

AD-A218 234

REPORT DOCUMENTATION PAGE

DTIC
ELECTE

21 1990

D

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION / AVAILABILITY OF REPORT
Available for public release.
Distribution unlimited.

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

#54

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION

The Pennsylvania State Univ.

6b. OFFICE SYMBOL
(if applicable)

7a. NAME OF MONITORING ORGANIZATION

Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)

Department of Chemistry
The Pennsylvania State University
University Park, Pa. 16802

7b. ADDRESS (City, State, and ZIP Code)

Arlington
Virginia 12217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION

ONR

8b. OFFICE SYMBOL
(if applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)

Arlington
Virginia 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO. NR	WORK UNIT ACCESSION NO.
N00014-84	K-0447	356/4-6-84	

11. TITLE (Include Security Classification)

Ring Expansion and Equilibration in Organophosphazenes, and the Relationship to Polymerization

12. PERSONAL AUTHOR(S)

Harry R. Allcock*, Gayann S. McDonnell, and James L. Desorcie

13a. TYPE OF REPORT

Preprint

13b. TIME COVERED

FROM TO

14. DATE OF REPORT (Year, Month, Day)

1990, February 15

15. PAGE COUNT

30

16. SUPPLEMENTARY NOTATION

Submitted to INORGANIC CHEMISTRY

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Polymers, polymerization, synthesis, mechanisms, thermal stability.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT

UNCLASSIFIED/UNLIMITED SAME AS RPT DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

Dr. Kenneth J. Wynne

22b. TELEPHONE (Include Area Code)

202-696-4410

22c. OFFICE SYMBOL

NC

Office of Naval Research

Contract N00014-84-K-0477
R&T Project Code 4132007---004

Technical Report No. 54

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AND THE RELATIONSHIP TO POLYMERIZATION

by

Harry R. Allcock^{*}, Gayann S. McDonnell and James L. Desorcie

Prepared for Publication in INORGANIC CHEMISTRY

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16801

February 15, 1990

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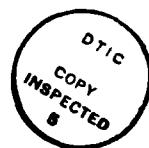
Ring Expansion and Equilibration in Organophosphazenes,
and the Relationship to Polymerization

Harry R. Allcock*, Gayann S. McDonnell, and James L. Desorcie

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

Received _____

Abstract. A series of cyclic trimeric phosphazenes that bear both halogen and organic side groups have been found to undergo ring expansion-equilibration reactions at elevated temperatures. Compounds non-gem $N_3P_3F_5CMe_3$, $N_3P_3F_5Ph$, $N_3P_3F_4(CMe_3)_2$, $N_3P_3F_4Ph_2$, $N_3P_3Cl_4Me_2$, $N_3P_3Cl_4Et_2$, $N_3P_3Cl_3Me_3$, and $N_3P_3Cl_3Et_3$ yield cyclic tetramers, pentamers, hexamers, and in some cases, heptamers, octamers, and nonamer when heated. The cyclic tetramers $(NPClMe)_4$ and $(NPClEt)_4$ also equilibrate to a range of cyclic species that range from trimer to hexamer. Several of these equilibrations also lead to the formation of high polymers. The results are discussed in terms of possible mechanisms for ring-ring equilibration and polymerization.



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It is known that certain cyclophosphazenes such as $(\text{NPF}_2)_3$ or $(\text{NPCl}_2)_3$ (1) polymerize to high polymers (2) when heated at temperatures between 250°C and 350°C (Scheme I). This is the starting point for the synthesis of a wide range of stable and useful organophosphazene high polymers.¹⁻⁷ On the other hand, cyclophosphazenes such as $(\text{NPMe}_2)_3$, $(\text{NPPH}_2)_3$, or $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_3$ (3)⁸⁻¹¹ undergo thermal ring-expansion reactions but do not give high polymers (Scheme II). This is a mechanistic anomaly that has an important bearing on attempts to synthesize new classes of phosphazene high polymers.

Schemes I and II near here

In this present work, we have selected a number of cyclophosphazenes that occupy an intermediate position: they contain both halogeno and organic side groups. When heated they can yield both small-molecule ring expansion products and high polymers. Seemingly minor changes within these structures can tip the balance in favor of either of the two extremes. By studying such systems we hoped to understand the relationship between side group structure in polyphosphazenes and their ability to polymerize.

The compounds studied are shown as 7-16. These were synthesized by methods described previously.^{10,12-16} The high polymers obtained from these cyclophosphazenes have been described in another paper.¹⁷ Here we discuss the macromolecules only with respect to their coexistence with the ring-ring equilibration products. Thus, the focus of this paper is on the small-molecule reaction products and on the relationship between the mechanisms of ring-ring equilibration and polymerization. This topic is of practical importance for three reasons. First, it is related to the choice of monomers for conversion to high polymers. Second, it provides

information that may allow an understanding of the high temperature thermal stabilities of phosphazene high polymers. Third, the ring expansion reactions provide a route to cyclic phosphazenes that are at present inaccessible by any other method.

Results and Discussion

Method of Study. Multiple samples of each compound 7-16 were heated at temperatures in the range of 210-300°C in evacuated sealed tubes for periods of time that ranged from 1 hour to 30 days. When high polymers were formed, the viscosity of the molten mixtures increased significantly. Otherwise the contents of the heated tubes remained fluid.

The main experimental problem in this work was to identify the various cyclic phosphazenes formed by ring-ring equilibration. An obvious technique, the use of ^{31}P NMR spectroscopy, could not be used to analyze all the mixtures because the chemical shifts were indistinguishable once the ring size exceeded five or six repeating units. However, cyclic trimers could be distinguished from tetramers, and the ^{31}P NMR spectra of these species were used to provide confirmatory evidence.

Vapor phase chromatography/mass spectrometry (VPC/MS) proved to be the most useful method of analysis. Two different approaches were employed. In the first, the cyclic oligomers formed by equilibration were solvent extracted from any high polymer present and were then subjected to VPC/MS analysis. The separation from the high polymer was necessary because of the extreme tendency of the polymer to crosslink when exposed to atmospheric moisture¹⁷ and the possibility that any high polymer present would depolymerize in the VPC inlet and thus distort the analysis. However, this

approach made it exceedingly difficult to compare the yields of cyclic oligomers and high polymer. The alternative approach involved an intermediate step to replace the halogen atoms in the equilibrated molecules by trifluoroethoxy groups, separation of the derivative cyclic oligomers from the high polymer, and analysis of the cyclic oligomers by VPC/MS techniques. This method had serious limitations because of the relatively high molecular weights of the trifluoroethoxy-substituted oligomeric products, which complicated both the VPC separations and the MS analysis. The only cases in which the oligomer ratios could be monitored by VPC/MS analysis of both the chloro- and trifluoroethoxy derivatives was for the products derived from 13-16 where only one type of repeating unit was incorporated into the products. In these cases a clean VPC separation and an accurate MS analysis of the trifluoroethoxy derivatives was possible.

In all these equilibration reactions, the total percentages of recovered cyclic oligomers and high polymers rarely exceeded 75% and, in a few experiments, was as low as 46%. This was attributed to losses incurred during extraction and recovery of the products and, in specific cases where long reaction times were employed, to side reactions that consumed equilibration products by crosslinking or side group transformations. Thus, the ratios of total cyclic oligomers to high polymers are less meaningful than the relative ratios of the various cyclic oligomers in the reaction mixtures. These values were reasonably reproducible and reflect the relative stabilities of the various cyclic phosphazenes in the equilibrate. However, the experimental difficulties were such that we prefer to compare most of the product ratios in terms of concentration zones - for example, "detected but <10%, 10-19%, 20-29%," etc - rather than by

drawing finer distinctions.

An exception is the case of products derived from $(\text{NPClR})_3$ or 4 where more precision was possible. Only one type of monomer unit is present in these systems, and this results in a considerable improvement in chromatographic resolution. As a result, relative concentrations could be estimated without the need to consider detector response factors.¹⁹ In addition, cross-correlation was possible between chromatographic data for the chloro- and trifluoroethoxy derivatives. Authentic samples of specific trifluoroethoxy-substituted cyclic trimers were easily prepared as controls via the reactions of 13-16 with sodium trifluoroethoxide. For these reasons, most of the mechanistic and thermodynamic arguments in this paper are based on these data.

General Behavior of Compounds 7-16. Compounds 7, 8, 11-13, and 15 underwent both ring expansion and polymerization reactions when heated. Species 9, 10, 14, and 16 yielded mainly small-molecule ring expansion (or contraction) products. No high polymers were formed. The reaction conditions employed and the relative yields of cyclic oligomers and high polymers are listed in Tables I and II.

Tables I and II near here

The presence of one bulky organic side group per trimeric ring, together with five fluorine atoms (7 or 8), allows ring expansion reactions to occur, together with ~50% conversion to high polymers. This is similar to results obtained earlier for a number of cyclotriphosphazenes with one organic group and five chlorine atoms per ring.²⁰⁻²⁴ However, when two t-butyl or phenyl groups are present at different phosphorus atoms (non-geminal), together with four fluorine atoms (9 or 10), high polymer formation is eliminated in

favor of small-molecule ring-expansion products. This effect was not detected if two non-gem-methyl or ethyl groups are present, together with four chlorine atoms (11 or 12). A third non-gem-methyl group (13) allows both polymerization and ring expansion, but a third ethyl group (14) blocks polymerization in favor of ring-expansion. A similar effect is seen in the cyclic tetrameric series (15 and 16). One methyl group on every phosphorus allows both ring-ring equilibration and polymerization, but one ethyl group per phosphorus inhibits polymerization. These results illustrate the powerful role played by the organic side groups in directing the reaction pathway in one direction or another.

In the following sections the ring-ring equilibrations will be discussed according to the structural type of the starting material. Reactions that originate from species with one organic group and five fluorine atoms per trimer ring will be described first. These will be followed by systems that contain progressively higher ratios of organic to halogen side groups. A summary of the data is given in Tables I and II.

Behavior of Systems with One Organic Unit Per Ring. In the following discussion, the numbers in parentheses represent the percentage of different cyclic phosphazenes in the oligomeric component detected by vpc-mass spectrometry.

First, when compound 7 was heated at 300°C for 4-6 days, an extensive redistribution of repeating units occurred to give different cyclic trimers, tetramers, pentamers, hexamers, and at least one cyclic heptamer. A total of 13 species were detected of which the starting material comprised less than 10% of the small-molecule mixture. The products can be understood in terms of a redistribution of NPF_2 and NPF_2CMe_3 units between the products.

The principal products were $N_4P_4F_6(CMe_3)_2$ (30-39%) and $N_6P_6F_{11}CMe_3$ (20-29%), together with $N_3P_3F_5CMe_3$, $N_3P_3F_4(CMe_3)_2$, $N_3P_3F_3(CMe_3)_3$, $N_4P_4F_7CMe_3$, $N_4P_4F_5(CMe_3)_3$, $N_5P_5F_9CMe_3$, $N_5P_5F_8(CMe_3)_2$, $N_5P_5F_7(CMe_3)_3$, $N_6P_6F_{10}(CMe_3)_2$, $N_6P_6F_9(CMe_3)_3$, and $N_7P_7F_{12}(CMe_3)_2$, each present at a level of less than 10% concentration. No evidence was found for the presence of even traces of $(NPF_2)_{3-8}$, which is surprising. It is speculated that these species, if formed in trace amounts, may be preferentially polymerized rather than oligomerized.

The evidence suggests that in this system each $NPF(CMe_3)$ unit retains its integrity--i.e. that exchange of side groups at phosphorus does not occur, and that only redistribution of repeating units takes place. This is consistent with the detection of products that mainly reflect the 2:1 ratio of NPF_2 : $NPFCMe_3$ in the starting material.

For 8, with a phenyl group in place of t-butyl, the distribution of products is very similar. Again, <10% of starting material (8) was detected, with the major product being the cyclic tetramer $N_4P_4F_7Ph$ (10-19%). All the other species (in the <10% concentration range) matched those derived from the t-butyl analogue, with the addition of the cyclic heptamers $N_7P_7F_{13}Ph$ and $N_7P_7F_{11}Ph_3$ (both <10%), and the octamers $N_8P_8F_{15}Ph$ and $N_8P_8F_{14}Ph_2$ (again <10%). Thus, here too the pattern indicates a very broad distribution of ring-ring equilibration products generated by the redistribution of a 2 : 1 ratio of NPF_2 : $NPFPh$ repeating units.

This does not imply that free monomer units are undergoing statistical redistribution, but rather that the conversion of rings to other rings allows the redistribution to take place. This is a similar situation to the one found in organocyclosiloxane equilibrations.

It should be noted that for compounds 7 and 8 the principle reaction product in each case is the high polymer, with the cyclic oligomers constituting only 15% of the isolated products from 7 and 13% from 8. It seems reasonable to suppose that the cyclic oligomers formed by redistribution are themselves capable of polymerizing to higher cyclic species or high polymers.

Compounds with Two Non-Geminal Organic Groups Per Ring. (a) Fluorophosphazenes. Fluorophosphazenes 9 and 10, with two t-butyl or phenyl side groups, gave no high polymers when heated at 300°C. Instead, the products consisted of a series of ring-expansion products. Species identified for the t-butyl system included cyclic trimers through heptamers, and for the phenyl system, trimers through hexamers. Again, the complex mixture of cyclophosphazenes was indicative of a broad redistribution reaction in which many of the possible combinations of NPF₂ and NPFR repeating units are represented.

For the t-butyl system, the trimeric species included N₃P₃F₅CMe₃ (<10%), N₃P₃F₄(CMe₃)₂ (starting material, 10-19%), and [NPF(CMe₃)]₃ (10-19%). Four tetramers were detected--N₄P₄F₇CMe₃ (<10%), N₄P₄F₆(CMe₃)₂ (20-29%), N₄P₄F₅(CMe₃)₃ (30-39%), and [NPF(CMe₃)₄] (<10%). Pentamers N₅P₅F₉CMe₃, N₅P₅F₈(CMe₃)₂, N₅P₅F₇(CMe₃)₃, N₅P₅F₆(CMe₃)₄, and [NPF(CMe₃)]₅, as well as hexamers N₆P₆F₁₁CMe₃, N₆P₆F₁₀(CMe₃)₂, N₆P₆F₉(CMe₃)₃ and heptamer N₇P₇F₁₂(CMe₃)₂ were detected, all at concentrations below 10%. No species of type (NPF₂)_x were detected. For the phenyl system derived from 10, a similar pattern of products was formed (Table I) but with only one species N₄P₄F₅Ph₃ (30-39%) present at levels above 10%.

Again, it appears that the cyclic products represent the results of a scrambling of NPF_2 and NPF_R repeating units as extensive ring-ring equilibration reactions occur. The absence of high polymers from these two systems is interesting, since the related chlorophosphazenes, 11 and 12, with smaller methyl or ethyl side groups generate substantial amounts of high polymer.

(b) Chlorophosphazenes. Chlorophosphazenes 11 and 12, with two non-gem methyl or ethyl groups per ring underwent equilibration at 250°C to give polymers (42-46%) and a mixture of ring-expansion oligomers (23-30%). For both systems, the cyclic products consisted of trimers through pentamers (Table I). For the methyl system, the main component of the oligomeric mixture was the starting material (11) (40-49%), together with less than 10% each of $\text{N}_3\text{P}_3\text{Cl}_5\text{Me}$ and $(\text{NPClMe})_3$; $\text{N}_4\text{P}_4\text{Cl}_6\text{Me}_2$, $\text{N}_4\text{P}_4\text{Cl}_5\text{Me}_3$, and $(\text{NPClMe})_4$; and $\text{N}_5\text{P}_5\text{Cl}_8\text{Me}_2$, $\text{N}_5\text{P}_5\text{Cl}_7\text{Me}_3$, $\text{N}_5\text{P}_5\text{Cl}_6\text{Me}_4$, and $(\text{NPClMe})_5$. The products obtained from the ethyl system (12) were identical to those from 11 with the exception that species $\text{N}_3\text{P}_3\text{Cl}_4\text{Et}_2$ (12) (20-29%), $(\text{NPClEt})_3$ (10-19%), $\text{N}_4\text{P}_4\text{Cl}_6\text{Et}_2$ (10-19%), and $\text{N}_4\text{P}_4\text{Cl}_5\text{Et}_3$ (20-29%) were present in the largest amounts. In addition, 12 gave $\text{N}_4\text{P}_4\text{Cl}_7\text{Et}$ and $\text{N}_5\text{P}_5\text{Cl}_9\text{Et}$. Once again, no cyclic species of type $(\text{NPCl}_2)_x$ were detected.

In these two methyl or ethyl chlorophosphazene systems, no cyclic hexamers, heptamers, or octamers were detected. This could be due to the ability of these species to readily polymerize or depolymerize to smaller rings. Direct comparisons with compounds non-gem $\text{N}_3\text{P}_3\text{F}_4\text{Me}_2$ or $\text{N}_3\text{P}_3\text{F}_4\text{Et}_2$ could not be made because, to our knowledge, synthetic routes to these species are not yet available. However, comparisons of 11 and 12 with the more highly organo-substituted species 13-16 are possible, and these are

discussed in the following sections.

Compounds of Formula $(\text{NPClMe})_3$ and $(\text{NPClEt})_3$. As discussed earlier, the equilibration reactions from species of type $(\text{NPClR})_x$ are simpler than those discussed in previous sections, since only one type of repeating unit is involved in the interchanges. Hence, a more detailed analysis was possible.

We first consider the situation for $(\text{NPClMe})_3$ (13). When heated at 210°C or 250°C this compound was converted to a mixture of cyclic oligomers and high polymer. Typical reaction conditions and results are shown in Table II.

For this system, the equilibration reaction was a slow and somewhat unpredictable process. However, a tendency was detected for the molecular weights of the isolated polymers to decrease if the equilibration reactions were allowed to continue for long periods of time. This suggests the presence of a general oligomer-polymer redistribution equilibrium in which the rates of redistribution are slow. However, it should be noted that, at very long reaction times (20-40 days at 250°C), side reactions occur that remove both oligomers and polymers from the system (perhaps by crosslinking), and this undoubtedly interferes with the analysis. Perhaps the most important result from this section of the work was the detection of the early formation of the cyclic hexamer $(\text{NPClMe})_6$ (22%) and nonamer $(\text{NPClMe})_9$ (3%) in the slower reactions carried out at 210°C (Table II). As the reaction progressed (or the temperature was raised), the hexamer decreased in concentration as the percentage of tetramer increased. This is strong evidence that the initial step during equilibration is a fusion of two trimer rings to form hexamer. Tetramer may then be formed by

ring-contraction from the hexamer. If this ring fusion process applies to the whole equilibration process, it implies that the high polymers may be macrocyclic rather than linear species.

When $(\text{NPClEt})_3$ (14) was heated at 210-250°C no high polymer was formed at all. Ring expansion reactions accounted for all the products. This provided an added simplification and allowed a more detailed examination of the ring-ring equilibration reactions without the complexity of a possible preferential loss of certain cyclic species to the polymerization process.

At 210°C the equilibration reaction was slow (Table II). After 25 days at this temperature the product mixture consisted of 93% trimer 14 and only trace amounts of tetramer, pentamer, and hexamer (Table II). At 250°C the equilibration rate increased markedly, with the principal product after 25 days being the cyclic tetramer (69%). Indeed, this provides the only route known at the present time for the preparation of $(\text{NPClEt})_4$. However, if the temperature was raised to 300°C the concentration of trimer increased at the expense of the tetramer (Table III).

Table III near here

Based on the concentration of trimer and tetramer in the equilibria at 248°C and 300°C (Table III), it was calculated that $\Delta H = -22.1$ kcal and $\Delta S = -36.7$ eu. Thus, the trimer is destabilized by about 1.8 kcal/monomer unit relative to the tetramer. This probably reflects the existence of ring strain in the trimer.

Careful monitoring of the reaction products as a function of consumed trimer indicated that the relative concentrations of cyclic oligomers is dependent on the extent to which the ring-expansion reaction has progressed. As shown in Figure 1, the concentrations of cyclic tetramer and pentamer

increased steadily throughout the course of the reaction, but the concentration of cyclic hexamer first increased to a maximum and then decreased. This suggests that, in the $(\text{NPClEt})_x$ system also, the cyclic hexamer may be an initial reaction intermediate from which trimer, tetramer, and pentamer can be formed.

Figure 1 near here

Cyclic Tetramers of Formula $(\text{NPClMe})_4$ and $(\text{NPClEt})_4$. The cyclic tetramer, $(\text{NPClMe})_4$ (15), polymerized at a slightly lower rate than did the trimer, $(\text{NPClMe})_3$. However, the polymers formed from the two cyclic species were essentially identical in molecular weight and molecular-weight-distribution. The distribution of cyclic oligomers, $(\text{NPClMe})_{3,4,5}$, and 6, at equilibrium (20 days at 250°C) was virtually identical irrespective of whether the trimer or tetramer was used as the starting material. The cyclic hexamer appeared to play a lesser role in the early stages of this equilibration than was the case in the system that originated from the trimer. This would tend to confirm an initial mechanism that involves trimer ring fusion in the $(\text{NPClMe})_3$ system. However, no octamer was detected from the reactions of $(\text{NPClMe})_4$. As discussed, the $(\text{NPClEt})_4$ system yielded the same mixture of oligomers at equilibrium as was formed from the trimer.

Reaction Mechanisms. Three questions are of special interest: (1) What is the overall pathway by which ring expansion or contraction or polymerization occur? (2) What is the initiation step and the detailed reaction pathway for ring-ring or ring-polymer interconversions? (3) Why do changes in side group structure allow polymerization in some cases but favor small-molecule ring expansions or contractions in others?

It appears unlikely that ring-expansion or polymerization proceeds via a mechanism that involves breakdown of the initial cyclophosphazenes into NPXR and/or NPX₂ monomer molecules, followed by subsequent recombination. If this occurred, detectable amounts of (NPF₂)_{3,4}.... or (NPCl₂)_{3,4}.... would be expected from species 7-12. No products of this type were found. Hence, unless species such as these are formed in substantial quantities but are rapidly and preferentially incorporated into the high polymer, it must be assumed that the initial steps involve the incorporation of trimer (or tetramer) molecules directly into larger rings or into a growing polymer chain. The formation of cyclic oligomers such as tetramer or pentamer from the trimer would then be a consequence of ring contraction reactions or depolymerization of the high polymer.

The generally accepted mechanism for polymerization of halogenocyclophosphazenes involves an ionization of a Cl⁻ or F⁻ group from phosphorus to generate a cyclic phosphazenium ion (17 in Scheme III), which then attacks another trimer molecule to cleave its ring (18) and begin a cationic linear chain propagation reaction (Scheme III, pathway a).²⁵

Scheme III near here

This mechanism explains why species such as (NPCl₂)₃ or (NPF₂)₃ polymerize to give high yields of very high molecular weight polymer, whereas compounds such as (NPMe₂)₃, (NPPH₂)₃, or [NP(OCH₂CF₃)₂]_n give no high polymers. However, it does not explain why the hexa-organo-substituted trimers undergo ring expansion reactions. Neither does it explain why compounds 9, 10, 14, and 16 undergo ring-expansion rather than polymerization.

With these facts in mind, we propose the existence of two closely related mechanisms, as shown in Scheme III. Pathway (a) is the classical

mechanism²⁵ that can lead to high polymer formation. It is favored when most of the side units are ionizable halogen atoms. The failure of ³¹P NMR spectroscopy to detect the cyclophosphazene end groups may reflect the low concentration of these units in a polymer that has 15,000 or more repeating units. However, progressive replacement of chlorine or fluorine side units in 1 by organic residues will have two polymerization-inhibiting effects. First, it will reduce the probability of initiation, since there are now fewer initiation sites (P-Cl or P-F units) in the system. Second, organic groups, especially bulky units, at the growing chain end, will sterically retard an attack by the active end on another trimer molecule. Finally, if the organic groups are bulky enough they may force the chain component of species such as 18 into a bent conformation that would bury the active chain end within the molecular coil and favor "backbiting" to split out a ring.

The alternative pathway (Scheme III, Pathway b) involves heterolytic cleavage of a P-N bond rather than a P-halogen bond. The electro-negativity difference within the P-N bond is sufficiently high to permit this step, especially if the side groups are electron-supplying (Me, Et, t-Bu, or Ph) rather than electron-withdrawing units. Thus, heterolytic ring cleavage would allow attack by the zwitterion on another ring (19) to generate expanded ring 20. The mutual attraction between the chain ends would favor cyclization at every step.

Both mechanisms could also provide a pathway for chain or ring contraction. Backbiting as shown in Scheme IV, structure 21, could yield small-molecule rings.²² Heterolytic cleavage of any ring or chain formed by pathway (b) could lead to ring contraction or depolymerization.

Scheme IV near here

The main point to be made is this. An increased loading of organic side groups will favor mechanism (b), which provides a bias in favor of small-molecule rings. An increased loading of P-halogen bonds favors mechanism (a), which provides a more efficient pathway for high polymer formation.

This interpretation explains two other facts discovered in previous studies. First, it explains why phosphazene cyclic trimers (such as 14 or 16), which ring-equilibrate but do not polymerize on their own, nevertheless give high polymers when copolymerized with $(\text{NPCl}_2)_3$. Second, it explains why phosphazene cyclic trimers that bear transannular ferrocenyl groups²⁶ and no halogen cosubstituents polymerize in the presence of traces of $(\text{NPCl}_2)_3$. Presumably even small amounts of $(\text{NPCl}_2)_3$ are sufficient to initiate polymerization via mechanism (a) if sufficient ring strain exists in the cyclophosphazene to escape from the manifold provided by pathway (b). However, when very bulky organic or organometallic side groups are the main side units present, pathway (b) is preferred, and small-molecule equilibration will be favored over polymerization.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$, was supplied by Ethyl Corp. Tetrahydrofuran (THF) was distilled into the reaction flask under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent. Hexane was distilled from calcium hydride before use. Trifluoroethanol (Halocarbon Products) was distilled and then dried over 3 Å molecular sieves. Sodium stick (Aldrich) was stored, cut, and weighed in a nitrogen-filled dry box equipped with a recirculating atmosphere system to remove oxygen and water.

Analytical Equipment and Techniques. ^{31}P NMR spectra were recorded with the use of a JEOL FX-90Q spectrometer operated at 36 MHz. Positive chemical shifts are downfield from external phosphoric acid. Vapor phase chromatography was carried out using a Varian 3700 gas chromatograph equipped with a flame ionization detector and a 2-m SP2100 (3%) column. Relative peak areas were determined using a Hewlett Packard 3392A integrator. VPC/MS data were obtained with the use of a Finnigan 3200 gas chromatograph/mass spectrometer. The thermodynamic data given in Table III were obtained from experiments in which the oven temperature was measured by means of a platinum thermocouple. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of Starting Materials, 7-16. Compounds 7-15 were prepared by methods in the literature (7, 8)^{15,16} or reported by us previously (10-15).¹⁰⁻¹⁴ Species $(\text{NPClEt})_4$ (16) was prepared by the thermal ring-expansion of $(\text{NPClEt})_3$ (14) (3.0 g, 0.027 mol) in an evacuated sealed Pyrex glass tube at 250°C for 25 days. The product mixture consisted of 69% of 16. It was isolated by column chromatography over silica gel, with hexane/methylene chloride (60-40) as eluent. Pure tetramer eluted first, followed by mixtures of tetramer, pentamer, and hexamer. The trimer was eluted last. The tetramer was further purified by sublimation at 0.05 torr. Isolated yield: 1.3 g, 43%, m.p. 65-67°C. ^{31}P NMR: 25.7, 19.8 ppm; ^1H NMR: CH_2 , δ 2.09, CH_3 , δ 1.22; IR: ν_{PN} 1305 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{N}_4\text{P}_4\text{Cl}_4$: C, 21.92; H, 4.57; N, 12.79; M.W. 435.9393. Found: C, 22.02; H, 4.34; N, 13.02; M.W. 435.9417.

All the starting materials used in this work were purified by vacuum distillation (7-10) or by two recrystallizations from heptane or hexane,

followed by three vacuum sublimations at 0.05 torr (11-16). These procedures yielded material that gave only one peak in the vpc analysis. The purified compounds were then stored in an inert-atmosphere dry box.

Preparation of Trifluoroethoxy-Substituted Cyclic Phosphazenes. These compounds were used for ^{31}P NMR monitoring of ring-ring equilibrates, and as controls for establishing the reaction conditions needed for halogen replacement of the equilibrate mixtures. The following example is typical.

A solution of $\text{N}_3\text{P}_3\text{F}_4(\text{CMe}_3)_2$ (9) (2.0 g, 6.2 mmol) in THF (30 mL) was added to a solution of $\text{NaOCH}_2\text{CF}_3$, prepared from Na (2.1 g, 0.091 mol) and HOCH_2CF_3 (9.0 mL, 0.124 mol) in THF (200 mL) at -78°C . The mixture was warmed to 25°C and was stirred at 25°C for 24 hours before deactivation with ClSiMe_3 . The product was isolated by addition to distilled water (200 mL), extraction with diethyl ether (3 x 150 mL), drying over MgSO_4 , solvent removal, and recrystallization from heptane and sublimation (0.05 mm Hg, 25°C). Yield: 1.8 g, 58%, m.p. $66-67^\circ\text{C}$. ^{31}P NMR: 15.3 (d) ppm, $\text{P}(\text{OCH}_2\text{CF}_3)_2$, 53.9 (d,t)_{ppm}, PF^tBu ; $J_{\text{PNP}} = 33.2$ Hz, $J_{\text{PF}} = 1026.8$ Hz. ^1H NMR: δ 4.3 (p) OCH_2CF_3 ; δ 1.2 (d) ^tBu ; $J_{\text{PH}} = 19.0$ Hz. IR (KBr): ν_{CH} 2960 cm^{-1} ; ν_{PN} 1165 cm^{-1} , 1205, 1250, 1290 cm^{-1} . Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_3\text{P}_3\text{OF}_8$: C, 29.7; H, 4.5; N, 8.6; F, 31.3. Found: C, 29.82; H, 4.42; N, 8.76; F, 31.61. Derivatives of 7, 8, and 10-16 were prepared in a similar way.

The same procedures were employed for replacement of fluorine or chlorine in the mixtures of cyclic oligomers (and polymers) formed by the thermal equilibration reactions.

Equilibration Reactions (Tables I and II). The equilibrations were carried out in Pyrex glass tubes, 220 mm long, 12 mm o.d., and 10 mm i.d. with a constriction 100 mm from the open end. The tubes were soaked in

ethanolic KOH for 24 h, followed by five washings each with tap water, 2% aqueous HCl solution, distilled water, and distilled/deionized water. The tubes were then dried at 140°C for 48 h. The tubes were charged with the appropriate cyclo-phosphazenes (~ 3.0 g) in the dry box, and were then connected to a vacuum line and evacuated for 30 min at 0.05 torr. The tubes were then sealed at the constriction, wrapped in aluminum gauze, and placed on a rocking device in a Freas thermoregulated oven preheated to the desired temperature. The viscosity of the molten reaction mixture increased significantly when high polymer was formed (i.e. during the equilibration of 7, 8, 11-13, and 15). No viscosity increase was detected during the ring expansion reactions of 9, 10, 14, and 16.

The polymerization tubes were opened in a nitrogen filled glove bag, and the contents were Soxhlet extracted with dry hexane for 48 h. The hexane was then removed from the extract under reduced pressure, and the recovered cyclic oligomers were subjected to VPC/MS analysis.

Alternatively, the contents of the polymerization tube were dissolved in dry THF and were treated with a solution of sodium trifluoroethoxide as described earlier.¹⁷ The product mixture was extracted with pentane to remove the cyclic oligomers which were then subjected to VPC analysis.

For the experiments summarized in Table III and Figure 1, Pyrex glass tubes (20mm x 6mm o.d.) were charged with 14 or 16 (0.05g), and were sealed and heated as described above. When removed from the oven, the tubes were allowed to cool to room temperature and were then opened. The contents were dissolved in CH₂Cl₂ and were subjected to VPC analysis.

Acknowledgments. This work was supported by the U.S. Office of Naval Research. We thank Linda W. Suszko for some of the preliminary experiments, and Robert Minard for the vpc/ms analyses.

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18. It was recognized that a potential error in the analysis was the possible equilibration of chloro- or fluorophosphazene small molecules

in the mass spectrometer. However, no evidence was found for equilibration when pure trimers or tetramers, 7-16, were injected into the instrument as controls.

19. A flame ionization detector was used for these measurements.
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Table I. Polymerization and Ring Expansion Reactions of
Cyclotriphosphazenes 7-12

	Starting Trimers					
	7	8	9	10	11	12
Temperature (°C)	300	300	300	300	250	250
Time	4-6 d	4-6 d	14 d	14 d	6-50 h	6-50 h
Yield Polymer (%)	49	59	0	0	46	42
Yield Oligomers (%)	15	13	100	100	30	23
<u>Detected Oligomers</u> ^a						
$N_3P_3X_5R$	<10	<10	<10	<10	<10	<10
$N_3P_3X_4R_2$	<10	<10	10-19	<10	40-49	20-29
$(NPXR)_3$	<10	<10	10-19	<10	<10	10-19
$N_4P_4X_7R$	<10	10-19	<10	<10	-	<10
$N_4P_4X_6R_2$	30-39	<10	20-29	<10	<10	10-19
$N_4P_4X_5R_3$	<10	<10	30-39	30-39	<10	20-29
$(NPXR)_4$	-	-	<10	<10	<10	<10
$N_5P_5X_9R$	<10	<10	<10	<10	-	-
$N_5P_5X_8R_2$	<10	<10	<10	<10	<10	<10
$N_5P_5X_7R_3$	<10	<10	<10	<10	<10	<10
$N_5P_5X_6R_4$	-	-	<10	<10	<10	<10
$(NPXR)_5$	-	-	<10	-	<10	<10

Table I (continued)

$N_6 P_6 X_{11} R$	20-29	<10	<10	<10	-	-
$N_6 P_6 X_{10} R_2$	<10	<10	<10	<10	-	-
$N_6 P_6 X_9 R_3$	<10	<10	<10	-	-	-
$N_6 P_6 X_8 R_4$	-	-	-	<10	-	-
$N_7 P_7 X_{13} R$	-	<10	-	-	-	-
$N_7 P_7 X_{12} R_2$	<10	<10	<10	-	-	-
$N_7 P_7 X_{11} R_3$	-	<10	-	-	-	-
$N_8 P_8 X_{15} R$	-	<10	-	-	-	-
$N_8 P_8 X_{14} R_2$	-	<10	-	-	-	-

^a X = fluorine or chlorine

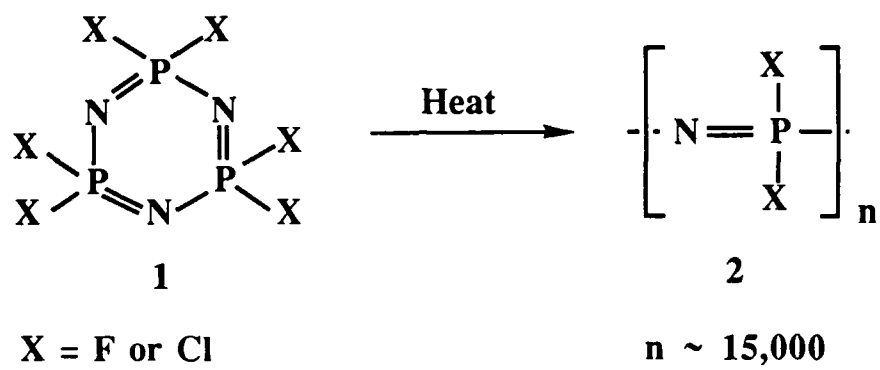
Table II. Polymerization and Ring Expansion and Contraction
Reactions of Cyclophosphazenes 13-15

	Starting Material									
	<u>13</u>	<u>13</u>	<u>13</u>	<u>13</u>	<u>14</u>	<u>14</u>	<u>15</u>	<u>15</u>	<u>15</u>	
Temperature (°C)	210	250	250	250	210	250	210	250	250	
Time	6-7 d	1 h	4-20 h	20 d	25 d	25 d	15 d	25 h	20 d	
Yield Polymer (%)	9	6	31	32	0	0	18	25	32	
Yield Oligomers (%)	68	68	44	16	91	95	52	42	14	
<u>Detected Oligomers</u> ^{a,b}										
(NPXR) ₃	51	53	45	10	93	21	10	14	12	
(NPXR) ₄	20	17	40	77	2	69	82	76	75	
(NPXR) ₅	4	4	5	10	1	9	6	8	10	
(NPXR) ₆	22	23	10	3	4	1	2	2	3	
(NPXR) ₇	3	3	-	-	-	-	-	-	-	

^a Percentages based on monomer units

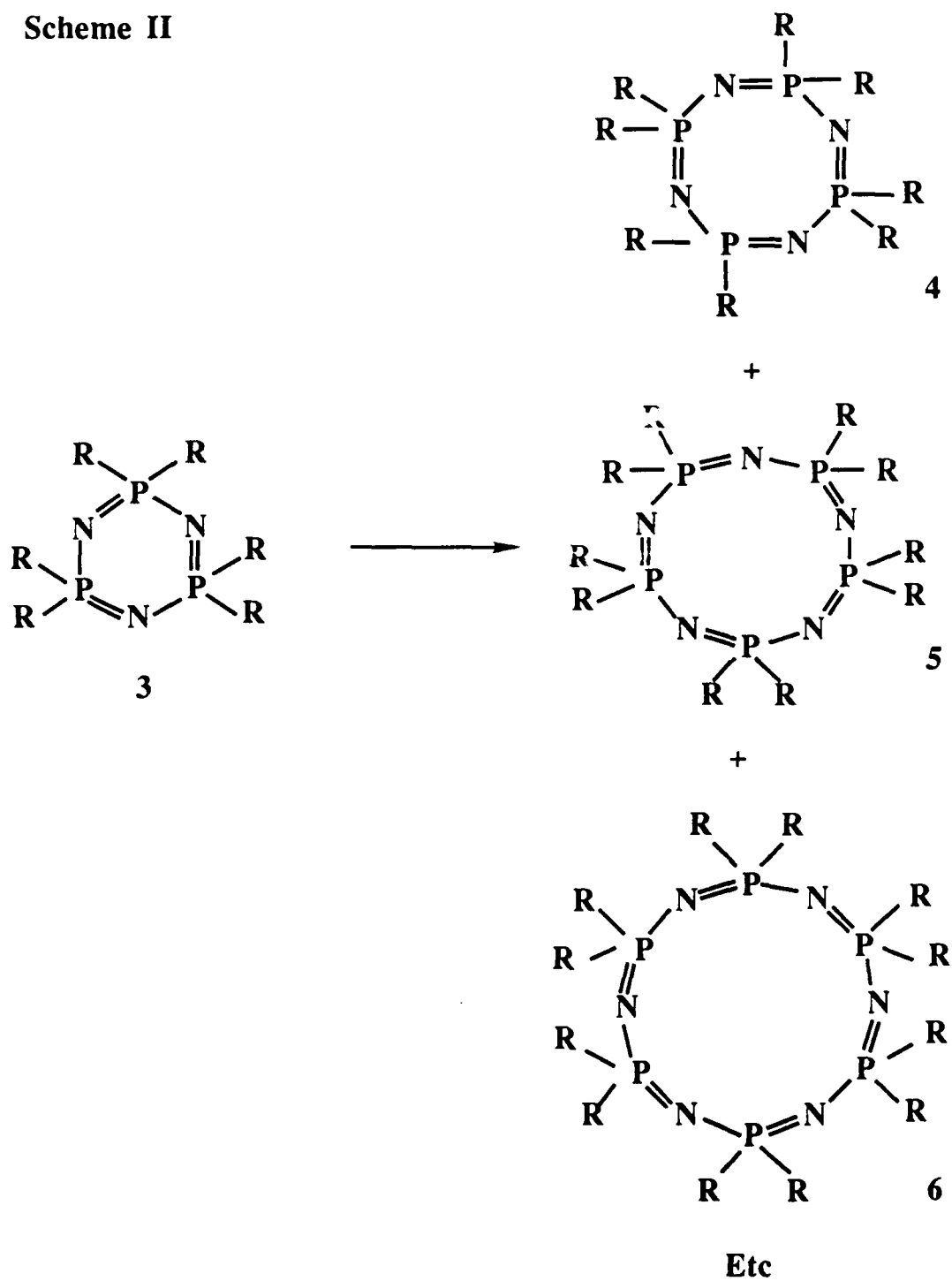
^b X = OCH₂CF₃

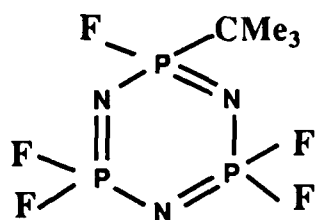
Scheme 1



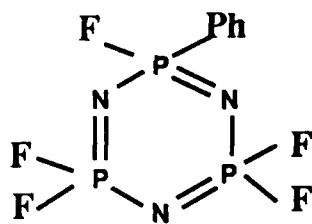
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Scheme II

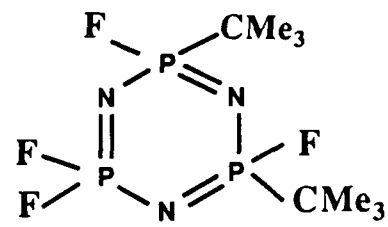




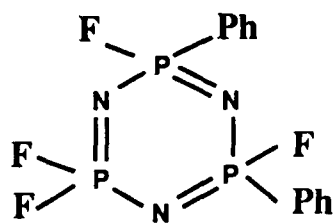
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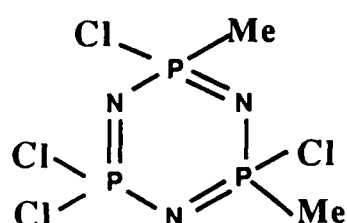
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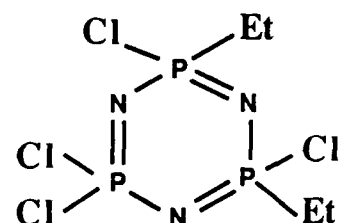
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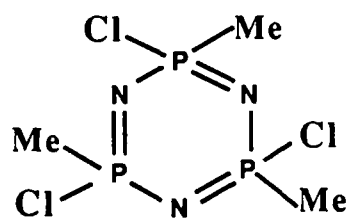
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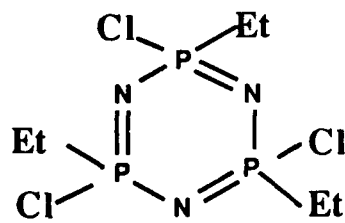
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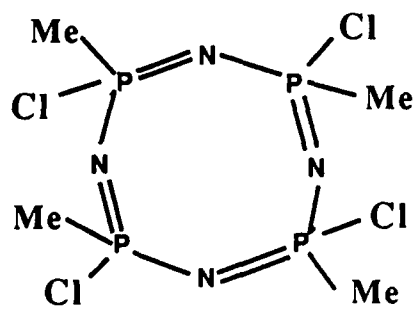
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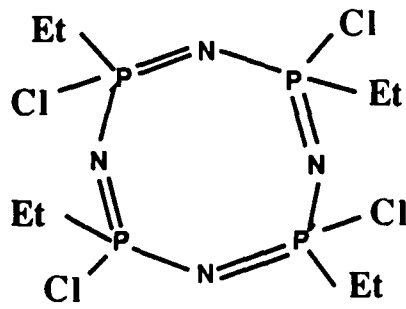
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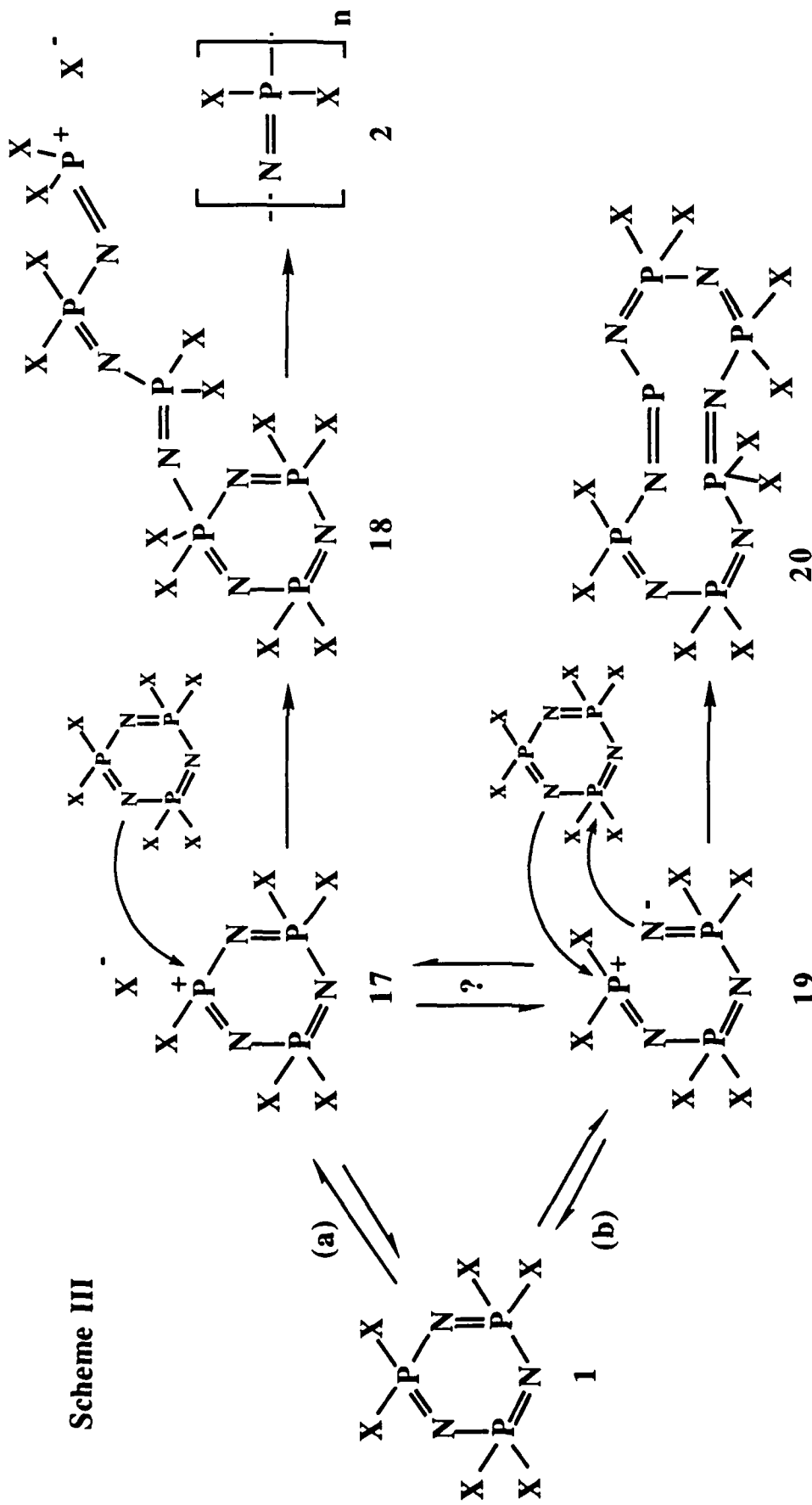


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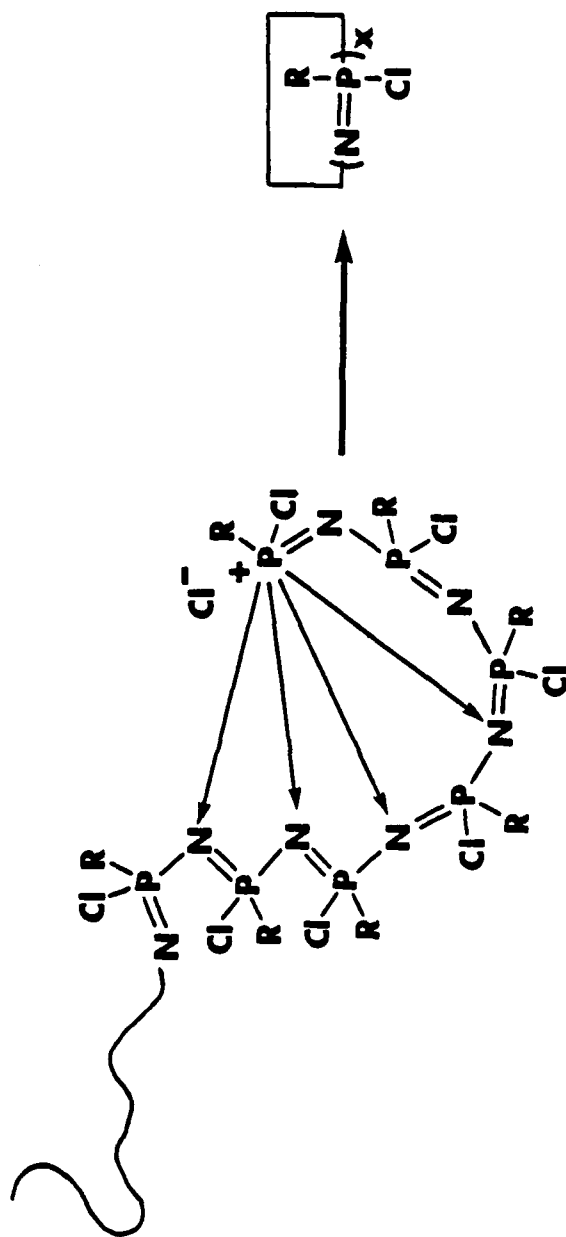
Scheme III



Pathway (a) would be favored if X is a readily ionizable group such as Cl, F, or perhaps OCH_2CF_3

Pathway (b) would be preferred if X is alkyl, aryl, or perhaps OCH_2CF_3

Scheme IV



21

Legend to Figure

Figure 1. Changes in the relative concentrations of cyclic phosphazenes as $(\text{NPClC}_2\text{H}_5)_3$ is heated at 250°C (● $(\text{NPClC}_2\text{H}_5)_4$; ■ $(\text{NPClC}_2\text{H}_5)_5$; ▲ $(\text{NPClC}_2\text{H}_5)_6$).

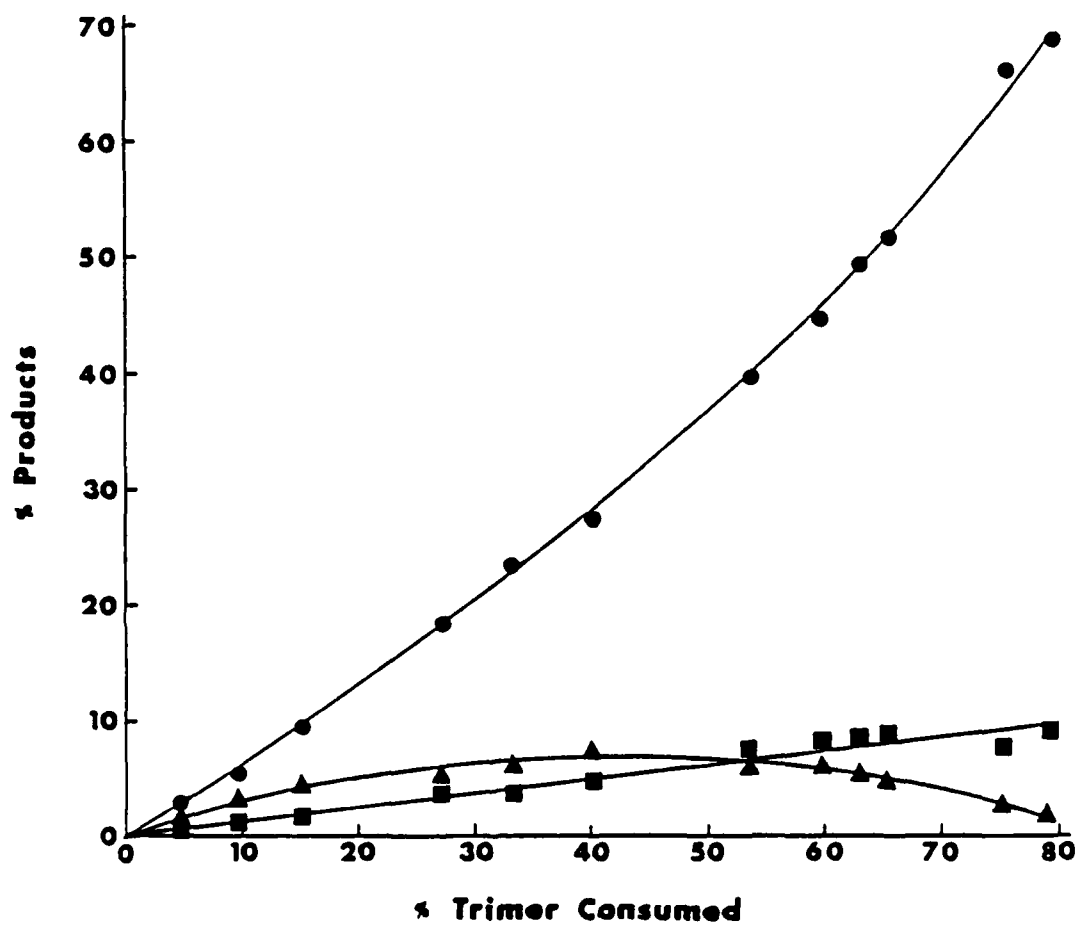


Figure 1

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Dr. Robert E. Cohen
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Annapolis, MD 21402

Dr. Curtis W. Frank
Department of Chemical Engineering
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Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

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413c037

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Case Western Reserve University
Cleveland, OH 44106-2699

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Dept. of Polymer Science & Engineering
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Amherst, MA 01002

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Department of Chemistry
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Blacksburg, VA 24061

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Dr. Kay L. Paciorek
Ultrasystems Defense and Space, Inc.
16775 Von Karman Avenue
Irvine, CA 92714

s400029srh

Dr. Martin Pomerantz
Department of Chemistry
University of Texas at Arlington
Box 19065
Arlington, TX 76019-0065
a400008df

Dr. T. J. Reinhart, Jr.
Nonmetallic Materials Division
Air Force Materials Laboratory (AFSC)
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333 Jay Street
Brooklyn, NY 11021

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Dr. Charles M. Roland
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Naval Research Laboratory
Washington, DC 20375-5000

413m009

Dr. Ronald Salovey
Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90089

413m010

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Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

413c004

Dr. Ferdinand Rodriguez
Department of Chemical Engineering
Cornell University
Ithaca, NY 14853

413c011

Dr. Michael F. Rubner
Materials Science & Engineering Dept.
Massachusetts Institute of Technology
Cambridge, MA 02139

413m007

Dr. Jacob Schaefer
Department of Chemistry
Washington University
St. Louis, MO 63130

413m001

Dr. Lawrence R. Sita
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

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Dr. Richard R. Schrock
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