alkoxy,[33] vinyloxy,[34] and aryloxy[30,35] reagents can also be rationalized by the substituent effect model. The formation of the nongeminal derivative (**10**) by 2-methoxyethylamine may reflect steric crowding by the methyl group decreasing the ability for effective oxygen-phosphorus interaction.

Alternatively, the source of the observed geminal selectivity may lie in a decrease in the rate of nongeminal attack. The ratio of geminal vs. nongeminal rates is responsible for the increased amounts of geminal product with increasing steric bulk of primary amines.[2,3] The rate of geminal isomer formation, via a dissociative process, is roughly constant. The rate of nongeminal isomer formation, via an associative process, is very dependent on the steric effects of the incoming reagent; thus, as the rate of the nongeminal process becomes slower, the geminal process becomes competitive. In 2-haloethylamines, the source of the rate retardation is electronic, not steric. It has previously been suggested that only the steric effect of the entering amine is significant but the range of basicity is extended when 2-haloethylamines are considered; e.g. $pK_b(BrCH_2CH_2NH_2) = 8.9$ vs. $pK_b(HCH_2CH_2NH_2) = 10.6$.[37] Thus, the weaker entering nucleophile (assuming nucleophilicity follows basicity) would have a higher activation energy so the alternative (dissociative) mechanism would be dominant, leading to the geminal product. It should be noted that this model does not preclude the operation of the substituent effect (proposed above) in the dissociative process. As one goes to more polar solvents, the rates of associative reactions of amines with $N_3P_3Cl_6$ increase,[3,35,38] hence, the appearance of the nongeminal product. The basicity of 2-methoxyethylamine ($pK_b = 9.44$) is greater than that of the haloethylamines, and hence, the formation of the nongeminal product is observed.

Acknowledgment. This work was supported by a grant (CA 24543) from the National Cancer Institute.

Supplementary Material Available: Table S1, showing a GC study of the solvent dependence of the reaction of 2-chloroethylamine with $N_3P_3Cl_6$, and Table S2, showing major mass spectral fragments and their intensities (5 pages). Ordering information is given on any current masthead page.

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Organophosphazenes. 21. Synthesis of ((α-Methylethenyl)phenyl)fluorocyclotriphosphazenes[1]

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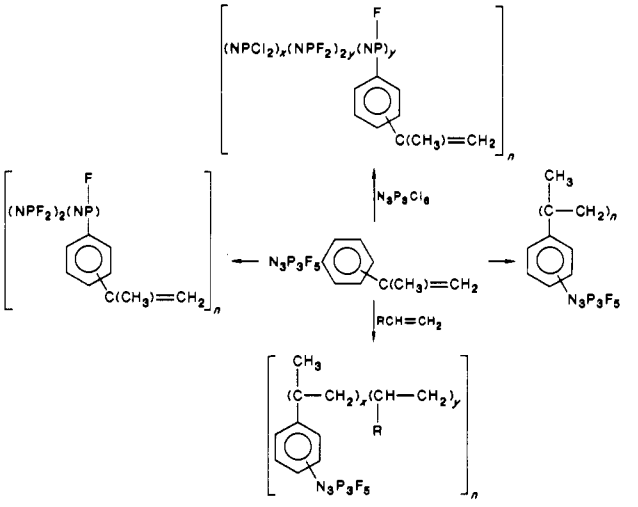
The reactions of (*m*-(α-methylethenyl)phenyl)- and (*p*-(α-methylethenyl)phenyl)lithium with hexafluorocyclotriphosphazene, $N_3P_3F_6$, lead to the formation of a series of ((α-methylethenyl)phenyl)fluorocyclotriphosphazenes, $N_3P_3F_{6-n}[C_6H_4C(CH_3)=CH_2]_n$ ($n = 1, 2$). At the bis stage of substitution both the geminal and non-geminal derivatives are obtained with the cis non-geminal species predominating. The cis to trans ratio is dependent on the position (meta vs. para) of the α-methylethenyl substituent on the phenyl ring. A model for the observed stereochemistry of the reaction is presented. The new compounds were characterized by mass spectrometry along with NMR (^1H, ^{13}C, ^{19}F, ^{31}P) and IR spectroscopy. Examination of the ^{13}C NMR spectra shows the modification in the phenyl charge distribution induced by the fluorophosphazene moiety.

Introduction

Organophosphazenes have become popular targets for synthesis in recent years[2-5] because of the inherent interest in this class of compounds and for more practical reasons, such as the development of new phosphazene monomers, which may be transformed into novel polymers.[3,4] Fundamental aspects of interest involve questions involving the factors that control the stereochemistry of the substitution reactions leading to organophosphazenes[2,6,7] and the synthesis of unique materials such as organometallic phosphazene derivatives.[4,5] Novel polymers from these monomers include polyphosphazenes with organic or organometallic substituents[4,8] and organic copolymers with cyclophosphazenes as substituents.[3] Monomers for this latter type of polymer have been olefinic phosphazenes. The high polarity of the olefin induced by the cyclophosphazene[9-11] has caused some difficulties in the

Scheme I



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polymerization process.[12] One approach to the successful reduction of olefinic polarity in these systems, which we have reported, is the introduction of an electron-donating function on the olefin to counterbalance the electron-withdrawing effect of the phosphazene.[7,13] An alternative approach to the problem of phosphazene-induced polarity is the introduction of an insulating function between the phosphazenes and the olefin. In this paper, we present the synthesis of α-methylethenyl phosphazenes with a phenyl group between the phosphorus and olefinic centers, i.e. phosphazene derivatives of α-methylstyrene. These materials can be potentially polymerized or copolymerized by two different routes as shown in Scheme I. The phosphazene ring processes would lead to linear phosphazene polymers while addition polymerization of the olefinic center would lead to carbon-chain polymers with the cyclophosphazene as a substituent. The addition copolymerization of α-methylethenyl pentafluorocyclotriphosphazenes with certain olefinic comonomers has been studied and will be reported in a subsequent publication.

Experimental Section

Materials and Methods. Hexafluorocyclotriphosphazene, $N_3P_3F_6$ (**1**),[14] obtained from hexachlorocyclotriphosphazene (Firestone Corp.), and both *m*- and *p*-bromo-α-methylstyrene,[15] (α-methylethenyl)phenyl bromide, were produced according to previously published procedures. *n*-Butyllithium (1.55 M in hexanes, Aldrich) was used as received. Diethyl ether was distilled from sodium/benzophenone, while petroleum ether (bp 30–60 °C) was distilled from sodium ribbon and stored over molecular sieves. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM 250 spectrometer operating at 250.1 (^{1}H), 62.9 (^{13}C), 235.2 (^{19}F), and 101.2 (^{31}P) MHz. Tetramethylsilane (^{1}H and ^{13}C) and hexafluorobenzene (^{19}F) were used as internal standards, while 85% H_3PO_4 (^{31}P) was employed as an external reference. Infrared spectra were obtained as thin films (NaCl disks) on a Nicolet 6000 series spectrophotometer. Mass spectra and GC mass spectra were recorded on a Finnigan 4610 spectrometer operating at 70 eV and equipped with a 30-m capillary column coated with SE-30. Other GC experiments were conducted on a Hewlett-Packard 5700A instrument equipped with a Chromasorb W (SE-30) column. Elemental analyses were conducted by Robertson Laboratory, Inc.

All reactions were performed in an anhydrous environment under a stream of N_2, and the reaction mixtures were magnetically stirred. Syringe techniques were used to transfer reagents where applicable.

Preparation of $N_3P_3F_5(C_6H_4$-*p*-$C(CH_3)=CH_2)$ (2). A previously described air-sensitive-reagent reaction vessel[16] was charged with 50 mL of diethyl ether and 37.3 mL (1.55 M, 0.0578 mol) of *n*-butyllithium in hexanes and cooled to 0 °C. A solution of 10.05 g (0.051 mol) of *p*-bromo-α-methylstyrene in 150 mL of diethyl ether was then added slowly to the butyllithium solution. The mixture was allowed to stir an additional 2 h after all the reagent had been added. The lithiated α-methylstyrene was then transferred dropwise to a solution of 12.70 g (0.051 mol) of $N_3P_3F_6$ (**1**) in 200 mL of diethyl ether at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. After removal of the solvent, petroleum ether was added to precipitate the lithium salts, which were subsequently removed by filtration through diatomaceous earth. The petroleum ether was then removed to give a yellowish oil, which, upon distillation, gave 9.72 g (54.9% of theory) of a clear liquid (bp 50–52 °C (0.02 mmHg)). Anal. Calcd for $C_9H_9N_3P_3F_5$: C, 31.14; H, 2.61; mol wt, 347. Found: C, 30.85; H, 2.75; mol wt, 347 (mass spectrum).[17] ^{1}H NMR:[18] δ_{CH_3} 2.16 (s, 3 H); δ_{H_a} 5.22 (s, 1 H); δ_{H_b} 5.45 (s, 1 H); $\delta_{H_{o,m}}$ 7.83 (d of d, 2 H), J_{HH} = 8.3, $^3J_{PH}$ = 15.9; δ_{H_m} 7.58 (d of d, 2 H), $^1J_{HH}$ = 8.3, $^4J_{PH}$ = 4.7. ^{13}C NMR:[19] δ_{C_1} 125.20, J_{PC} = 210; δ_{C_2} = 130.96, $^2J_{PC}$ = 12.9; δ_{C_3} 126.21, $^3J_{PC}$ = 18.3; δ_{C_4} 147.56, $^4J_{PC}$ = 3.3; δ_{C_5} 142.38; δ_{C_6} 115.86; δ_{C_7} 21.50. ^{19}F NMR: δ_{PFR} −54.99, $^1J_{FP}$ = 986; $\delta_{PF_2,cis}$ −69.96, $^1J_{FP}$ = 916; $\delta_{PF_2,trans}$ −71.97, $^1J_{FP}$ = 904. ^{31}P NMR: δ_{PFR} 35.44, $^1J_{PF}$ = 985, $^2J_{PP}$ = 78.1, $^3J_{PF}$ = 19.5; δ_{PF_2} 9.25, $^1J_{PF}$ = 913, $^2J_{PP}$ = 78.1. IR:[20] 1630 (m, $\nu_{C=C}$), 1603 (m, $\nu_{c=c}$), 1268 (vs, $\nu_{P=N}$), 945 (s, $\nu_{PF,asym}$), 835 (s, $\nu_{PF,sym}$).

Preparation of $N_3P_3F_5(C_6H_4$-*m*-$C(CH_3)=CH_2)$ (3). The preparation was allowed to proceed as above with the exception that *m*-bromo-α-methylstyrene was used in place of *p*-bromo-α-methylstyrene. In a typical experiment the following quantities of materials were used: *m*-bromo-α-methylstyrene, 12.84 g (0.0652 mol) in 200 mL of diethylether; *n*-butyllithium, 48.1 mL (1.55 M in hexanes, 0.0720 mol); **1**, 16.30 g (0.0655 mol) in 200 mL of diethyl ether. The resulting oil was distilled to give 11.23 g (49.6% of theory) of a clear liquid (bp 75–77 °C (0.04 mmHg)). Anal. Calcd for $C_9H_9N_3P_3F_5$: C, 31.14; H, 2.61; mol wt, 347. Found: C, 31.47; H, 2.70; mol wt, 347 (mass spectrum).[17] ^{1}H NMR:[18] δ_{CH_3} 2.18 (s, 3 H); δ_{H_a} 5.21 (s, 1 H); δ_{H_b} 5.44 (s, 1 H); δ_{H_o} 7.80 (m, 1 H), $^3J_{PH}$ = 17.4; $\delta_{H_{o'}}$ 7.95 (m, 1 H), $^3J_{PH}$ = 15.9; δ_{H_m} 7.51 (m, 1 H); δ_{H_p} 7.77 (m, 1 H). ^{13}C NMR:[21] δ_{C_1} 126.86, $^1J_{PC}$ = 205; δ_{C_2} 127.64, $^2J_{PC}$ = 13.0; $\delta_{C_{2'}}$ 129.43, $^2J_{PC}$ = 12.6; δ_{C_3} 142.60, $^3J_{PC}$ = 16.7; $\delta_{C_{3'}}$ 129.13, $^3J_{PC}$ = 18.2; δ_{C_4} 131.44, $^4J_{PC}$ = 3.1; δ_{C_5} 142.10; δ_{C_6} 114.80; δ_{C_7} 21.64. ^{19}F NMR: δ_{PFR} −55.12, $^1J_{FP}$ = 941; $\delta_{PF_2,cis}$ −69.93, $^1J_{FP}$ = 905; $\delta_{PF_2,trans}$ −71.99, $^1J_{FP}$ = 905. ^{31}P NMR: δ_{PF_2} 9.31, $^1J_{PF}$ = 909, $^2J_{PP}$ = 76.9; δ_{PFR} 35.58, $^1J_{PF}$ = 989, $^2J_{PP}$ = 76.9, $^3J_{PF}$ = 19.5. IR:[20] 1632 (m, $\nu_{C=C}$), 1607 (m, $\nu_{C=C}$), 1270 (vs, $\nu_{P=N}$), 943 (s, $\nu_{PF,asym}$), 837 (s, $\nu_{PF,sym}$).

Preparation of $N_3P_3F_4(C_6H_4$-*p*-$C(CH_3)=CH_2)_2$ (4). The preparation was allowed to proceed as above, except that 2-equiv amounts of *n*-butyllithium and *p*-bromo-α-methylstyrene are employed. In a typical experiment, the following quantities were used: *p*-bromo-α-methylstyrene, 9.85 g (0.0500 mol) in 200 mL of Et_2O; *n*-butyllithium, 35.5 mL (1.55 M in hexanes, 0.055 mol); **1**, 6.23 g (0.0250 mol) in 200 mL of diethyl ether. After removal of the lithium salts, the oil was subjected to flash chromatography[22] (petroleum ether) to give 9.50 g (42.7% of theory) of a mixture of isomers. Anal. Calcd for $C_{18}H_{18}N_3P_3F_4$: C, 48.55; H, 4.07; mol wt, 445. Found: C, 47.69; H, 4.13; mol wt, 445 (mass spectrum).[17] A gas chromatographic analysis of the mixture revealed the isomer ratio to be 1:6.1:1.5 for the geminal, cis, and trans isomers, respectively. Unfortunately, while the cis isomer could be recrystallized from a dilute heptane solution, the geminal and trans isomers resisted further separation. The melting point of the cis isomer was 104.0–105.1 °C. Anal. Calcd for $C_{18}H_{18}N_3P_3F_4$: C, 48.55; H, 4.07; mol wt, 445. Found: C, 48.13; H, 4.20; mol wt, 445 (mass spectrum).[17] ^{1}H NMR (mixture of isomers):[18] δ_{CH_3} 2.13–2.16; δ_{H_a} 5.17–5.22; δ_{H_b} 5.42–5.47; $\delta_{H_{ar}}$ 7.51–7.95. ^{1}H NMR (*cis*-**4**):[18] δ_{CH_3} 2.16 (s, 3 H); δ_{H_a} 5.22 (s, 1 H); δ_{H_b} 5.46 (s, 1 H); δ_{H_o} 7.85 (d of d, 2 H), J_{HH} = 8.3, $^3J_{PH}$ = 15.5; δ_{H_m} 7.58 (d of d, 2 H), $^1J_{HH}$ = 8.3, $^3J_{PH}$ = 4.2. ^{19}F NMR (*cis*-**4**): δ_{PFR} −52.39, $^1J_{FP}$ = 984; $\delta_{PF_2,cis}$ −68.17, $^1J_{FP}$ = 920, $^2J_{FF}$ = 77.5; $\delta_{PF_2,trans}$ −71.71, $^1J_{FP}$ = 899, $^2J_{FF}$ = 77.5, $^3J_{FP}$ = 18.8, $^4J_{FF}$ = 12.1. ^{31}P NMR (*cis*-**4**): δ_{PF_2} 7.25, $^1J_{PF}$ = 919, $^2J_{PP}$ 61.1, $^3J_{PF}$ = 2.9; δ_{PFR} 33.50, $^1J_{PF}$ = 974, $^2J_{PP}$ = 61.1, $^3J_{PF}$ = 3.1. ^{19}F NMR (*trans*-**4**): δ_{PFR} −51.93, $^1J_{FP}$ = 986; δ_{PF_2} −70.43, $^1J_{FP}$ = 932. ^{31}P NMR (*trans*-**4**): δ_{PF_2} 6.03, $^1J_{PF}$ = 912, $^2J_{PP}$ = 68.8, $^3J_{PF}$ = 7.2; δ_{PFR} 33.67, $^1J_{PF}$ = 973, $^2J_{PP}$ = 68.8, $^3J_{PF}$ = 9.6. ^{19}F NMR (*gem*-**4**): δ_{PF_2} −70.44, $^1J_{FP}$ = 891. ^{31}P NMR (*gem*-**4**): δPF_2 8.30, $^1J_{PF}$ = 878, $^2J_{PP}$ = 52.0; δ_{PR_2} 26.35, $^2J_{PP}$ = 52.0, $^3J_{PF}$ = 6.3.

Preparation of $N_3P_3F_4(C_6H_4$-*m*-$C(CH_3)=CH_2)_2$ (5). This preparation was allowed to proceed as above with the exception that *m*-bromo-α-methylstyrene is used in place of the *p*-bromo analogue. In a typical experiment, the following quantities of reagents were used: *m*-bromo-α-methylstyrene, 7.88 g (0.040 mol) in 200 mL of diethyl ether; *n*-butyllithium, 36.0 mL (1.23 M in hexanes, 0.0443 mol); and **1**, 5.00 g (0.0200 mol) in 200 mL of diethyl ether. The salt-free oil was purified via flash chromatography (petroleum ether) to give 4.59 g (51.5% of theory) of a mixture of isomers. Anal. Calcd for $C_{18}H_{18}N_3P_3F_4$: C, 48.55; H, 4.07; mol wt, 445. Found: C, 47.24; H, 4.07; mol wt, 445

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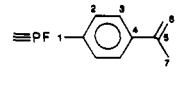
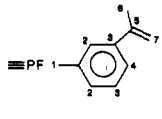
(17) Mass spectrometry data are available as supplementary material.
(18) All NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) coupling constants are in Hz. The positional designations, o, m, and p, are with respect to the phosphazene. H_a and H_b refer to the olefinic protons trans and cis to the phenyl ring, respectively.
(19) Numbers refer to



(20) In cm^{-1}.
(21) Numbers refer to



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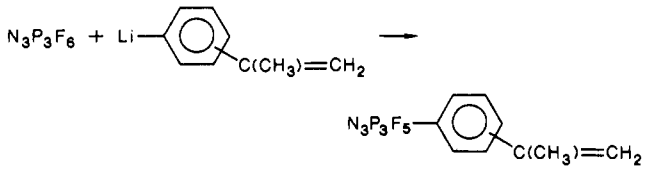
(mass spectrum).[17] Further preparative-level separation of the isomers could not be achieved. A gas chromatographic analysis of the mixture revealed the geminal to cis to trans ratio 1:2.8:1.1. ^{1}H NMR (mixture of isomers):[18] δ_{CH_3} 2.14–2.19; δ_{H_a} 5.16–5.20; δ_{H_b} 5.43–5.48; δ_{H_a} 7.41–8.02. ^{19}F NMR (*cis*-**5**): δ_{PFR} −52.73, $^1J_{FP}$ = 995; $\delta_{PF_2,cis}$ −68.50, $^1J_{FP}$ = 909; $\delta_{PF_2,trans}$ −72.01, $^1J_{FP}$ = 903. ^{31}P NMR (*cis*-**5**): δ_{PF_2} 7.29, $^1J_{PF}$ = 924, $^2J_{PP}$ = 62.6, $^3J_{PF}$ = 3.1; δ_{PFR} 33.64, $^1J_{PF}$ = 994, $^2J_{PP}$ = 62.6, $^3J_{PF}$ = 8.7. ^{19}F NMR (*trans*-**5**): δ_{PFR} −51.88, $^1J_{FP}$ = 989; δ_{PF_2} −70.67, $^1J_{FP}$ = 926. ^{31}P NMR (*trans*-**5**): δ_{PF_2} 5.42, $^1J_{PF}$ = 911, $^2J_{PP}$ = 67.6, $^3J_{PF}$ = 7.9; δ_{PFR} 33.64, $^1J_{PF}$ = 994, $^2J_{PP}$ = 67.6, $^3J_{PF}$ = 14.5. ^{19}F NMR (*gem*-**5**): δ_{PF_2} −70.51, $^1J_{PF}$ = 900. ^{31}P NMR (*gem*-**5**): δ_{PF_2} 8.48, $^1J_{PF}$ = 914, $^2J_{PP}$ = 58.4; δ_{PR_2} 26.69, $^2J_{PP}$ = 58.4, $^3J_{PF}$ = 11.68. IR (mixture of isomers):[20] 1631 (m, $\nu_{C=C}$), 1602 (m, $\nu_{C=C}$), 1246 (vs, $\nu_{P=N}$), 925 (s, $\nu_{PF,sym}$).

Results and Discussion

The reaction of hexafluorocyclotriphosphazene, $N_3P_3F_6$ (**1**), with either *m*- or *p*-lithio-α-methylstyrene produces the corresponding ((α-methylethenyl)phenyl)pentafluorocyclotriphosphazenes in good yield:

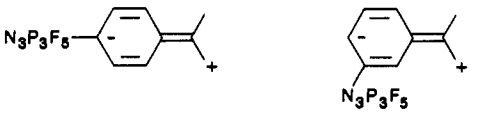


2, para isomer
3, meta isomer

The compounds are clear, colorless liquids that are easily purified via distillation at reduced presure. They were characterized by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy as well as infrared spectroscopy, mass spectrometry, and elemental analysis.

The ^{1}H NMR spectra resemble those of the parent hydrocarbon with additional phosphorus–proton coupling present in the aromatic region. In both **2** and **3**, the proton chemical shifts appear downfield of α-methylstyrene, due to the strong electron-accepting nature of the fluorophosphazene unit.[9,10] The ^{31}P and ^{19}F NMR spectra confirm the assignment of a monosubstituted phosphazene by exhbiting resonances due to two $\equiv PF_2$ centers and one $\equiv PFR$ center. The magnitudes of the chemical shifts are consistent with those of previously reported aryl-substituted fluorophosphazenes.[23] Finally, the ^{13}C NMR data support the assignment of the substitution pattern about the phenyl ring. The carbon spectra of **2** and **3** display four and six aryl carbon resonances, respectively, which is consistent with the para and meta derivatives.

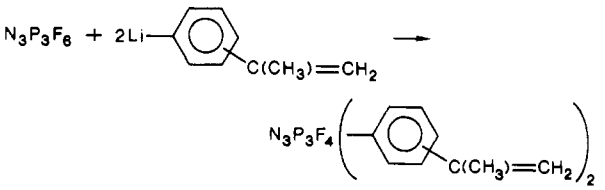
Some features of the ^{13}C NMR spectra bear further discussion. Previous aryl carbon chemical shifts for fluorophosphazene derivatives were assigned by assuming that J_{PC} decreases with an increase in the number of intervening bonds between the atoms in question.[10] However, by consideration of the spectrum of **3** and by use of selective decoupling techniques[24] it was found that $^3J_{PC} > {}^2J_{PC}$. The β-carbon chemical shift of the vinylidene carbon of styrene and α-methylstyrene derivatives has been used as a measure of the electronic perturbation induced by the substituent.[25] With use of this criterion, the $N_3P_3F_5$ moiety (δ_{C_β} 115.9) is comparable to the strongly electron-withdrawing nitro group (δ_{C_β} 115.8 for *p*-$NO_2C_6H_4C(CH_3)=CH_2$[26]). This is consistent with previous studies of the electron-withdrawing effect of the fluorophosphazenes.[9,10] Another feature of the ^{13}C NMR data of interest is the difference in β-carbon chemical shift (Δδ) between the meta (**3**) and para (**2**) isomers. The Δδ value (1.00 ppm) is midway between those of α-methylstyrenes with substituents that exhibit strong mesomeric interactions (e.g. NO_2) and those with substituents with no significant interaction (e.g. CF_3). This observation could be interpreted as showing a small to moderate conjugative ability of the posphazene unit. A similar suggestion was made by Harris et al. to rationalize NMR data of various arylphosphazenes.[11] Since a UV-photoelectron spectroscopy study of arylfluorophosphazenes indicates little or no phosphazene–aryl mesomeric interaction,[10] we prefer an alternative and simpler model to rationalize the ^{13}C data. If one considers the two canonical structures representing removal of electron density from the olefin (and hence the β-carbon atom) by the phenyl group



it is clear that electrostatic stabilization of the negative charge by the strongly electron-withdrawing $N_3P_3F_5$ moiety is favored for the para isomer (**3**). Thus, the electronic effect of the phosphazene is transmitted through the σ system.

The mass spectra of these new organophosphazenes are complex and are dominated by ions generated from the organic moieties. However, a few salient features can be extracted. The base peak in the spectra of **2** and **3** is the molecular ion. The predominant fragmentation mode involves cleavage of the exocyclic group, leaving the phosphazene intact, which may be contrasted with the case for phenylfluorophosphazenes, where aryl migration to a nitrogen atom and formation of linear phosphazene ions is observed.[27] The relative intensities are similar in both isomers except that the intensity for loss of C_3H_5 is 5 times greater in **3** than in **2**. This may be ascribed to the steric repulsion between the propenyl moiety and the phosphazene ring. Substitution in the meta position brings the propenyl residue into closer contact with both the geminal fluorine atom and the two transannular fluorine atoms, thus leading to a steric destabilization of **3**.

If 2 equiv of lithio-α-methylstyrene is allowed to react with **1**, reasonable yields of the bis derivatives may be isolated:



4, para isomer: **a**, geminal; **b**, cis; **c**, trans
5, meta isomer: **a**, geminal; **b**, cis; **c**, trans

While all three possible isomers of **4** and **5** were present in the crude reaction mixtures, only the *cis*-bis(*p*-α-methylstyryl)phosphazene **4b** could be isolated in the pure state. The presence of the other isomers was confirmed by GC, GC–mass spectrometry, and NMR spectroscopy. The ^{1}H and ^{13}C spectra of the mixtures were not particularly helpful in this regard as they consist of numerous overlapping multiplets. However, the ^{31}P NMR spectra are definitive. The trans isomer gives rise to a downfield second-order doublet and an upfield first-order triplet from the $\equiv PFR$ and $\equiv PF_2$ centers, respectively. In the case of the cis isomer, the spectrum contains the downfield doublet but the upfield triplet is now transformed into a doublet of doublets since the two fluorine atoms of the $\equiv PF_2$ center are no longer equivalent. The geminal isomer is readily identified by the pressure of a relatively small triplet arising from the $\equiv PR_2$ phosphorus atom interacting with the two equivalent $\equiv PF_2$ centers. The ^{19}F NMR data corroborate the existence of all three isomers in the reaction mixture. The spectra of the cis, trans, and geminal isomers contain three, two, and one unique fluorine resonance, respectively.

The ^{31}P and ^{19}F NMR spectra of the mixtures of isomers in both **4** and **5** show that the cis non-geminal isomers, **4b** and **5b**, are the major components in each case. A quantitative measure of the individual amounts of each isomer was obtained via GC and GC–mass spectrometry. Comparison of the gas chromato-

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(24) Only one proton was irradiated while the carbon atom was accumulated; as a result, the resonance of the carbon atom attached to the irradiated proton will remain a doublet due to phosphorus–carbon coupling while all the other carbon resonances will collapse into complex multiplets due to carbon–hydrogen coupling. Thus, if the proton assignments are known, each carbon atom may be correctly identified.
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gram of **4b** with that of the mixture of isomers of **4** confirmed the cis isomer as the major constituent. The GC–mass spectrometry analysis of **5** shows the expected three components with the largest GC peak assigned to (on the basis of the ^{31}P NMR spectrum) the cis isomer, **5b**. The first eluted compound shows a major fragmentation route involving cleavage of the aryl–phosphazene bond. This behavior is typical of a geminal isomer[27] and so allows assignment of **5a**. Geminal phosphazene isomers generally have the smallest GC retention times. The non-geminal isomers **5b** and **5c** show the expected fragmentation patterns[27] with formation of linear phosphazene ions being an important feature. The intensities of the peaks assigned to the cis isomer are greater than those of the trans isomer. This is in agreement with the behavior of phenyl fluorocyclotriphosphazenes,[27] thus adding addition evidence to the GC peak assignments. The isomer ratio (from GC) for **5a**:**5b**:**5c** is 1:2.8:1.1. The GC–mass spectrometry analysis of **4** shows the gen (**a**):cis (**4b**):trans (**4c**) ratio to be 1:6.1:1.5. A curious feature of the mass spectrum of the geminal, **4a**, isomer is the importance of the loss of a propenyl group and the formation of linear ions becoming competitive with phosphazene–aryl cleavage. The reason for the selective cleavage of the propenyl group in this case is unclear, but once it is severed from the aryl ring, there will be a more pronounced positive charge on that ring and it will be more likely to migrate to the adjacent ring nitrogen atom and eliminate as an aryl nitrene, a process which ultimately produces the linear phosphazene fragment seen in the mass spectrum.[27]

The observed substitution pattern for reactions of lithio-α-methylstyrenes with **1** is similar to that of the corresponding phenyllithium reaction;[23] i.e., regio- and stereoisomers are observed with non-geminal regioselectivity and cis stereoselectivity being observed. We have previously shown[6] that steric effects are reasonable for the formation of non-geminal, as opposed to the expected[2,7] geminal, products in the reactions of organolithium reagents with **1**. Further evidence for the importance of steric effects is found in the cis:trans ratio for the para vs. meta (**5a**,**b**) α-methylstyrene derivatives. The cis selectivity is significantly reduced with the propenyl substituent in the meta position, where it might be expeected to experience significant transannular repulsions with another substituent in a cis configuration. The question of the cis preference in these reactions is an interesting one. If only steric effects were involved, then one would expepect a strong trans preference, as is shown in the reactions of *tert*-butyllithium with **1**.[6] We believe the observed cis preference is due to an electrostatic interaction of the electron-deficient aryl substituent on the phosphazene ring[9,10] and the electron-rich incoming organolithium reagent. This interaction favors approach of the incoming reagent on the same side of the ring as the aryl substituent, which is in place, thus leading to the formation of the cis isomer. The fact that an approximately 1:1 cis:trans ratio is observed in the formation of (*p*-(dimetylamino)phenyl)tetrafluorocyclotriphosphazenes[28] is related to the exceptionally strong electron-donating ability of the dimethylamino group. The transfer of electron density from the dimethylamino group to the phenyl ring reduces the electron-deficient nature of the aryl groups, and hence, less electrostatic attraction with the incoming reagent occurs.

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Supplementary Material Available: Table I (major mass spectral fragments and their relative intensities) (3 pages). Ordering information is given on any current masthead page.

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Kinetic and Isotopic Studies on the Reaction between Trioxodinitrate and the Hexaammineruthenium(III) Cation

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The reaction between trioxodinitrate and the hexaammineruthenium(III) cation has been studied over the pH range 4.7–13.4. The products are nitrite, N_2O, NO, and a trace of N_2. Isotopic-labeling experiments confirm that the major source of the gaseous products is the N-1 nitrogen atom in trioxodinitrate, with a small contribution from the N-2 (two-oxygen-containing) position. The reaction is first order in both ruthenium complex and in trioxodinitrate. The rate exhibits a maximum at about pH 11.2, with a second-order rate constant $k_2 = 45.8\ M^{-1}\ s^{-1}$ at 2 °C. Variation of rate constant with pH allows the determination of pK_a values of 9.25 and 13.20 for $HN_2O_3^-$ and $Ru(NH_3)_6^{3+}$, respectively, in good agreement with literature values. The kinetic data are consistent with pathways involving $N_2O_3^{2-}$ and $Ru(NH_3)_6^{3+}$ as reactive species, or $HN_2O_3^-$ and $Ru(NH_3)_5(NH_2)^{2+}$. The latter alternative leads to an unreasonably high value of the second-order rate constant ($k_2' = k_2K_a(HN_2O_3^-)/K_a(Ru) = 2.5 \times 10^5\ M^{-1}\ s^{-1}$), however, and is considered unlikely.

Aspects of the solution chemistry of trioxodinitrate have been clarified in recent years. These include the mechanism of self-decomposition[2,3] and the stabilization of the $HN_2O_3^-$ ion by added nitrite.[4,5] The decomposition in the range pH ≥4 occurs by cleavage of the N–N bond in the monoprotonated anion $HN_2O_3^-$, with formation of nitrosyl hydride (HNO) and nitrite, followed by rapid dimerization of HNO to yield N_2O. A recent proposal that the primary products are HNO_2^- and NO, rather than HNO and NO_2^-,[6] has been subjected to a direct experimental test and disproven.[7] Under more acidic conditions (pH <3) decomposition occurs by a nitrous acid catalyzed free-radical process to yield NO exclusively.

We now describe the previously unreported reaction between trioxodinitrate and hexaammineruthenium(III) trichloride over the pH range 4.7–13.4. Our interest in this reaction arose from studies of the reaction of the nitrosylpentaammineruthenium(II)

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