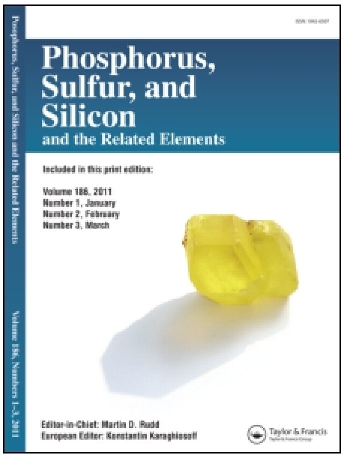

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Vinyloxycyclophosphazenes

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VINYLOXYCYCLOPHOSPHAZENES

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Abstract Numerous vinyloxyphosphazenes, $N_yP_yX_{2y-n}(OCH=CH_2)_n$ (y=3,4; X=Cl,F;n=1-2y) are available via reactions of the enolate anion of acetaldehyde with halocyclophosphazenes. We have now shown that the cis stereoisomer is the predominant species formed in many of these reactions. An electrostatic model has been proposed to account for this observation. The reaction of vinyloxyphosphazenes with other nucleophiles has been examined. Mixed vinyloxy/trifluoroethoxy derivative have been prepared. Studies involving ^{13}C nmr spectroscopy and vinyl addition polymerization show that the electron distribution in the vinyl group is strongly influenced by the electron donor ability of the geminal phosphazene substituent. The methacryloyl ethylenedioxy derivative, $N_3P_3Cl_5OCH_2CH_2OC(O)C(CH_3)=CH_2$, was prepared. This material undergoes a slow phosphazene-phosphazane rearrangement.

Compared to the numerous studies of the reactions of amines with cyclophosphazenes, few corresponding studies of the chemistry of organo oxyanions have been noted.[1] Systems receiving detailed examination include reactions of the chlorocyclophosphazenes, $(NPCl_2)_{3,4}$, with the phenoxide [2-4] p-cresoxide[2] and trifluoroethoxide ions [5,6]. In recent years, we have introduced a new class of cyclophosphazene derivatives derived from enolate anions.[7-10] The simplest nucleophile in the series, the enolate of acetaldehyde, has been studied in detail with derivatives of $(NPX_2)_3$ ($X=F$[9], Cl[8]) and $(NPCl_2)_4$[10] being reported. We have previously shown that the regio control in these

$$N_3P_3X_6 + nLiOCH{=}CH_2 \longrightarrow N_3P_3X_{6-n}(OCH{=}CH_2)_n$$

$$X=F,Cl; n=1-6$$

$$N_4P_4Cl_8 + nLiOCH{=}CH_2 \longrightarrow N_4P_4Cl_{8-n}(OCH{=}CH_2)_n$$

$$n=1,2$$

reactions ranges from predominately[8,10] to exclusively[9] non-geminal. In this paper, we wish to discuss the issue of stereochemical control of the reaction and the electronic interactions between the vinyloxy function and the phosphazene entity.

In the case of the trisubstituted derivative, $N_3P_3Cl_3(OCH{=}CH_2)_3$, the ^{31}P NMR spectrum unambiguously allows for identification of the cis (A_3) and trans (AB_2) isomers and a cis preference (over the ratio expected on a statistical basis) is observed.[10] In the case of the disubstituted chlorophosphazene moieties, the preparation of the dimethylamino derivatives, $N_3P_3(NMe_2)_4(OCH{=}CH_2)_2$ allowed for determination of the cis/trans ratio from ^1H and ^{31}P NMR spectroscopy and again a cis preference is observed. The dimethylaminolysis of $N_4P_4Cl_6(OCH{=}CH_2)_2$ did not give unambiguous results. If the pattern of the cis isomer having a greater downfield ^{31}P NMR shift which is observed in the vinyloxy[8], phenoxy[2,4] etc. system is preserved in the tetramer, then the cis isomer predominates in 2,4-$N_4P_4Cl_6(OCH{=}CH_2)_2$. The cis preference in these reactions is contrasteric and may be compared to the trifluoroethoxide system in which the trans isomer is heavily favored[5]. The model we have developed to rationalize the cis preference in arylcyclophosphazenes[11] is applicable to these systems. The cyclophosphazene unit exerts a strong electron withdrawing influence[12] on the bound vinyloxy substituent thereby allowing for a weak change transfer interaction between the bound and entering (electron rich) oxyanion leading to a cis preference. Similar interactions would be expected in the phenoxide and cresoxide systems where a cis preference is also observed[2-4]. We are conducting further tests of this hypothesis by preparing the mixed trifluoethoxide/vinyloxy derivatives, $N_3P_3Cl_4(OCH_2CF_3)(OCH{=}CH_2)$. In this system we observe a preponderance of one isomer of unknown (as yet), but presumably trans, stereochemistry.

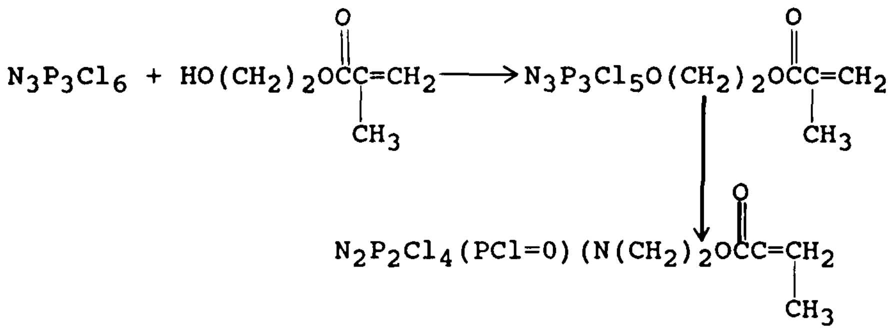
As noted above reactions of the remaining halogen atoms in the vinyloxyphosphazenes proceed in a facile manner. Using standard substitution reactions[1] a series of vinyloxyphosphazene derivatives, $N_3P_3R_5(OCH{=}CH_2)$ ($R{=}OCH_2CF_3$, OCH_3, NC_2H_4, $N(CH_3)_2$) were prepared and studied along with the previously known species, $N_3P_3X_5(OCH{=}CH_2)$ (X=F[9],Cl[8]) and $N_4P_4Cl_7(OCH{=}CH_2)$[10]. The ^{13}C NMR shifts of the β-vinyloxy carbon atom show a progressive upfield shift, indicating electron withdrawl from the vinyl group, on going from electron donor cosubstituents (amines) to electron withdrawing cosubstituents (halides). The corresponding ^{31}P NMR shifts for the $PR(OCH{=}CH_2)$ centers show a progressive downfield trend which exhibits an approximate linear correlation to the ^{13}C shifts. A reasonable model for these observations involves competition between the vinyl group and the phosphazene for vinyloxy oxygen atom electron denisty. As the cosubstituent donates electron density to the phosphazene, the vinyloxy oxygen atom donates electron density to the vinyl group making it a more electron rich species.

While the use of vinyloxyphosphazenes as monomers in olefin radical addition polymerization

$$N_3P_3X_5(OCH{=}CH_2) \xrightarrow[R\cdot]{} \underset{\displaystyle ON_3P_3X_5}{(\overset{}{C}HCH_2)_n}$$

has been a focus of our attention[13], the aspect of interest in this paper is how the polymerization behavior reflects the electronic effects measured in spectroscopic studies. We have observed that when the vinyloxy function is electron donating to the phosphazene, $N_3P_3R_5(OCH{=}CH_2)$ ($R{=}F,Cl,OCH_3,OCH_2CF_3$) facile polymerization occurs whereas electron rich olefins ($R{=}NR_2$) do not polymerize. This behavior is similar to organic monomers where electron rich species, such as vinyl ethers, do not undergo radical addition polymerization.

Given the intimate relationship between olefin electronic structure and the phosphazene, we decided to prepare vinyloxyphosphazenes where the vinyl group would be insulated from contact with the phosphorus centers. The reaction of $(NPCl_2)_3$ with hydroxyethylmethacrylate using pyridine as a base leads to the monosubstituted derivative.



Suprisingly, over a period of weeks, this material undergoes a phosphazene/phosphazane rearrangement. Freshly prepared samples of the monosubstituted oxyethylmethacrylate derivative undergo facile polymerization or copolymerization with methylmethacrylate either thermally, or with radical initiation. Reactivity ratio determinations in the copolymerization reaction indicate that the polarity of the vinyl group is significantly modified (relative to methylmethacrylate) by the presence of the phosphazene.

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