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The Mechanism of a Phosphazene-Phosphazane Rearrangement.

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ABSTRACT

The phosphazene-phosphazane rearrangement of $N_3P_3Cl_5O(CH_2)_2OC(=O)CMe=CH_2$ (**8**)has been examined in detail using one and two dimensional NMR (^{31}P, ^{1}H) spectroscopy and mass spectrometry. The mixed phosphazene-phosphazane $[NPCl_2]_2[N((CH_2)_2OC(=O)CMe=CH_2)P(O)Cl]$(**14**), $[NPCl_2]_2[NHP(O)Cl]$ (**13**) and a two ring assembly $[NPCl_2]_2[NP(O\{(NPCl_2)_2(N((CH_2)_2OC(=O)CMe=CH_2)P(O)\}]$ (**15**) have all been detected in the product mixture. The rate of the rearrangement has been measured at five temperatures by ^{31}P and ^{1}H NMR. The reaction is first order in **8** ($T_{1/2}$ at 111^0 is 4.65 hours). The activation enthalpy is positive and the activation entropy is negative. A mechanism involving competing intra and inter molecular processes which fits the product distribution and kinetic data has been proposed. Several other methyacrylphosphazenes were examined under the same thermolysis conditions. The rearrangement was observed and the rates obtained in cases where the $(CH_2)_2$ spacer unit of the methacrylate was replaced by linear and branched propyl units. The rearrangement was not observed when the methacrylate was appended to a spirocyclic unit, the spacer unit was extended to the n-butyl group and when the methacrylate unit was replaced by a methoxy group. These results are all consistent with the proposed mechanism. This investigation resolves conflicting results previous reported for the rearrangement.

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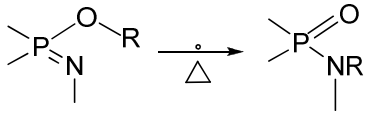
INTRODUCTION

The phosphazene-phosphazane rearrangement is a process in which the formal double bond in a phosphazene unit rearranges to a formal phosphorus-nitrogen single bond (phosphazane) accompanied by the migration of a hydrogen atom or alkyl group from a POR center to the phosphazene nitrogen atom leaving formal phosphorus–oxygen double bond. [1-6] This process has been known for



a long time and plays an important role in cyclo- and polyphosphazes[3] but a full understanding of the mechanism by which the process occurs has yet to be presented. The simplest system in the cyclophosphazenes is in the degradative hydrolysis of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**)(Scheme 1), where the rearrangement of the hydroxyphosphazene(**2)** eventually leads to

-Insert Scheme 1-

trimetaphosphinic acid, $[NHP(O)OH]_3$(**3)**.[2,7-9] Semi empirical calculations confirm the energetically favorable nature of the hydrolysis rearrangement and suggest a proton stabilized by both the oxygen and nitrogen centers in the intermediate.[10] The hydrolytic rearrangement has also been studied by solid state NMR and the results reproduced by *ab initio* methods.[11] The most widely examined system has been $N_3P_3(OMe)_6$(**4)**[1-6,11,12] which undergoes the rearrangement in the distillation temperature range to give the cyclophosphazane (**5**). The process can be catalyzed by added alkyl halides.[3] Substituent exchange has been observed in the thermolysis of the $N_3P_3(OMe)_6/N_3P_3(OCD_3)_6$ mixture suggesting an intermolecular process.[13] The rearrangement occurs in the larger per methoxy substituted cyclophosphazenes, $[NP(OMe)_2]_n$ up to the hexamer.[13,14] The rearrangement of mixed substituent trimers such as 2,2-$N_3P_3R_2(OMe)_4$(**6**) leads to six membered rings with both phosphazene and phosphazane bonds(**7)**.[14,15] Certain of these have been examined by X-ray crystallography and the relative orientations of the phosphoryl and methoxy groups was established.[3,15,16] The fact that poly(dimethoxyphosphazene) also undergoes this rearrangement[12,17] has significant implications for the stability of poly(phosphazenes). The replacement of the methyl group with larger alkyl groups leads to decomposition in the thermolysis of $N_3P_3(OR)_6$ (R= Et,Pr).[14] Detailed investigations of the alkoxy phosphazene-phosphazane rearrangement processes in mixed substituent, alkoxy and (p-methylphenoxy), derivatives have been reported.[14,15] An increase in the number of aryloxy groups or lengthening of the alkoxy chain leads to an increase in the temperature required for the rearrangement to occur. Evidence for both inter- and intramolecular pathways was obtained as was evidence that the first rearrangement in a molecule undergoing multiple rearrangements is the slowest step. [15] While there have been some kinetic studies, they have been on systems with a high impurity level. Furthermore, the order of the kinetics was not determined.[12] We have previously noted that a phosphazene-phosphazane rearrangement may be occurring in attempts to purify the monomer, $N_3P_3Cl_5O(CH_2)_2OC(=O)CMe=CH_2$(**8**) by distillation.[18,19] If this were to be the case, this would be a system with only one opportunity for the rearrangement and would be an excellent candidate for a detailed product and kinetic analysis allowing for a detailed understanding of the phosphazene-phosphazane rearrangement. This study is reported in this paper.

EXPERIMENTAL SECTION

Materials and Methods. Organic compounds were purchased from Aldrich Chemical Company and used as delivered except where noted. Solvents such as anhydrous diethyl ether, hexanes, tetrahydrofuran, toluene, benzene and methylene chloride were purchased from J.T. Baker, Inc. THF and benzene were dried by distillation over potassium metal prior to use. 4-Hydroxybutyl methacrylate, hydroxypropyl methacrylate, and were purchased from Polysciences, Inc..
Hexachlorocyclotriphosphazene (**1**) was received from Nippon Soda Co. and was sublimed prior to use.

Spiro(2,3-dioxypropylmethacryl)tetrachlorocyclotriphosphazene(**9**) was prepared by a previously reported procedure.[20] Deuterated solvents ($CDCl_3$, C_6D_8, d_8-toluene, d_8-THF) were purchased from Cambridge Isotope Labs, Inc. and used as delivered except where noted.

NMR spectra were acquired on a Bruker ARX-500 spectrometer equipped with an Aspect Station Computer. Data work-up was done using Bruker UXNMR software running under the UNIX/X11 operating system. Spectrometer operating frequencies were 500.13 MHz(^{1}H), 202.46 MHz(^{31}P), and 125.76 MHz(^{13}C). Tetramethylsilane was used as an internal reference for ^{1}H and ^{13}C spectra and 85% H_3PO_4 as an external reference for ^{31}P spectra. Broad band (Waltz16) ^{1}H decoupling was used for ^{13}C experiments. Gated decoupling experiments utilized standard Bruker parameter sets and pulse programs as did two dimensional experiments (COSY and HETCOR). Time domain data sizes for COSY experiments were adjusted as needed for adequate resolution and zero filling in the f_1 domain was used to square the frequency domain data matrix when necessary. NMR spectra were simulated using the UNEANMR[21] and WinDaisey[22] programs. Infrared spectra were recorded on a Perkin Elmer System 2000 FT-IR. Mass spectral analysis was done on a Finnigan 4610 spectrometer operating at ionization energy of 70 eV.

The rate of the rearrangement process was followed by ^{31}P and ^{1}H NMR spectroscopy. A 10.0mL volumetric flask was charged with 0.30g of (2-oxyethyl methacryl)pentachlorocyclotriphosphazene **(8**) and ~ 2mL of d_8-toluene and the phosphazene was dissolved. The flask was brought up to volume, sealed and the contents mixed. NMR tubes were loaded with ~ 1mL of the solution and the head space purged with dry nitrogen before sealing the cap. The tubes were placed in an immersion finger containing silicon oil which in turn was inserted into solvent in a three necked round bottom flask, equipped with a reflux condenser and a stopper in the remaining neck. The kinetic runs were accomplished by holding the sample at the reflux temperature of the solvent. The solvents employed were: toluene (111 ^{0}C), isopropyl acetate (89 ^{0}C), hexane (70 ^{0}C), cyclopentane (50 ^{0}C) and diethyl ether (35 ^{0}C). Samples were removed at timed intervals, cleaned of oil and analyzed by NMR. For each measurement, the probe was tuned matched and shimmed. The receiver gain was held constant so that the absolute value of the difference in integrations would accurately reflect concentration changes. The signals for the unreacted material were followed as a function of time to a point which was two to three times that of the reaction half-life. A series of samples were prepared with reduction of trace moisture. In these cases, ~ 2mL of dry benzene was added to the monomer and removed under vacuum three times in order to remove water as the benzene –water azeotrope. After the toluene solution was prepared, a few 3Å molecular sieves were added and the sample was allowed to sit for ~14 hrs. then ~1mL was transferred to a predried, evacuated NMR tube fitted with a septa/stopcock (Wilmad Glass Co.) and the headspace flushed with dry nitrogen.

Preparation of (2-oxyethyl methacryl)pentachlorocyclotriphosphazene (8). This synthesis is a modification of a previously reported procude.[15] Freshly distilled pyridine (7.0 mL, 0.087 moles) was added under an inert atmosphere to a solution of hexachlorocyclotriphosphazene (15.00 g, 0.043 moles) and p-methoxyphenol (~5 mg) in anhydrous diethyl ether (100 mL). A solution of hydroxyethyl-methacrylate (5.4 mL, 0.043 moles) in anhydrous diethyl ether (50 mL) was then added over 0.5 hour period to the phosphazene-pyridine solution. Stirring was started while adding the alcohol and was

continued for 48 hours at room temperature as the reaction was allowed to proceed. The reaction mixture was filtered to remove the pyridine hydrogen chloride and then washed sequentially with 2M HCl, saturated $NaHCO_3$ solution, and water. The ethereal solution was dried over $MgSO_4$ then filtered through a plug of Celite. The ether was removed by rotoevaporation to yield 17.80g of a white paste. Flash chromatography (20% diethyl ether in low boiling petroleum ether)of 2.50 g of the crude solid yielded 0.79 g of 5 (31%) as a pale yellow oil. Anal. Calcd. For $C_6H_9O_3N_3P_3Cl_5$: C, 16.33; H, 2.06; N, 9.52; mol wt 441.34. Found: C, 17.28; H, 2.29; N, 9.19; mol wt 442 (mass spec). ^{1}H NMR (d_8-toluene): δ_{Hc}6.28 (d of q, 1 H), $^2J_{HcHt}$=1.6, $^4J_{HcHMe}$=1.0; δ_{Ht} 5.40 (d of q, 1 H), $^4J_{HtHMe}$=1.6; δ_{Et}4.00 (m, 4 H); δ_{Me} 1.98 (d of d, 3 H). ^{13}C NMR ($CDCL_3$); $\delta_{carbonyl}$ 167.5; δ_{vinyl} 136.2; δ_{vinyl} 127.2; $\delta_{-CH2OP-}$67.5 (d), $^2J_{CP}$=6.54; $\delta_{-COCH2-}$62.9 (d), $^3J_{CP}$=9.31; δ_{Me} 18.8. ^{31}P NMR (d_8-toluene); δ_{PCl2} 24.2 (d), $^2J_{PP}$=63.9; δ_{POCl} 16.9 (t of t), $^3J_{PH}$=9.7. IR (neat); 2959 (m, CH str); 1725 (s, C=O Str); 1638 (m, C=C str); 1452, 1437 (M, CH_2 scsr); 1297 (vs, PN str); 1201, 1122 (vs, CO str); 1066, 1041 (vs, PO str); 876 (m, PCl asym); 752 (m, PCl sym).

Preparation of (3-oxypropyl methacryl)pentachlorocyclotriphosphazene (10). Under an inert atmosphere (N_2) freshly distilled pyridine (2.8 mL, 0.035 moles) was added to a diethyl ether (50 mL) solution of hexachlorocyclotriphosphazene (11.29 g, 0.032 moles) and p-methoxyphenol (~5 mg) standing over 4Å molecular sieves (~3 g). A solution of 3-hydroxypropyl methacrylate (3.16 g, 0.022 moles) in anhydrous diethyl ether (5 mL) was then added over 10 minute periods to the phosphazene-pyridine solution. Stirring was started while adding the alcohol and was continued for 72 hours as the reaction was allowed to proceed at room temperature. The reaction mixture was filtered to remove the pyridine hydrogen chloride and then washed sequentially with 2M HCl, saturated $NaHCO_3$ solution, and water. The ethereal solution was dried over $MgSO_4$ then filtered through a plug of Celite. The ether was removed by rotoevaporation to yield 11.01g of a white paste. Flash chromatography (25% diethyl ether in low boiling petroleum ether) of 2.67 g of the crude solid yielded 0.90 g of **6** (34%) as a pale yellow oil. Anal. Calcd. For $C_7H_{11}O_3N_3P_3Cl_5$: C, 18.64, H, 2.43; N, 9.23; mol wt 455.37. Found C, 18.42; H, 2.39; N, 9.19; mol wt 556 (mass spec). ^{1}H NMR (C_6D_6); δ_{Hc} 6.30 (d of q, 1 H), $^2J_{HcHt}$=1.6, $^4J_{HcHMe}$=0.8; δ_{Ht} 5.43 (d of q, 1 H), $^4J_{HtHMe}$=1.6, δ_{-OCH2-} 4.12 (t, 2 H), $^3J_{HH}$=6.0 ; δ_{-OCH2-} 4.04 (d of t, 2H), $^3J_{HH}$=6.3 ; $^3J_{HP}$=9.3; δ_{Me} 2.04 (d of d, 3 H); δ_{-CH2-} 1.69 (d of d of d, 2 H), $^4J_{HP}$=1.6. ^{13}C NMR (C_6D_6); $\delta_{carbonyl}$ 167.2; δ_{vinyl}137.3, δ_{vinyl} 126.1; $\delta_{-CH2OP-}$ 67.2 (d), $^2J_{CP}$=7.6; $\delta_{-COCH2-}$ 60.9; δ_{-CH2-} 29.6 (d), $^3J_{CP}$=9.2; δ_{Me} 19.0 ^{31}P NMR ($CDCL_3$); δ_{PCL2} 23.4 (d), $^2J_{PP}$=62.9; δ_{POCl} 15.8 (t of t), $^3J_{PH}$=9.3. IR(neat); 2965 (m, CH str); 1722(s, C=O str); 1639 (m, C=C str); 1470, 1453 (m, CH_2 scsr); 1297 (vs, PN str); 1202 (vs, CO str); 1042 (vs, PO str); 878 (m, PCl asym); 743 (m, PCl sym).

Preparation of (4-oxybutyl methacryl)pentachlorocyclotriphosphazene (11). Under an inert atmosphere (N_2) freshly distilled pyridine (1.8 mL, 0.023 moles) was added to a solution of hexachlorocyclotriphosphazene (7.68 g, 0.022 moles) and p-methoxyphenol (~5 mg) in anhydrous diethyl ether (50 mL). A solution of 4-hydroxybutyl methacrylate (3.37 g, 0.021 moles) in anhydrous diethyl ether (50 mL) was then added over 0.5 hour period to the phosphazene-pyridine solution. Stirring was started while adding the alcohol and continued for 68 hours at room temperature as the reaction proceeded. The reaction mixture was filtered to remove the pyridine hydrogen chloride and then washed sequentially with 2M HCl, saturated $NaHCO_3$ solution, and water. The solution was dried over $MgSO_4$ then filtered through a plug of Celite. The ether was removed by rotoevaporation to yield

9.63 g of an off white paste. Flash chromatography (25% diethyl ether in low boiling petroleum ether) of 2.53 g of the crude solid yielded 1.18 g of 7 (47%) as a clear viscous liquid. An attempt was made to vacuum distill the material too but it decomposed in the pot before pure compound could be collected. Anal. Calcd for $C_8H_{13}O_3N_3P_3Cl_5$: C, 20.47; H, 2.79; N, 8.95; mol wt 469.40. Found: C, 21.56; H, 2.81; N, 8.69; mol wt 470 (mass spec.). ^{1}H NMR (C_6D_6): δ_{Hc} 6.32 (d of q, 1 H), $^2J_{HcHt}$=1.8, $^4J_{HcHMe}$=0.9; δ_{Ht} 5.45 (d of q, 1 H),$^4J_{HtHMe}$=1.7; δ_{-OCH2-} 4.07 (t, 2 H), $^3J_{HH}$=6.1; $\delta_{-CH2OP-}$ 3.96 (d of t, 2H), $^3J_{HH}$=6.0, $^3J_{HP}$=9.4; δ_{Me}2.06 (d of d, 3 H); δ_{-CH2-} 1.49 (m, 4 H). ^{13}C NMR (C_6D_6); $\delta_{carbonyl}$ 167.4; δ_{vinyl} 137.5; δ_{vinyl} 125.8; $\delta_{-CH2OP-}$ 70.0 (d), $^3J_{CP}$=9.6; $\delta_{-COCH2CH2-}$ 25.4; δ_{Me} 19.0. ^{31}P NMR (C_6D_6); δ_{PCl2} 23.4 (d), $^2J_{PP}$=62.6, δ_{POCl} 15.7 (t of t). IR(neat); 2961 (m, CH str);1720 (s, C=O str); 1639 (m, C=C str); 1471, 1452, 1437 (m, CH_2 scsr); 1247 (vs, PN str); 1206 (vs, CO str); 1041 (vs, PO str); 876 (m, PCl asym); 764 (m, PCl sym).

Preparation of (2-(1-oxypropyl) methacryl)pentachlorocyclotriphosphazene (11a) and (1-(2-oxypropyl) methacryl)pentachlorocyclotriphosphazene (11b). Under an inert atmosphere (N_2) freshly distilled pyridine (5.9 mL, 0.073 moles) was added to a solution of hexachlorocyclotriphosphazene (10.12 g, 0.029 moles) and p-methoxyphenol (~5 mg) in anhydrous diethyl ether (40mL). A 4.15 g (0.029 mol) solution of hydroxypropyl methacrylate (a mixture of 30% 2-(1-hydroxypropyl)methacrylate and 70% 1-(2-hydroxypropyl)methacrylate) in anhydrous diethyl ether (10mL) was then added over 1.5 hour period to the phosphazene-pyridine solution. Stirring was started while adding the alcohol and was continued for 48 hours at room temperature as the reaction was allowed to proceed. The reaction mixture was filtered to remove the pyridine hydrogen chloride and then washed sequentially with 2M HCl, saturated $NaHCO_3$ solution, and water. The ethereal solution was dried over $MgSO_4$ then filtered through a plug of Celite. The ether was removed by rotoevaporation to yield 10.53 g of a white paste. Flash chromatography (22% diethyl ether in low boiling petroleum ether) of 2.52 g of the crude solid yielded 0.83 g of a mixture of 4a and 4b (33%) as a clear viscous liquid. Anal. Calcd for $C_7H_{11}O_3N_3P_3Cl_5$: C, 18.46; H, 2.43; N, 9.23; mol wt 455.37. Found: C, 19.98; H, 2.70; N, 8.99; mol wt 455 (mass spec.).

(2-(1-oxypropyl) methacryl)pentachlorocyclotriphosphazene (11a); ^{1}H NMR (C_6D_6): δ_{Hc} 6.35 (d of q), 1 H), $^2J_{HcHt}$=1.6, $^4J_{HCHMe}$= 1.0; δ_{Ht} 5.42 (d of q, 1 H), $^4J_{HtHMe}$= 1.6; δ_{CH} 5.16 (m, 1 H), $^3J_{HH(-CH2-)}$=3.4, 5.5, $^3J_{HHMe}$=6.5; δ_{-CH2-} 4.02 (m, 2 H), $^3J_{HP}$=9.2; δ_{Me} 2.03 (d of d, 3 H); δ_{Me} 1.12 (d, 3 H). ^{13}C NMR ($CDCl_3$); $\delta_{carbonyl}$ 167.1; δ_{vinyl} 137.1; δ_{vinyl} 126.6; $\delta_{-CH2OP-}$ 71.2 (d), $^2J_{CP}$=7.6, δ_{-COCH-} 68.9 (d), $^3J_{CP}$=9.6; $\delta_{-CH(CH3)-}$ 16.3; δ_{Me} 18.9. ^{31}P NMR(C_6D_6); δ_{PCl2} 23.6 (d), $^2J_{PP}$=63.8; δ_{POCl} 16.5 (t of t).

(1-(2-oxypropyl) methacryl)pentachlorocyclotriphosphazene (11b); ^{1}H NMR (C_6D_6); δ_{Hc} 6.41 (d of q, 1 H), $^2J_{HcHt}$=1.6, $^4J_{HcHMe}$=1.0, δ_{Ht} 5.46 (d of q, 1 H), $^4J_{HtHMe}$=1.6; δ_{CH} 4.82 (m, 1 H), $^3J_{HH(-CH2-)}$=6.5, $^3J_{HP}$=11.7; δ_{-CH2-} 4.08 (m, 2 H0; δ_{Me} 2.06 (d of d, 3 H); δ_{Me} 1.16 (d, 3 H). ^{13}C NMR (C_6D_6); $\delta_{carbonyl}$ 166.8; δ_{vinyl} 136.8; δ_{vinyl} 127.0; $\delta_{-CH2OP-}$ 77.4 (d), $^2J_{CP}$ = 8.0; $\delta_{-COCH2-}$ 66.9 (d), $^3J_{CP}$ = 7.2; $\delta_{-CH(CH3)-}$ 18.0, $^3J_{CP}$ = 7.2; $\delta_{-CH(CH3)-}$ 18.0, $^3J_{CP}$ = 3.2; δ_{Me} 18.9. ^{31}P NMR(C_6D_6); δ_{PCl2} 23.3 (d), $^2J_{PP}$ = 63.1; δ_{POCl} 14.8 (t of d of d), $^4J_{PH}$ =3.3.

Mixture of isomers; IR(neat); 2986 (m, CH str); 1724 (s, C+O str); 1639 (m, C=C str); 1452 (m, CH_2 scssr); 1247 (vs, PN str); 1203 (vs, CO str); 1042 (vs, PO str); 873 (m, PCL asym); 764 (m, PCl sym).

Preparation of (2-methoxy-1-oxyethyl)pentachlorocyclotriphosphazene(12). Under an inert atmosphere (N_2) methoxyethanol (5.6mL, 0.71mol) was added slowly to sodium metal in anhydrous

diethyl ether (50mL) and allowed to react until all of the metal was consumed. The resulting solution was added slowly to hexachlorocyclotriphosphazene (12.53g, 0.036mol) in anhydrous diethyl ether (125 mL) over 2.0 hours. After stirring for 12 hours at room temperature, the solution was washed sequentially with 2M HCl, saturated $NaHCO_3$ solution and water. The ethereal phase was dried over $MgSO_4$ and filtered through a plug of Celite. The ether was removed by rotoevaporation to yield 18.47g of a creamy white liquid. Flash chromatography (methylene chloride) of 2.52 g of the crude liquid yielded 1.67 g (66%) of **5** as a white solid (mp 30.5-31.5 ^{0}C) . Anal.calcd for $C_3H_7O_2N_3P_3Cl_5$: C,9.30;H,1.82; N, 10.85;mol wt 387.29. Found: c, 9.59;H, 1.71;N,10.82; mol wt 388 (mass spec.). ^{1}H NMR ($CDCl_3$): $\delta_{-CH2OP-}$ 4.32(m,2H), $^3J_{HP}$= 10.2; $\delta_{-COCH2-}$3.68(m,2H); δ_{Me} 3.419 S,3H). ^{13}C NMR (CDCl3: δ_{-OCH2-}71.0(d), $^3J_{CP}$= 9.0 ; $\delta_{-CH2OP-}$69.0(d), $^2J_{PC}$ 7.7, δ_{Me} 59.8. ^{31}P NMR: δ_{PCl2} 23.23(d), $^2J_{PP}$ 62.8; δ_{POCl} 16.2 (t of d). IR(neat): 2889(m,CH str);1451(m,CH_2 scsr); 1245(vs,PN str);1201(vs,CO str); 1051(vs,PO str); 891,875(m, PCl asym); 754(m, PCl sym).

RESULTS AND DISCUSSION

A series of methacrylcyclophosphophazens (Scheme 2) has been prepared for investigation of the rearrangement process proposed for **8**.[18] The identity of each was confirmed by NMR (^{1}H,^{13}C,^{31}P) and IR

-Insert Scheme 2-

spectroscopy and mass spectrometry. Elemental analyses deviated slightly from optimal values which is most like due to rearrangement and/or residual solvent from the purification procedure. The first step in understanding the rearrangement process was to identify the products of the thermolysis of **8**. The ^{31}P NMR spectra of **8** before and after heating at 111 ^{0}C for 10 hours are shown in Figure 1. The initial spectrum is the expected doublet and triplet arising from a mono substituted cyclophosphazene.

- Insert Figure 1 -

The sample was heated until there was no further change in the relative peak heights in the spectrum. The resulting spectrum showed evidence for several components. The combination of high hydrolytic sensitivity and polarity potentially made isolation of the products difficult, however they could be identified using NMR spectroscopy and mass spectrometry. A ^{31}P COSY spectrum (Figure S1) showed four components. The spectrum of **8** was easily identified from the starting material and the published NMR parameters. [15] The simplest spectrum (doublet, triplet) of the remaining products does not show any coupling from a CH_2 site and matches the known[7,8] spectrum reported for $(NPCl_2)_2P(O)NH$ (**13**). The spectra for the remaining two products, **14** and **15** are shown in Figures 2 and 3 respectively. Since precise measurements of the NMR parameters were complicated by signals arising from other components, the spectra were also simulated and the NMR data are reported in Table S.1.

-Insert Figure 2-

-Insert Figure 3-

Compound **14** was identified as the diphosphazene, 1-(N-ethylmethacryl)-2-oxo-2,44,4,6,6 – pentachlorocyclo-3,5-diphosphazene, obtained from the phosphazene-phosphazane rearrangement of **8.** The ^{31}P NMR spectrum shows three unique phosphorus centers. The chemical shift of the alkoxy center in **8** (16.9 ppm) is replaced by the phosphoryl center of **14** at -10.7 ppm. The PCl_2 centers are no longer equivalent (29.2 and 17.6 ppm). Identification of the high frequency center to the 6 position (adjacent to the substituted nitrogen center) was based on the observation of PH coupling from the methylene center attached to the nitrogen. Similar coupling is seen for the phosphoryl center. The J_{PP} values in **14** are noticeable lower than those observed in **8** due to the decreased s character at nitrogen upon going from a sp^2 nitrogen in **8** to a sp^3 nitrogen atom in **14.** The ^{13}C and ^{1}H NMR data (Table S.1.) are all consistent with the assignment of the structure of **14**. The ^{31}P NMR spectrum of 15 which shows five unique phosphorus centers suggested a multi ring assembly. The mass spectrum of the mixture shows a fragment at m/e of 735 and an isotope pattern from nine chlorine atoms. The connectivity of the phosphorus centers was established by the ^{31}P COSY spectrum. A comparison of Figures 2a and 3a shows a phosphazane unit in **15** which is equivalent to that in **14.** The phosphoryl center (Figure 3e) shows additional phosphorus coupling relative to that in **14**. The J_{PP} values for phosphorus atoms a, c and e are in the range noted for **14** while those for d and b are typical of phosphazenes. The chemical shifts for d and b are very similar to the previously reported values for $(N_3P_3Cl_5)_20$. [7] These data allow for assignment of **15** to the oxo bridged dimer shown in Figure 3. Examination of the ^{1}H NMR spectrum shows, in addition to the resonances arising from **8**,**14**and **15**, the spectrum of 2-chloroethylmethacrylate, CH_2=C(Me)C(O)O$(CH_2)_2$Cl (**16**) which was confirmed by comparison to an authentic sample of same and the observation of the parent ion (m/e 148) in the mixture mass spectrum. The concentration of **16** undergoes a significant increase in the late stages of the rearrangement.

The rearrangement process proceeds slowly enough that rates can be reliably measured by NMR spectroscopy. Changes in the intensities of both ^{31}P and ^{1}H NMR spectra of the same sample of **8** were recorded. A second set of ^{31}P NMR measurements on a sample of **8** that was not as rigorously dried were also obtained. The rates were followed at five temperatures (111^0, 89^0, 70^0, 50^0 and 35^0C) and always found to fit a first-order rate law. The data and the details of the kinetic fit analyses can be found in Tables S2, S3 and S4 for the ^{31}P "dry" sample, ^{31}P "wet "sample and ^{1}H respectively. The rate vs. temperature data was used to generate Eyring plots (Figure S2). The plots exhibited some curvature especially in the low temperature region so the 35^0C data was not used in the regression analysis. The curvature may be related to competing reactions (polymerization and/or hydrolysis) or the activation parameters may be temperature dependant.[23] The Eyring plot and calculations are found in Table S5. Half life and activation parameter data can be found in Table 1. The internal consistency of the ^{31}P and

-Insert Table 1-

^{1}H NMR data for the dry sample confirms the accuracy of the results. The parameter variation on going to the less rigorously dried sample demonstrates the importance of the solvent properties in the rearrangement process. The first order rate behavior and the negative entropy of activation indicate a dissociative process which somewhat counter intuitively goes to a more organized transition state. The endothermic enthalpy of activation is consistent with bond breaking in the transition state. A

mechanism which fits all of the kinetic data and the product distribution is shown in Scheme 3. The proposed first step involves formation of an intimate ion pair through a transition state where the developing carbocation is stabilized by an electrostatic interaction with the carbonyl oxygen.

-Scheme 3-

The increased structural organization generated by the carbocation stabilization contributes to the positive entropy of activation. In general formation of ions from a neutral species results in an entropic increase which is attributed to ordering of solvent around the developing ion.[24] This effect is more pronounced in low dielectric effect solvents such as toluene which is used in this study. The intimate ion pair intermediate consists of the well-known [7,8] oxyphosphazene anion and a dioxolane(dioxoenium) cation which is stabilized by allylic resonance of the positive charge. This type of carbocation has been observed in other systems [25] and is known to exist in acidic media. These carbocations have been implicated in other degradation processes [26]and can be formed by ring closure reactions.[27] There are two potential outcomes of the collapse of the intimate ion pair via reaction of the oxyphosphazene anion at the 4 position of the dioxolane (the position which leads to the thermodynamically stable products). If the attack is by the oxygen end of the ambident anion, the starting material, **8**, is regenerated. If the attack is by the nitrogen end then the phosphazane, **14** is obtained. If the ions diffuse out of the solvent cage, then the oxyphosphazene anion can attack **15** generating the observed oxo linked phosphazene-phosphazane **15**. Capture of a chloride ion by the dioxolane leads to the observed 2-chloroethylmethacrylate, **16**. Preliminary ^{31}P NMR data suggests the possibility of reaction of the oxyphosphazene anion with **16** to yield a three ring system. This additional level of reaction has been proposed in the hydrolysis of hexachlorocyclophosphazene.[8] The observation that the relative concentration of **15** continues to increase relative to that of **14** is consistent with the formation of the three ring system**.**

The mechanism proposed in Scheme 3 fits the observed product distribution, the kinetic order of the reaction and the activation energies. In order to further test this hypothesis, we have explored the thermolysis of a series of phosphazene derivatives related to **2.** These species are shown in Scheme 2. The spiro(2,3-dioxypropylmethacryl)tetrachlorocyclotriphosphazene(**9**) contains the basic (2-oxyethyl methacryl) unit which undergoes the rearrangement in **8** however as a result of being incorporated into a spirocyclic unit it has two points of attachment to the phosphazene ring. Phosphazenes with five membered spirocyclic ring substituents have been shown to undergo a spiro to ansa (2,2 to 2,4 attachment) rearrangement but only under the influence of alkoxide anions.[28] Exposure of **9** to elevated temperatures for extended periods of time left the molecule unchanged. In order to undergo the rearrangement process shown in Scheme 3, the developing carbocation in the transition state and the ion pair would be significantly constrained by the second point of attachment to the phosphazene. This constraint provides sufficient barrier to prevent the rearrangement. The stability of the methacrylate on spirocyclic unit allowed for use of certain of these derivatives to be employed as monomers in polymerization reactions.[29] The next set of mechanistic test reactions involved investigation of the effect of elaboration of the alkyl chain of the methacrylate unit, specifically to propyl (2-oxypropyl(**10**)), isopropyl (1-2-oxypropyl(**11a**) and 2-(1-oxypropyl (**11b**))and butyl groups (n-butyl,**11**). Complete resolution of the ^{31}P NMR signals in 11a and 11b mixture was not possible and the chemical shifts are

reported as the average of the pair except where clearly resolved. Products analogous to those obtained from **8** i.e. the rearranged (phosphazane) and dimeric specie as well the chloromethacrylate were observed. Partial assignments and knowledge of the isomer ratio available in the parent methacylates allowed for monitoring of the rearrangement of a mixture of **11a** and **11b** by ^{31}P and ^{1}H NMR at 111^0 under conditions identical to those employed for **8.** The structural changes were clearly reflected in the kinetic data (half lives, Table 1).[30] In each case, an increase in rate is observed which can be ascribed to the electron releasing methyl group stabilizing the developing carbocation. The effect is stronger in **11b** (**11b** > **11a** > **8**) where the methyl group is directly attached to the carbon atom which is the site of the developing carbocation. In **10**, the rearrangement does occur and the products analogous to those observed for **8** were observed by NMR (^{31}P and ^{1}H) and mass spectrometry. The extension of the carbon chain to an n-propyl unit between the phosphazene and the methacrylate moiety results in a 20 fold rate reduction (Table1).[30] Due to increased conformational possibilities in **10** relative to **8** (and the related **11a** and **11b**), the formation of the dioxoenium ion requires a larger loss on configurational entropy and hence a higher energy transition state. Further extension of the length of the alkyl chain to the n-butyl derivative (**11**) increases the cost of loss of configurational entropy to a degree that it is unchanged after heating of **11** for 12 hrs at 111^0. This has allowed for the use of phosphazenes related to **11 to** serve as a monomers in radical initiated olefin polymerization.[31-33] The role of the ester carbonyl was examined by investigating the thermolysis of **12** where the methacrylate group is replaced by a methoxy group. Even under forcing conditions (111^0, 48 hrs), no rearrangement was observed. The multifunctional derivative, $N_3P_3(O(CH_2)_2OC(=O)CMe=CH_2)_6$ has been reported to undergo polymerization at multiple olefin sites to yield a highly cross linked (cyclomatrix)phosphazene polymer. The resulting hard film has been proposed to be of value in coatings. [34] However, we have examined the thermolysis of $N_3P_3(O(CH_2)_2OC(=O)CMe=CH_2)_6$ and have observed preliminary evidence for the phosphazene-phosphazane rearrangement which may contribute to a decrease of the long term stability of the films by introducing the more reactive phosphazane component . The corresponding polymerization of $N_3P_3[O(CH_2)_4OC(=O)CMe=CH_2]_6$ has been reported to yield a hard film which can be plasma etched.[33]

The mechanism described above and in Scheme 3 fits all of the product distribution and kinetic data. The structure activity studies involving a range of modification of the organic substituents are all consistent with the proposed mechanism. The observation of pathways both within and outside of the solvent cage allow for understanding of the evidence for both inter and intramolecular pathway in the rearrangement of alkoxyphosphazenes.[13,15] The importance of solvent cage effects in other cyclophosphazene systems will be reported in a future publication. The stability of the oxyphosphazene anion, $N_3P_3Cl_5O^-$ is one of the major diving forces for the reaction and is a commonly observed (or presumed) products of numerous cyclophosphazene decomposition reactions.[2,35] This stability combined with the stabilization of a developing carbocation , the other major factor identified in this investigation, allows for understanding of the relative instability of tertiary (and to some degree secondary) alcohol phosphazene derivatives since the increased number of alkyl groups provide stabilization for a developing carbocation. Finally, this study allows for the rational design of methacyl phosphazene monomers suitable for olefin polymerization.

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REFERENCES

(1) Shaw,R.A. *Z.Naturforsch.* **1976**,*31b,641*

(2) Allen,C.W. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc,I.,Sowerby,D.B.,Eds.;Academic Press:London,1987; Vol 2, Chapter 20,p 501.

(3) Shaw,R.A. *J.Organomet.Chem.* **1988**,*341*,357.

(4) Allen,C.W. *Chem.Rev.* **1991**,*91*,119.

(5) H. R. Allcock*, Chemistry and Applications of Polyphosphazenes; Wiley-Interscience: New York, 2003.*

(6) V. Chandrasekhar*, Inorganic and Organometallic Polymers; Springer-Verlag: Berlin, 2005.*

(7) De Ruiter,B.; Winter,H.; Wilting,T.; van de Grampel,J.C.*J.Chem.Soc.,Dalton Trans.* **1984**,1027.

(8) Gabler,D.G.;Haw,J.F. *Inorg.Chem.* **1990**,*29*,4018.

(9) Murray,M.; Boulajoun *Phosphorus Research Bulletin* **1996**,*6*,155.

(10)Alekseiko,L.N.;Gorchakov,V.V.;Ivanov,Yu. V.; Murashov,D.A.;Rozanov,I.A. *Russ.J.Inorg.Chem*.**1989,**34,1958.

(11)Thomas,B.;Paasch,S.;Boehme,U. *Z.Anorg.Allg.Chem*.**2005**,631,85.

(12)Cheng,T.C.;Mochel,V.D.;Adams,H.E.;Longo,T.F. *Macromolecules* **1980**,13,158.

(13) Ferrar,W.T.;DiStefano,F.V.;Allcock,H.R. *Macromolecules* **1980,**13,1345.

(14) Dhathathreyan,K.S.; Krishnamurthy,S.S.;Vasudeva Murthy, A.R.; Shaw,R.A.; Woods,M.*J.Chem.Soc.,Dalton Trans.***1981**,1928.

(15) Karthikeyan,S.;Krisnamurthy,S.S.*J.Chem.Soc.,Dalton Trans.* **1991**,299.

(16) Bullen,G.;Williams,S.J.;Paddock,N.;Patmore,D.J. *Acta Crystallogr.,Sect.B: Stuct.Crystallogr.Cryst.Chem.***1981**,B37,607.

(17) Mochel,V.D.;Cheng.T.C. *Macromolecules* **1978**,11,176.

(18) Brown,D.E.; Allen,C.W. *J.Inorg.Organomet.Polym.***1991**,1,189.

(19) Hayes,R.F.;Allen,C.W.*Phosphorus,Sulfur,Silicon* **1994**,93-94,269.

(20) Hayes,R.F.;Allen,C.W.*Heteroatm.Chem.***1998**,9,669.

(21) The original version of DNM-3 is in the following: (a) Kleier,D. A.;Binsch,G. *J. Magn. Reson. Relat. Phenom., Proc. Congr. Ampere, 16th* **1971**,3, 146. Local modifications are described in the following:(b) Bushweller, C.H.; Bhat, G.; Lentendre, L.; Brunelle, J. A.; Bilofsky, H. S.; Rubin, H.; Templeton, D. H.; Zalkin, A. J. *J. Am. Chem. Soc.* **1975**, 97, 65.

(22) Weber,U.;Thiele,H., *NMR Spectroscopy: Modern Spectral Analysis*;Wiley-VCH:Weinheim,Germany,1998.

(23) Conners, K.A., *Chemical Kinetics, The Study of Reaction Rates in Solution;* VCH Publishers: New York,1990,251-253.

(24) Issacs, N., *Physical Organic Chemistry, 2nd e.*; John Wiley and Sons,inc.: New York,1995,113-16.

(25) (a) Hart,H.; Tomalia,D.A. *Tetrahedron Lett.***1967**,1347. (b) Hart,H.; Tomalia,D.A.*Terahedron Lett.***1966**,3383. (c)Hart, H.; Tomalia,D.A. *Tetrahedron Lett.***1966**,3389.

(26) Capon, B: Ghosh,A.K. *J.Am.Chem.Soc.***1981**,103,1765.

(27) (a)Wilen,S.H.; Delguzzo,L.; Saferstein,R. *Tetrahedron* **1987**,43, 5089. (b) Pittman,C.U.; McManus,S.P. *Tetrahedron Lett.***1969**, 339.

(28) (a) Besli,S.; Coles,S.J.; Coles,L.S.; Davies,D.B.; Kilic,A. *Polyhedron* **2012**,43,176.(b) Besli,S.; Coles,S.J.: Davies,D.B.;Hursthouse,M.B.;Kilic,A.; Shaw,R.A. *J.Chem.Soc., Dalton Trans.***2007**,26,2792.

(29) Hayes,R.F.;Allen,C.W. *J.Inorg.Organomet.Polym.Mater.* **2010**,20,528.

(30) Kinetic data available on request.

(31) Allen,C.W. *Inorg.Chim.Acta* **2011**,372,32.

(32) Myer, C.N. *J.Inorg.Organomet.Polym.Mater.***2007**, 17,143.

(33) Hagberg, E.C.; Hart, M.W.; Cong, L.; Allen, C.W.; K.R. Carter, *J.Inorg. Organomet. Polym. Mater.***2007**,17,377.
17, 377(2007).

(34) Yaguchi, A.; Mori,S.; Kitayama, M.; Onda,T.; Kurahashi, A.; Ando ,H Thin Solid Films , **1992**,216,123.

(35) Nataro,C.; Myer,C.N.; Cleaver, W.M.;Allen,C.W.*J. Organomet. Chem.***2001**,637-639, 284.

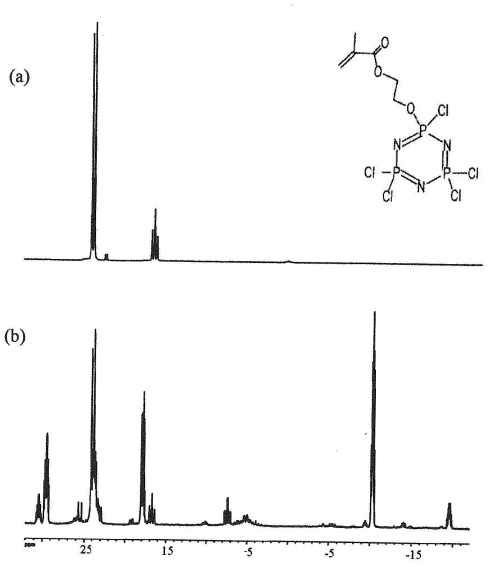


Figure 1. ^{31}P NMR spectra of **8** (a) before and (b) after heating at 110 C for 10 hours.

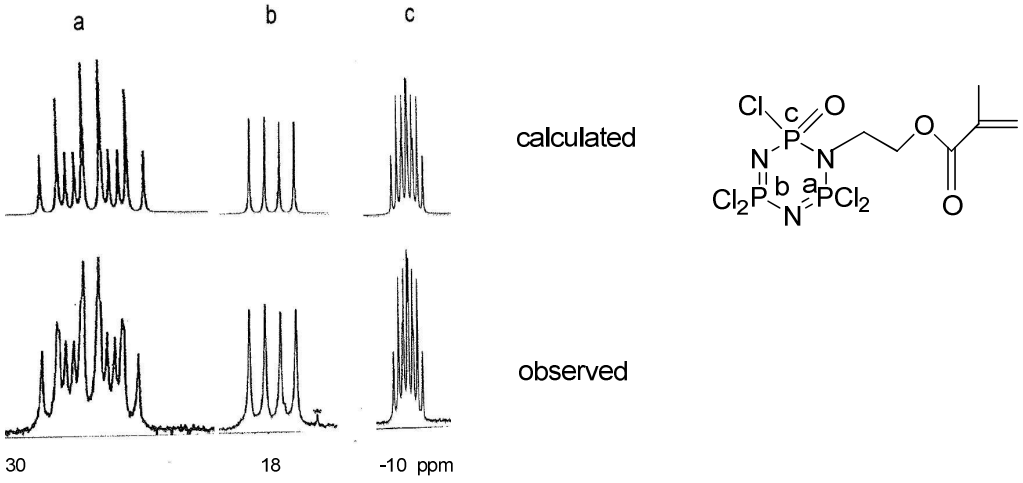


Figure 2. Calculated and Observed ^{31}P NMR Spectrum for 14

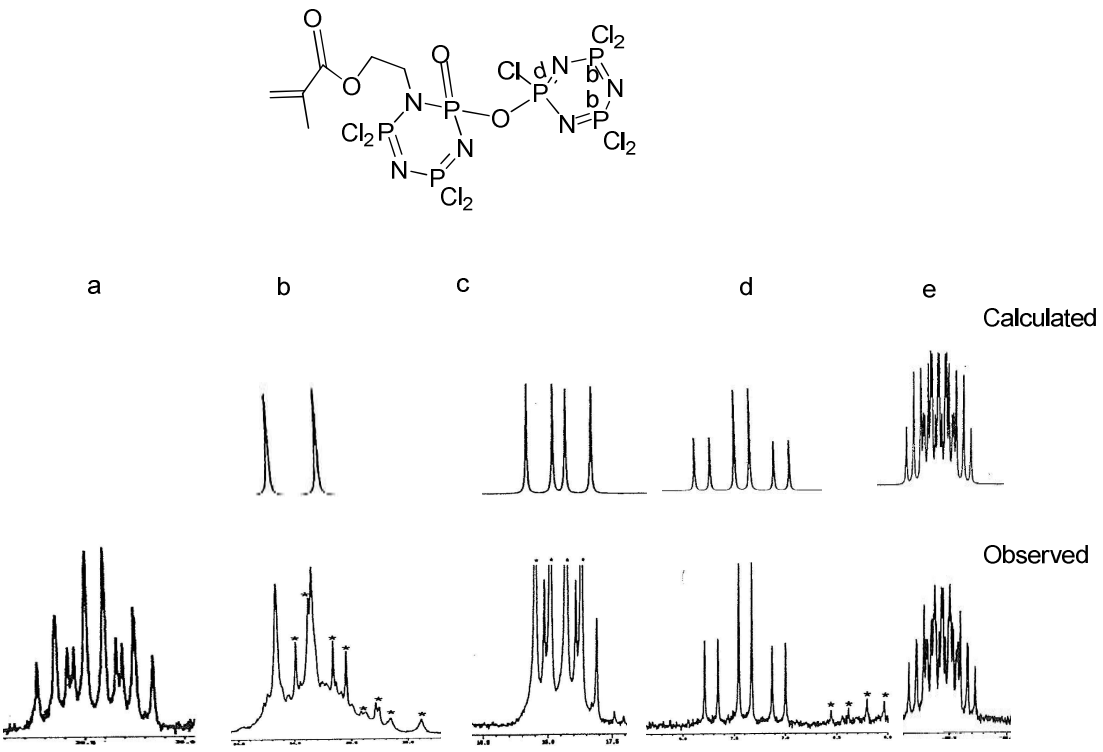
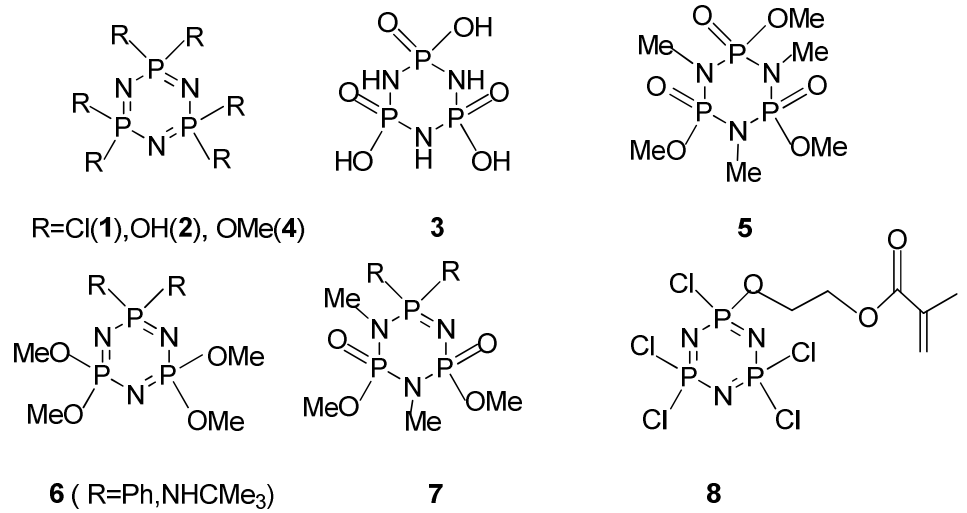


Figure 3.Calculated and observed ^{31}P NMR spectrum of **15**. Peaks marked with * are overlapping from other species.

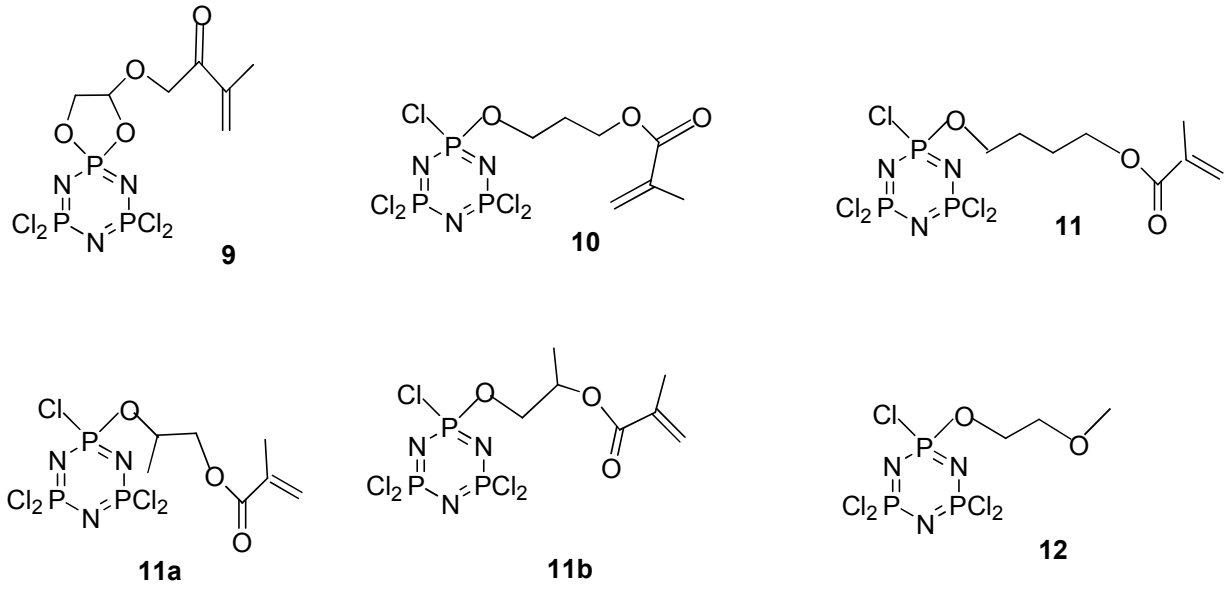
Table 1. Selected Rearrangement Kinetic Data

Compound	**8** "Dry Sample"			**8** "Wet" Sample	**10**	**11a**	**11b**
Parameter		^{31}P	^{1}H	^{31}P			
Half life [a]	111[b]	4.65	5.06	4.42	89.5	4.03	3.61
	89	67.1	73.8	20.3			
	70	343	376	67.0			
	50	1210	1230	215			
	35	1940	3620	387			
$\Delta H^{\pm}$ [c]		90.1	89.0	62.6			
$\Delta S^{\pm}$ [d]		-100	-104	-169			

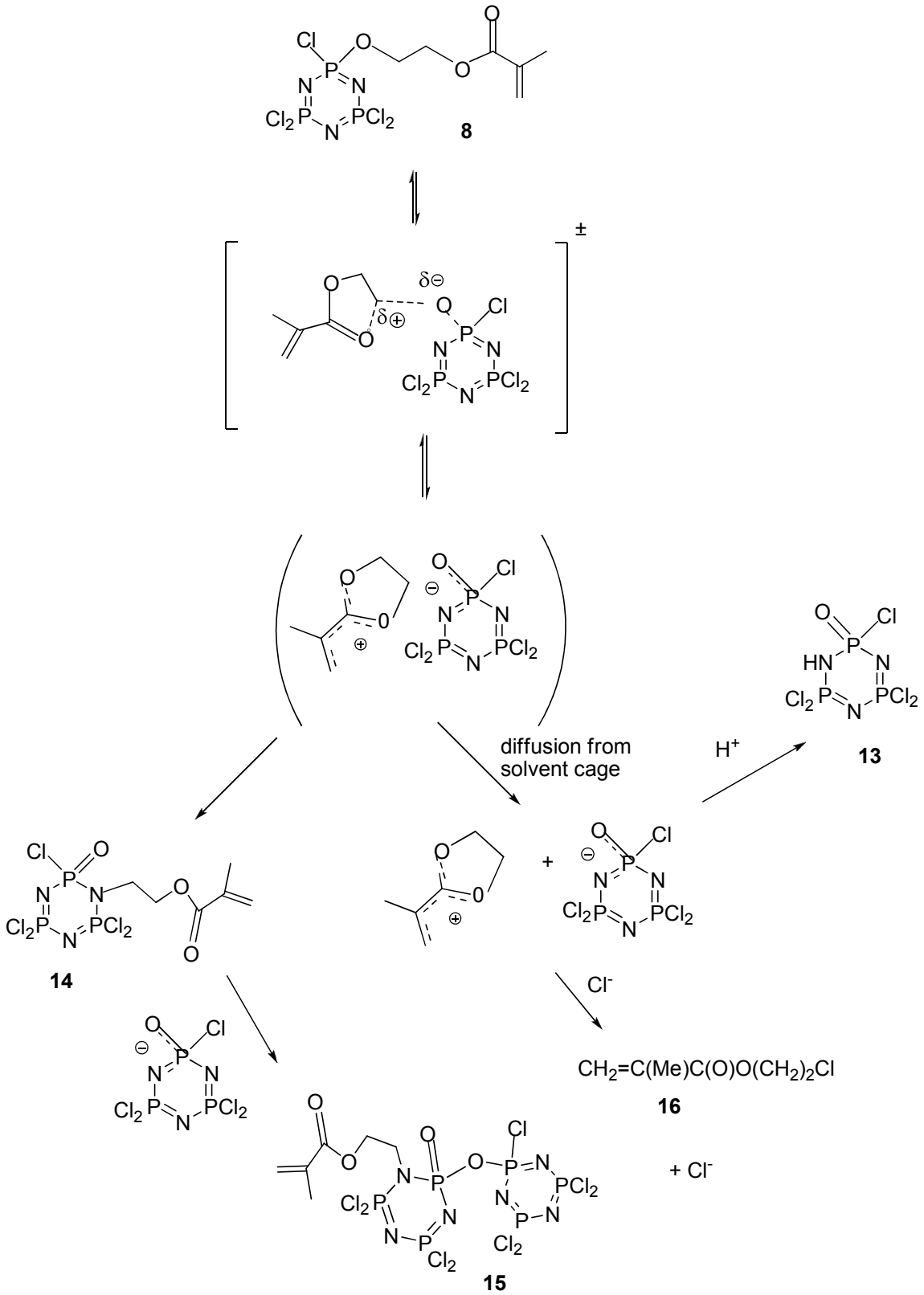
[a] hours. [b] ^{0}C. [c] KJ/mole. [d] J/mole



Scheme 1. Selected Cyclophosphazenes and Cyclophosphazenes



Scheme 2. Methacrylcyclophosphazanes



Sceme 3. Proposed Mechanism for the Rearrangement of 8

The mechanism showing both inter- and intramolecular pathway of the phosphazene-phosphazane rearrangement of $N_3P_3Cl_5O(CH_2)_2OC(=O)CMe=CH_2$ (**8**) has been determined.