would occur which would correspond to a $\equiv PF_2$ center. No such signal is observed. The ^{19}F spectrum of the tetrakis derivative, $N_3P_3F_2(OCH{=}CH_2)_4$ (Table II), shows a complex doublet in the $\equiv PF(OCH{=}CH_2)$ range arising from the large phosphorus–fluorine coupling. A geminal isomer would show a signal corresponding to a $\equiv PF_2$ center. Since no such signal is seen, the trend which is observed for the lower members of the series is followed at the stage of tetrakis substitution, *i.e.*, non-geminal isomers are formed exclusively. The ^1H NMR spectrum of the tetrakis derivative, shows extra signals which are due to the presence of a $\equiv P(OCH{=}CH_2)_2$ center in the molecule.

The pentakis derivative, $N_3P_3F(OCH{=}CH_2)_5$, exhibits a large doublet and a small multiplet in the ^{31}P NMR spectrum (Table II). Both resonances exhibit extensive coupling and second order effects. The doublet arises from the single $\equiv PF(OCH{=}CH_2)$ resonance, while the singlet corresponds to the two $\equiv P(OCH{=}CH_2)_2$ centers. The spectrum may be more appropriately viewed as a second-order AB_2X system. The ^{19}F NMR (Table II) consists of a doublet with extensive second order effects. The structure of the molecule is confirmed by the ^1H NMR spectrum (Table I), which shows signals corresponding both to the $\equiv P(OCH{=}CH_2)_2$ and the $\equiv PF(OCH{=}CH_2)$ centers. Integration of these regions shows the relative abundance of 4:1 respectively, appropriate for the pentakis derivative.

It should be noted that all attempts to prepare the hexakis derivative, $N_3P_3(OCH{=}CH_2)_6$, were unsuccessful. Several reactions were carried out with a 10 molar equivalent of the enolate anion, and reaction times of up to 120 hours. The major product obtained with these reactions was the tetrakis derivative. Small amounts of tris and pentakis were also isolated.

The product distribution observed in the preparation of the vinylfluorocyclotriphosphazenes indicates that substitution occurs preferentially at a $\equiv PF_2$ rather than a $\equiv PF(OCH{=}CH_2)$ center. Evidence for this assertion is the complete absence of the geminal substitution pathway, the reluctance of the reaction to proceed past the trisubstituted stage and the inability to go past the pentasubstituted material. The decreasing reactivity at higher levels of substitution has been observed in other systems following a non-geminal pathway and has been ascribed to decreased electrophilicity of the phosphorus centers due to electron release to the ring from the substituent [13].

Non-geminal substitution is favored when the substitution is electron releasing relative to the halogen. The availability of the non-geminal pathway in the preparation of $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ [4] but not in $N_3P_3F_{6-n}(OCH{=}CH_2)_n$ can be related to the poor leaving group ability of the fluoride ion in phosphazene substitution reactions [14]. If the product distribution is kinetically controlled, then the low yield of geminal products in the chlorophosphazene reaction indicates a higher activation energy for the geminal pathway. The large energy associated with phosphorus–fluorine bond cleavage makes the formation of the geminal isomers energetically prohibitive in the fluorophosphazene reactions.

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