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STRAINED INORGANIC HETEROCYCLIC COMPOUNDS AND THEIR
CONVERSION TO MACROCYCLES AND HIGH POLYMERS

by

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Prepared for publication as a chapter in
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Strained inorganic heterocyclic compounds and their conversion to macrocycles and high polymers

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Abstract

The ring expansion or contraction reactions of inorganic cyclic molecules often depend on structural features such as ring strain or side group intramolecular interactions. The ability of an inorganic cyclic system to undergo ring-opening polymerization to open-chain macromolecules usually depends on the same factors. In this paper the influence of transannular structures or heteroelements in the ring on ring-ring or ring-polymer interconversions will be discussed. Particular emphasis is placed on the way in which certain side groups switch the reaction pathway from ring expansion to polymerization. Polymers formed from these ring systems are of interest as electroactive or elastomeric materials, and structure-property relationships are discussed.

1. THE IMPORTANCE OF RING-OPENING POLYMERIZATION AND RING EXPANSION REACTIONS

The ring-opening polymerization of organic compounds such as tetrahydrofuran, trioxane, lactams, cyclic anhydrides, epoxides, or oxazolines¹ constitutes one of the most important methods for the synthesis of organic macromolecules. This is true also for the synthesis of inorganic high polymers from inorganic ring systems, although the polymerization chemistry of inorganic systems has received far less attention.

The two classical examples of ring-opening polymerization in the inorganic field are the polymerization of methylcyclsiloxanes to poly(dimethylsiloxane)² and the conversion of hexachlorocyclotriphosphazene to poly(dichlorophosphazene),³ a reaction that will be discussed in later sections. However, ring-opening polymerization also plays a major role in the synthesis of poly(sulfur nitride) (polythiazyl), polysilanes, and several other inorganic macromolecular systems.⁴ It appears likely that the general ring-opening polymerization process will be the main pathway used in the future for the preparation of yet-unsynthesized inorganic polymer systems.

Ring-opening polymerization is one extreme in a series of processes that start from inorganic small-molecule rings. Another important, and closely-related, reaction is ring expansion in which, for example, a six-membered ring is

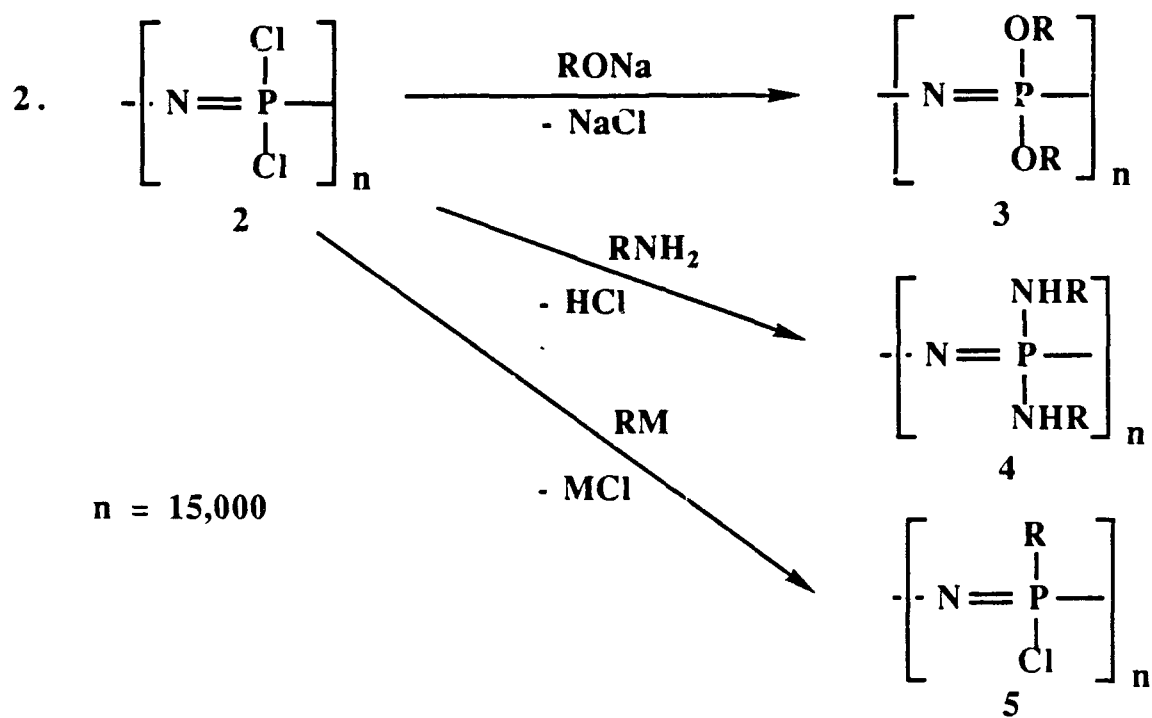
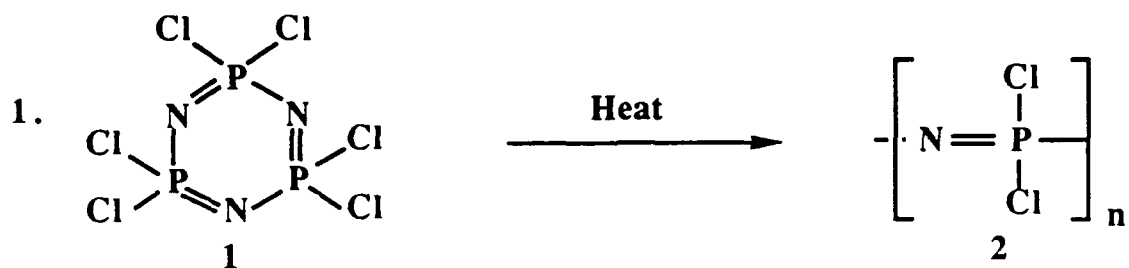
converted to an eight- or ten-membered macrocycle. The ring-expansion reaction may be the only practical pathway for the preparation of the macrocyclic species.

2. RING OPENING POLYMERIZATION OF CHLORO-CYCLOPHOSPHAZENES: THE CLASSICAL ROUTE TO POLY(ORGANOPHOSPHAZENES)

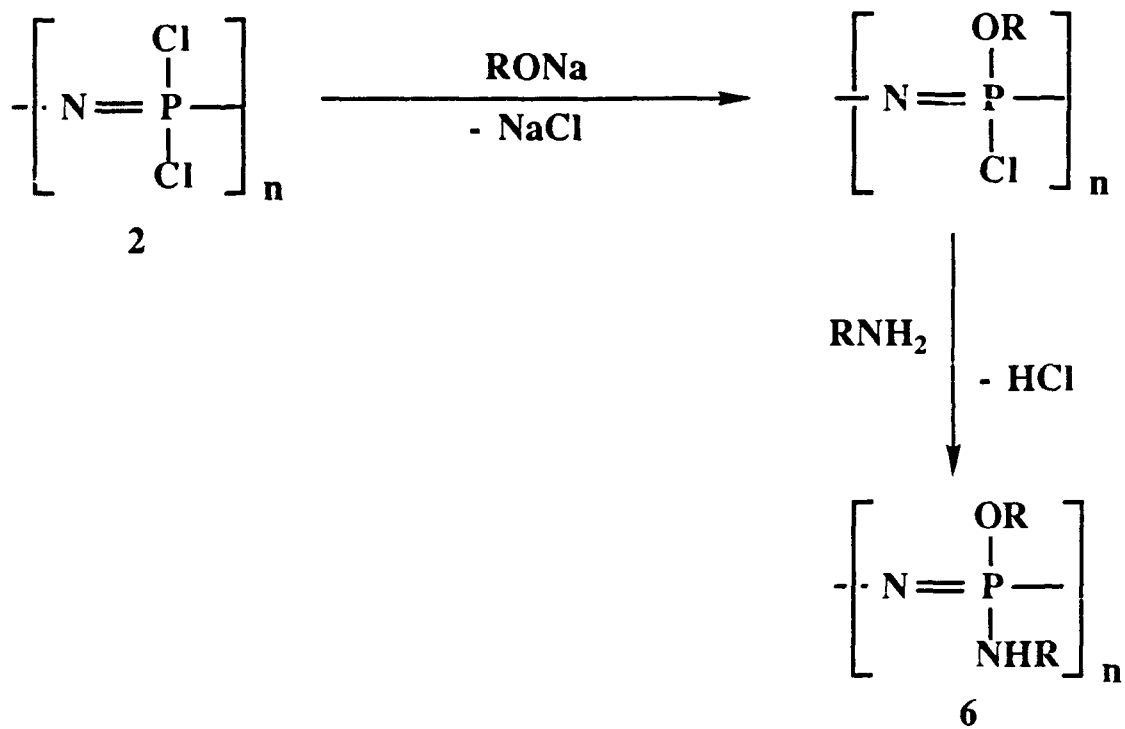
The ability of hexachlorocyclotriphosphazene (1) to polymerize when heated has been recognized in general terms since the 1890's, when Stokes described the conversion of the molten trimer to a hydrolytically unstable elastomer known as "inorganic rubber"⁵ Subsequent X-ray diffraction studies on the elastomer, carried out by Meyer, Lotmar, and Pankow in 1936⁶ indicated that the Stokes' material was composed of essentially linear chlorophosphazene chains. However, it was not until the 1960's that it became clear from the work of Allcock, Kugel, and Valan⁷⁻⁹ that inorganic rubber, as synthesized by the Stokes method, is a *crosslinked* polymeric material. The interchain crosslinks have a powerful and detrimental effect on the usefulness of the polymer. Specifically, the crosslinks prevent the polymer from dissolving in any solvent. This precludes clean chemical reactions from being carried out on the polymer. The need for chemical reactions arises from the hydrolytic sensitivity of *chlorophosphazenes*. Only by carrying out reaction chemistry on a chlorophosphazene polymer would it be possible to replace the chlorine atoms by hydrolytically stable organic side groups.

The solution to this problem, as discovered and developed in our research program,⁷⁻¹⁰ is summarized in Scheme I. First, it was found that the heating of *highly purified* hexachlorocyclotriphosphazene (1) at 250°C brings about polymerization in two stages. Initially, the cyclic trimer molecules undergo ring-opening polymerization to yield a generally linear high polymer (2). The reaction can be terminated at this stage. Beyond a certain point (typically after 70% conversion to the polymer) the macromolecules undergo crosslinking reactions. The uncrosslinked polymer is soluble in organic solvents such as benzene, toluene, or tetrahydrofuran, and in solution it functions as a highly reactive macromolecular intermediate for halogen replacement reactions of the types shown in Schemes I and II.⁷⁻⁵⁸ These organo-substituted polyphosphazenes (3-6) are generally stable to moisture, and have properties that, in many instances, are superior to those of classical organic polymers. A key feature of this synthesis route is that the side groups can be varied with ease, and changes in side group structure result in dramatic changes in polymer properties. By mid 1991 more than 300 different types of polyphosphazenes had been synthesized and characterized, with properties that range from those of elastomers to films, fibers, glasses, and with practical applications in aerospace engineering, biomedicine, and electro-optical devices. Approximately 2,000 papers and patents have now been published on polyphosphazenes, with the number increasing at a rate of about 200 per year. This is now a rapidly expanding area of polymers and materials science, and it represents one of the few clear examples in recent years of the way in which fundamental inorganic synthesis work can lead to tangible practical benefits. At the scientific level, the challenge is in the use of molecular design to correlate macromolecular and

SCHEME I
TWO STEP SYNTHESIS



SCHEME II
SEQUENTIAL SUBSTITUTION



$n = 15,000$

materials properties to specific molecular structural features, so that a set of target properties can form the basis of a program in macromolecular synthesis.

3. EXTENSION OF THE RING-OPENING POLYMERIZATION PROCESS TO OTHER CYCLOPHOSPHAZENES

The polymerization of hexachlorocyclotriphosphazene to the high polymer is but one of many possible access routes to poly(organophosphazenes). Fluoro- and bromo-cyclophosphazenes are also known, as are many species with both halogeno- and organic side groups. Can these cyclic trimers also be polymerized to high polymers? Chart 1 contains examples of several cyclotriphosphazenes that undergo ring-opening polymerization. The overall conversion of cyclic trimer to linear high polymer is the same in each case, although the details of the reaction conditions may be different.

The conversion of hexafluorocyclotriphosphazene (7) to poly(difluorophosphazene) was reported in 1956 by Seel and Langer^{59,60}. This reaction follows a similar sequence to that originally reported by Stokes. Thus, the heating of 7 at 350°C in an autoclave yielded a rubbery material that was insoluble in all solvents. We were subsequently able to show that termination of the polymerization before crosslinking occurs gives a form of poly(difluorophosphazene) that is soluble in fluorocarbon media.⁶¹⁻⁶³ Further heating leads to crosslinking. In solution the uncrosslinked polymer functions as a macromolecular intermediate and can be used as the starting point for the preparation of a wide variety of organophosphazene high polymers. However, the reactivities and substitution pathways that exist for the fluoro-polymer sometimes differ from those found for the chlorophosphazene system, and this provides additional opportunities for fine-tuning the structures of the final macromolecules.^{62,63} An advantage of poly(difluorophosphazene) over poly(dichlorophosphazene) is its ability to react with organometallic reagents without undergoing extensive skeletal cleavage. This provides an access route to polymers in which alkyl, aryl, or organometallic units are linked to the chain via P-C or P-metal bonds.⁶²⁻⁶⁵

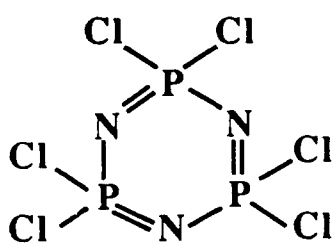
Hexabromocyclotriphosphazene (8) also forms a rubbery polymer when heated at 220°C, but the crosslinked form is the only modification yet isolated.^{66,67}

The remaining cyclic trimers shown in Chart 1 polymerize when heated, but their structures differ sufficiently from those of 1, 7, and 8 to raise some interesting questions. Isothiocyanatophosphazenes such as the cyclic trimer shown as 9 were polymerized first by Audrieth and coworkers in 1958.^{68,69} However, again the rubbery polymer appeared to have been crosslinked. Recently we have reexamined this reaction and have been able to isolate uncrosslinked poly[di(isothiocyano)phosphazene] by a careful control of the reaction conditions.⁷⁰ This polymer is a useful macromolecular intermediate in the sense that the isothiocyano side groups are capable of reacting with alcohols or amines to yield thiourethane and thiourea derivative polymers.⁷⁰ This chemistry was developed first at the cyclic trimer level, before transposition to the macromolecular system.

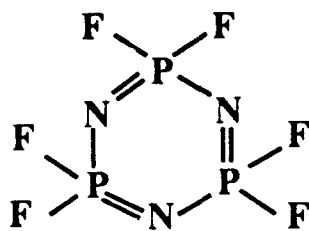
Small-molecule *phosphazocyclophosphazenes*, such as the two examples shown as 10 and 11, have been known for several years.⁷¹⁻⁸⁰ However, it has

CHART 1

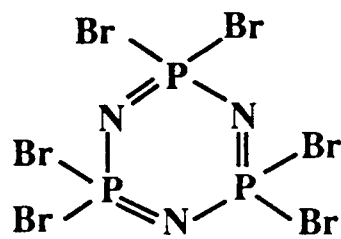
POLYMERIZABLE CYCLOPHOSPHAZENES



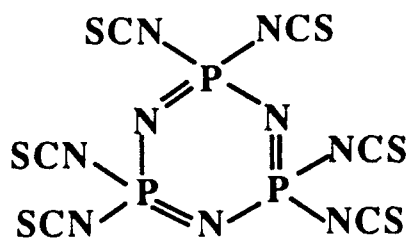
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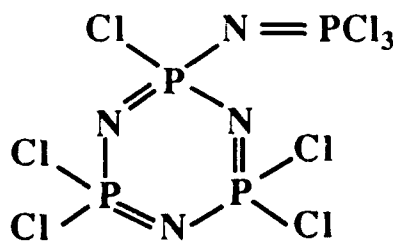
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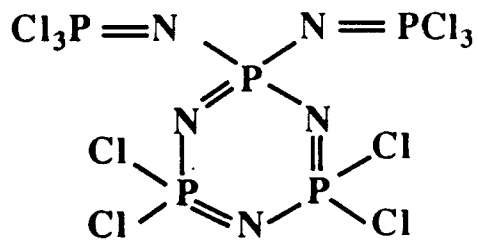
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9

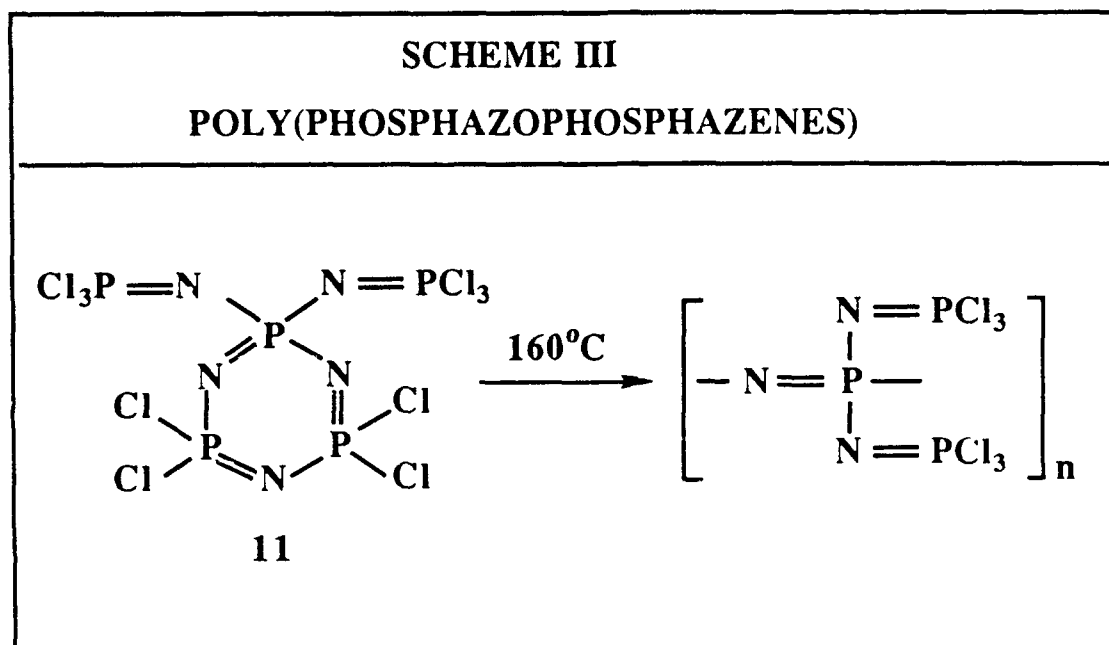


10



11

only recently been demonstrated that these cyclic trimers also undergo ring-opening polymerization when heated to give polymers of the types shown in Scheme III.⁸¹ In these, the phosphazo groups retain their integrity during the polymerization process and provide "controlled branch points" along the polymer chain. Chlorine replacement by oxo- or nitrogen-nucleophiles occurs, with the phosphazo-chlorine atoms being replaced first. The organic derivatives of these polymers constitute a new class of polyphosphazenes that promise to provide additional properties and uses.⁸²

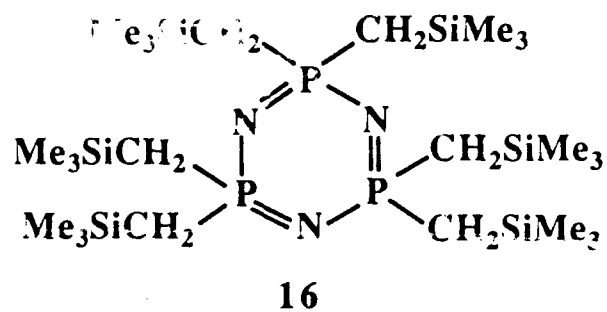
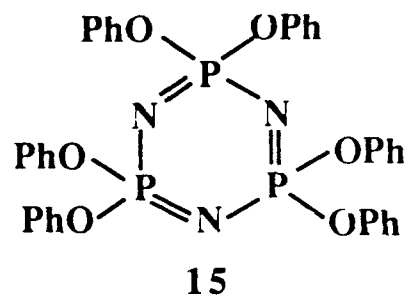
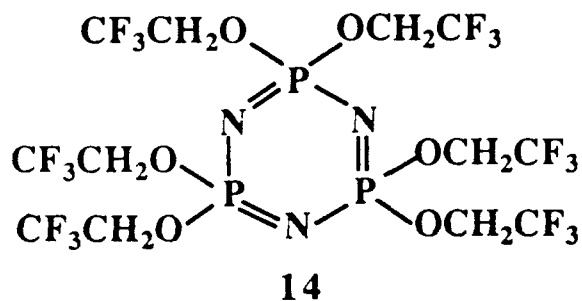
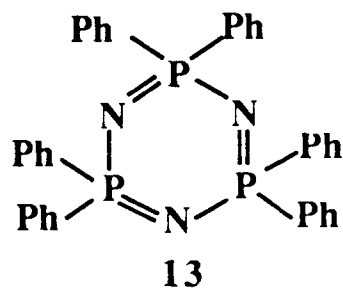
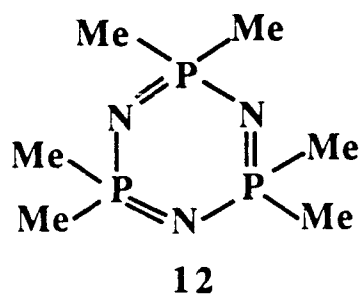


The cyclic trimers shown as 1 and 7-11 require different reaction conditions to induce polymerization. In particular, the temperature required for polymerization differs as the side units are changed. Thus, the minimum temperature required for the uncatalyzed polymerization decreases with different side units in the following order: $(\text{NPF}_2)_3$ (350°C) > $(\text{NPCl}_2)_3$ ($240\text{--}250^{\circ}\text{C}$) > $(\text{NPBr}_2)_3$ (220°C) > $\text{N}_3\text{P}_3\text{Cl}_5(\text{NPCl}_3)$ (180°C) > $\text{N}_3\text{P}_3\text{Cl}_4(\text{NTPCl}_3)_2$ (160°C) > $[\text{NP}(\text{NCS})_2]_3$ (100°C). As will be discussed, this trend may reflect the different ease with which the various side groups can thermally separate from phosphorus as anions, but this is not the only factor, as will be described later.

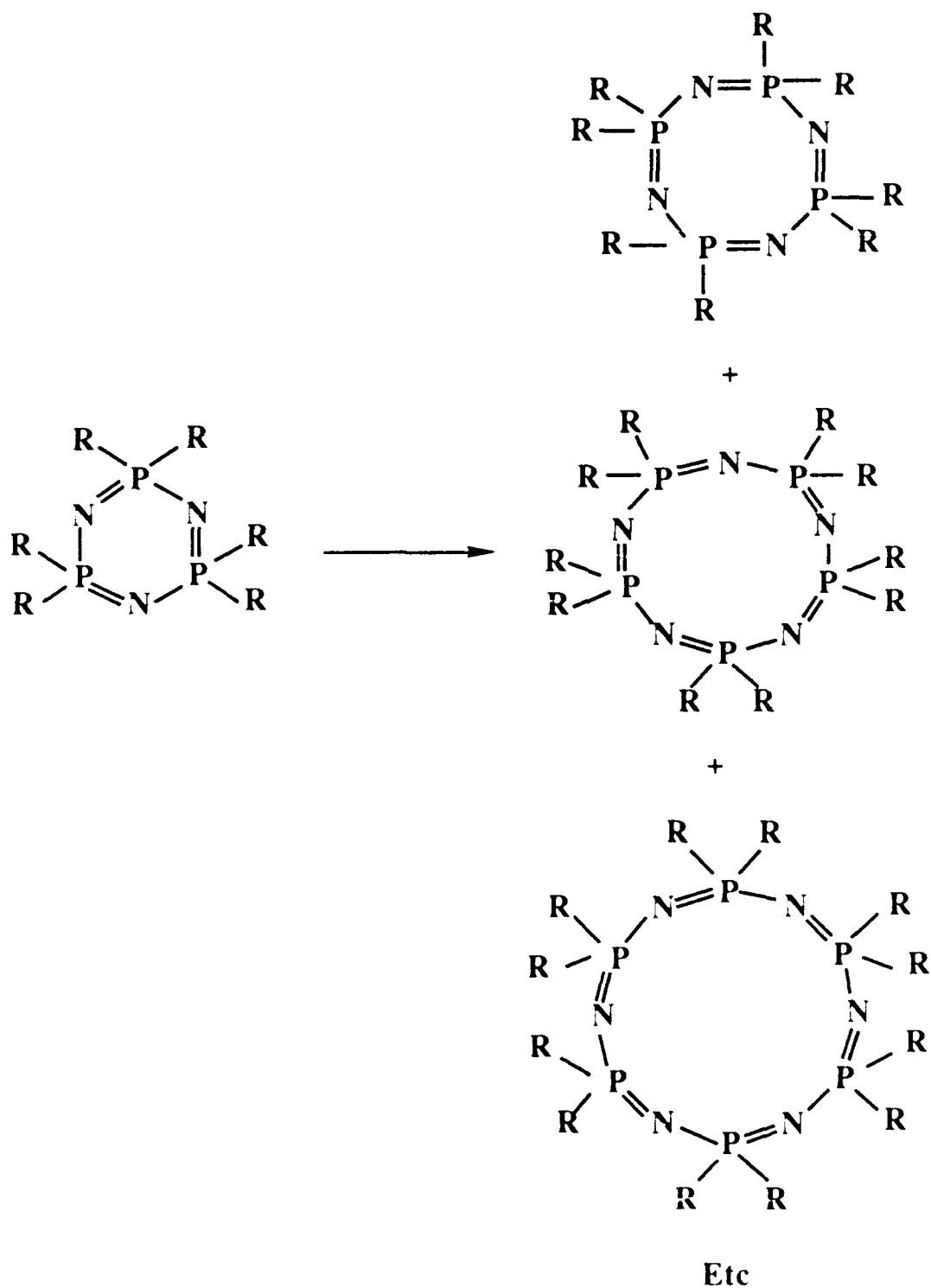
4. CYCLOPHOSHAZENES THAT RESIST POLYMERIZATION

A logical extension of the above reactions would be the polymerization of phosphazene cyclic trimers or tetramers that have organic side groups linked to phosphorus. Such a process would allow the synthesis of high polymers without the need for a subsequent macromolecular substitution step. Because substitution reactions are often easier to carry out at the small-molecule stage

CHART 2
NON-POLYMERIZABLE CYCLOPHOSPHAZENES



SCHEME IV
RING EXPANSION AND EQUILIBRATION



than at the high polymer level, this would constitute a considerable advantage. The compounds shown in Chart 2 are typical cyclophosphazenes that, in principle, could yield important high polymers.

Unfortunately, heating of these compounds does not lead to the formation of high polymers. Ring-expansion processes, as depicted schematically in Scheme IV, occur with species 12-14. Specifically, hexamethylcyclotriphosphazene (12), when heated, forms a cyclic trimer-cyclic tetramer equilibrate.⁸³ Similar ring-ring equilibrations occur with the phenyl (13) and trifluoroethoxy (14) trimers,^{84,85} and these reactions provide a marginally efficient route for the synthesis of cyclic tetramers, hexamers, and higher homologues without the need to prepare the corresponding halogeno-derivatives as intermediates. Hexaphenoxy-cyclotriphosphazene (15) apparently equilibrates but also undergoes a concurrent side group condensation process that leads to the linkage of cyclic trimeric rings.⁸⁶ Hexakis(trimethylsilylmethyl)-cyclotriphosphazene (16) neither ring expands nor undergoes side group condensation.⁸⁷

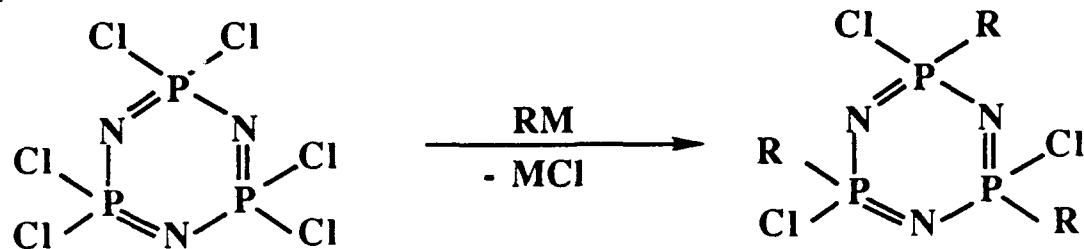
Why is the polymerization process apparently blocked when all the side groups attached to a cyclotriphosphazene are organic units? The most obvious explanation is that polymerization requires the presence of P-halogen or P-pseudohalogen units to provide a site for side group ionization and initiation of chain growth. It can be argued that P-O or P-C bonds are less prone to ionize, and that the polymerization mechanism is therefore blocked. This argument is not entirely valid, as will be discussed later for strained cyclophosphazenes. Moreover, the presence of P-O or P-C side units does not block the *ring expansion* process. Thus the possibility exists that polymerization and ring expansion may follow different mechanisms or be subject to different thermodynamic constraints. The failure of the organosilicon derivative 16 to either polymerize or ring expand is attributed to steric crowding by the bulky organosilicon side groups. Ring-opening or ring expansion may be inhibited because either reaction would bring the side groups into closer proximity and would generate a higher enthalpy system. This factor may also favor the conversion of 12-14 to cyclic tetramers, hexamers, or octamers, without the formation of linear high polymers. In polymer language, bulky side groups raise the ceiling temperature of the system to the point that polymers are thermodynamically unstable relative to small-molecule cyclic oligomers.

5. CYCLIC TRIMERS THAT BEAR BOTH HALOGENO- AND ORGANIC SIDE GROUPS

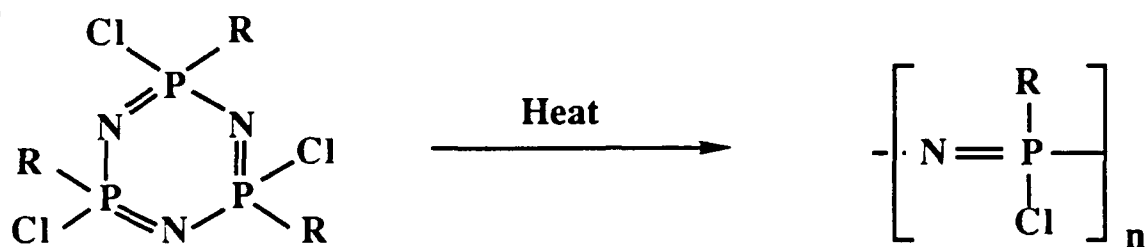
If perhalogeno-cyclophosphazenes undergo ring-opening polymerization, but the per-organo derivatives do not, what is the behavior of species that bear both halogen and organic side groups? We have devoted considerable attention to this question^{67,84,88-100} since, even if only a fraction of the side groups in a cyclic trimer are organic units, the polymerization process would still provide access to polymers that cannot be prepared by other routes. The long-range purpose of these studies is summarized in Scheme III. The exact behavior of the system depends on the ratio of organic to halogeno groups and on the steric dimensions of the organic components. Steric hindrance effects may tip the

SCHEME III
THREE STEP SYNTHESIS

1



2



3

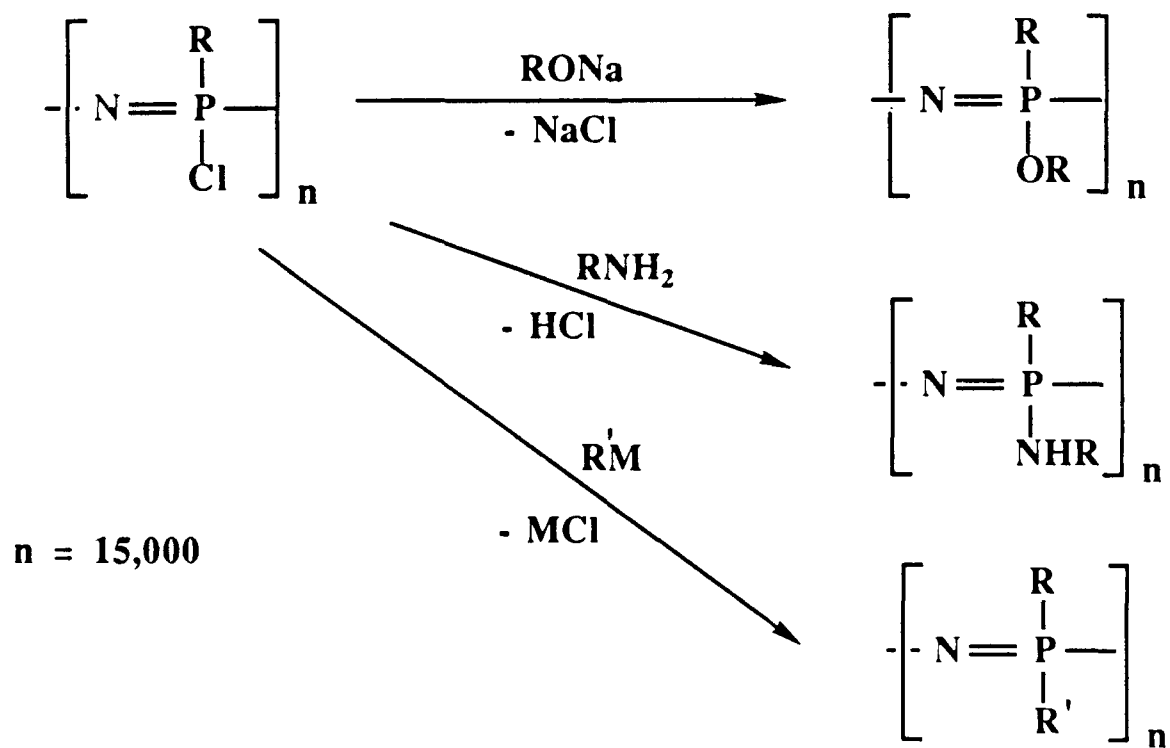
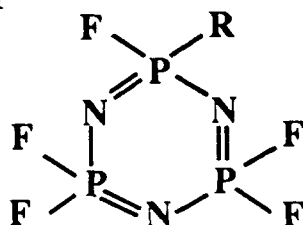


CHART 3

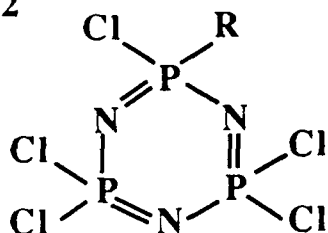
POLYMERIZATION AND RING-EQUILIBRATION REACTIONS OF NON-GEMINAL ALKYL-CYCLOPHOSPHAZENES

1



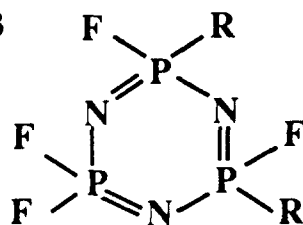
When R = Me, Et, t-Bu, or Ph, both polymerization and ring expansion occur.

2



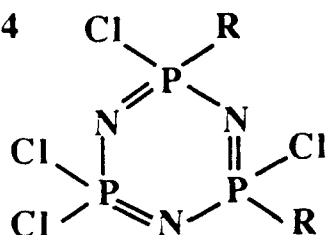
When R = Me, Et, n-Pr, n-Bu, CH₂CMe₃, CH₂SiMe₃, or phenyl-o-carborane, polymerization occurs. However, when R = i-Pr or t-Bu, side group reactions take place.

3



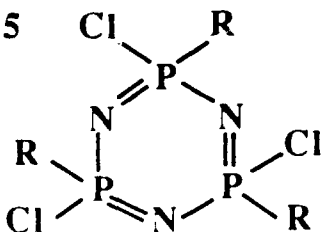
When R = CMe₃, or Ph, ring expansion is the main reaction.

4



When R = Me or Et, both polymerization and ring expansion occur.

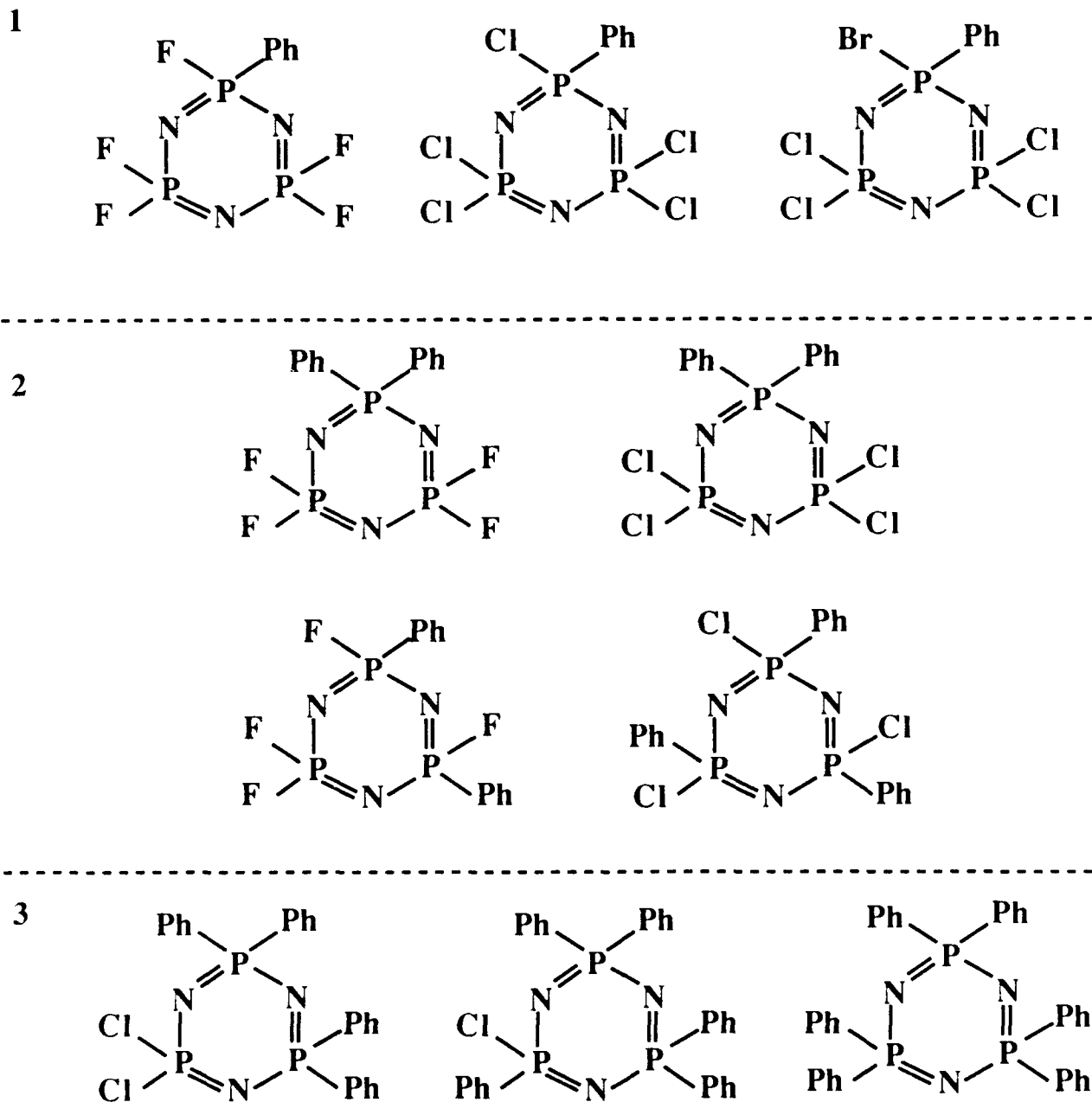
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When R = Me, polymerization and ring expansion are found, and the compound also copolymerizes with (NPCl₂)₃. However, when R = Et ring expansion predominates and polymerization occurs only during copolymerization with (NPCl₂)₃.

CHART 4

PHENYL-CYCLOPHOSPHAZENES



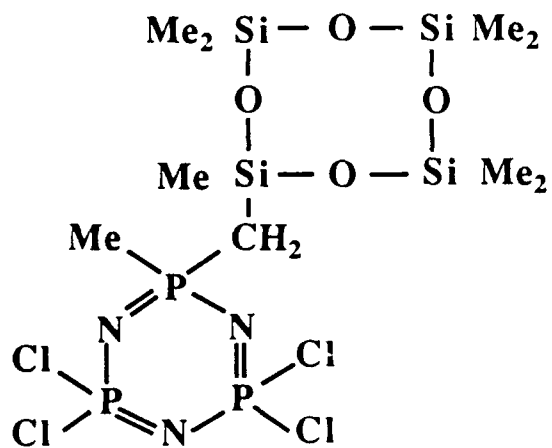
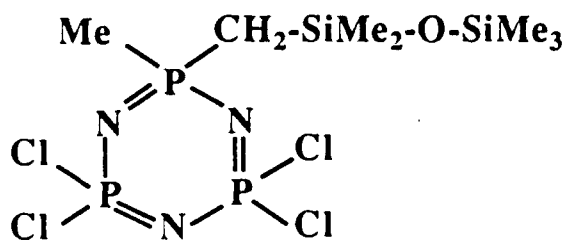
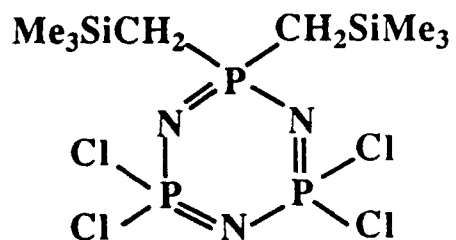
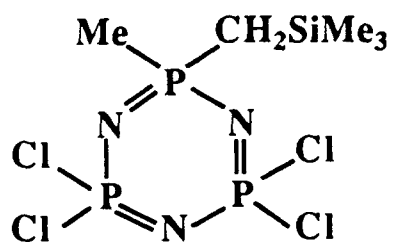
1 = Polymerize thermally, and copolymerize with $(\text{NPCl}_2)_3$.

Compound 18 also undergoes ring expansion.

2 = Do not homopolymerize, but copolymerize with $(\text{NPCl}_2)_3$, and undergo ring expansion.

3 = Do not homopolymerize, and inhibit polymerization of $(\text{NPCl}_2)_3$.
Undergo ring expansion.

CHART 5
GEMINAL ORGANOSILYL-CYCLOPHOSPHAZENES



balance between polymerization and ring expansion, as illustrated in the following examples.

Charts 3-5 show a number of alkyl- and aryl- halogeno phosphazene cyclic trimers prepared in our program by a variety of organometallic substitution routes.^{67,84,88-100} First, it should be noted that, when only one organic group is present per ring, polymerization usually proceeds unencumbered by the presence of the organic unit. The only exceptions are found when the organic side group can undergo reactions with the P-halogen bonds that are also present. For example, *i*-propyl- or *t*-butyl- groups eliminate alkyl chlorides and induce simultaneous ring-linkage reactions. Note that ring-expansion reactions also take place, especially when the halogen present is fluorine.

The presence of two organic groups per ring places some restrictions on the polymerization process. As shown in Chart 4, two geminal or non-geminal phenyl groups favor ring expansion rather than polymerization, but allow copolymerization with $(\text{NPCl}_2)_3$. Similar patterns are evident in the alkylphosphazene series, where increasing numbers of alkyl groups per molecule and increasing dimensions of the side groups favor ring-ring equilibration rather than polymerization. Non-gem- $(\text{NPClEt})_3$, for example, equilibrates to the cyclic tetramer and polymerizes only in the presence of $(\text{NPCl}_2)_3$, whereas the methyl analogue undergoes polymerization as well as ring expansion.^{99,101} Apart from the practical implications of these results and their influence on the design and synthesis of useful new materials, the data provide clues to the underlying mechanistic and thermodynamic factors that are at work. This aspect is considered in the following section.

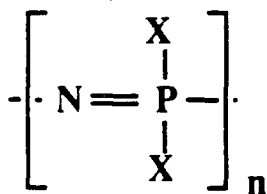
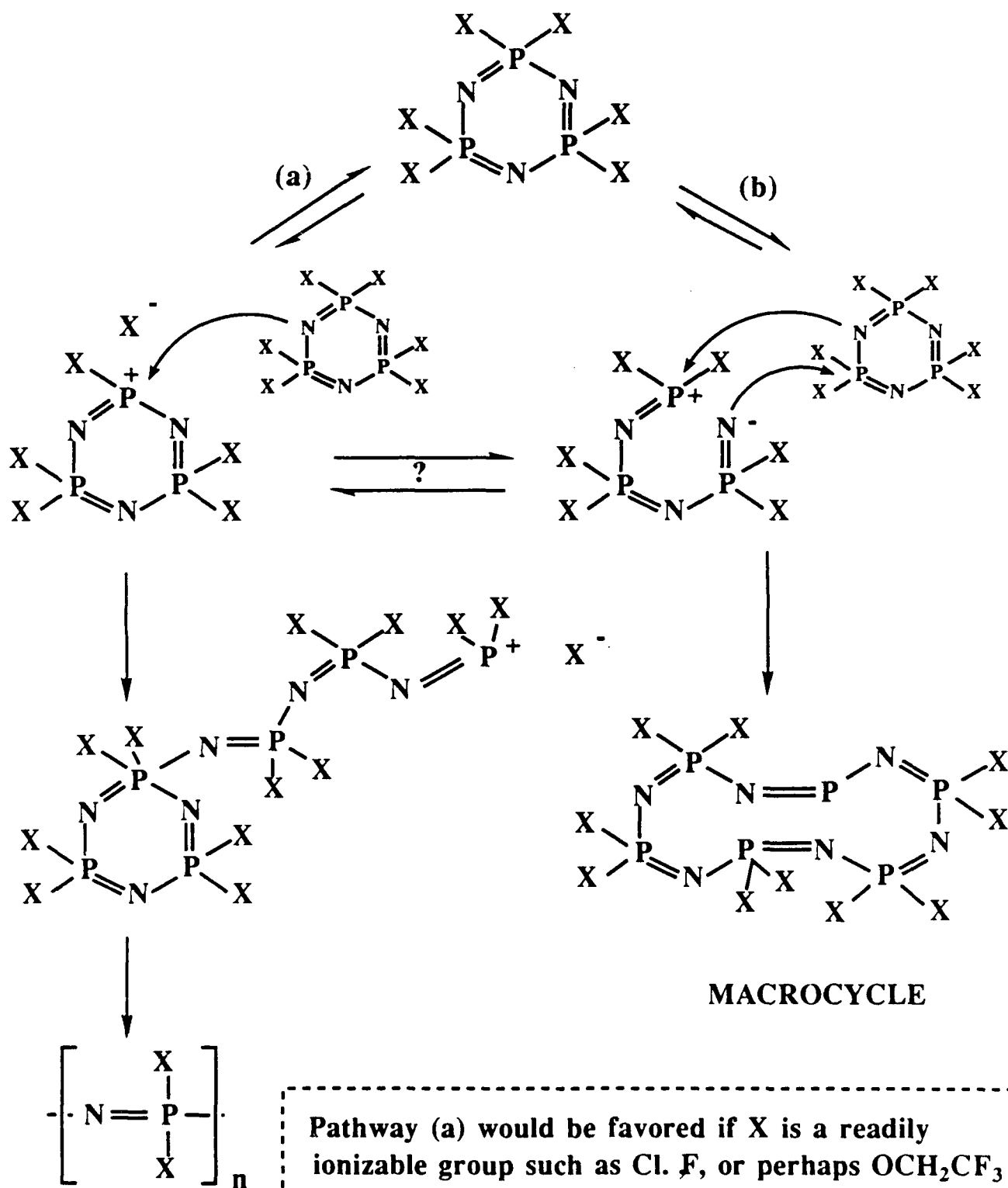
6. TWO POSSIBLE MECHANISMS

The earliest mechanistic studies on the polymerization of $(\text{NPCl}_2)_3$ drew attention to the role played by halogen ionization from phosphorus in these reactions.¹⁰²⁻¹⁰⁴ The ring-opening polymerization process proposed at that time is shown in mechanism a of Scheme V. Thermally-induced halogen ionization leads to the formation of a phosphazanium cation, which then attacks the ring nitrogen atom of a neighboring molecule to open that ring and initiate a cationic chain propagation process. Chain growth can lead to as many as 5,000 trimer molecules being incorporated into each macromolecule.

Alternatively (mechanism b), the possibility exists that the phosphorus-nitrogen bond will break instead of the bond to the side groups. If this occurs, the product will be a zwitterion that can attack another ring in a ring-fusion process. Thus, apart from the existence of a (presumably) unstable linear zwitterion, the ring equilibration reaction proceeds first by fusion of trimers to give cyclic hexamer, then nonamer, and so on. Intermediate sized rings arise in the later phases by ring contraction to cyclic tetramer, pentamer, etc. The pattern of ring formation detected in our studies provides some evidence for this mechanism.⁹⁹

Thus, a working hypothesis is that those side groups that favor side group ionization will favor polymerization, whereas those that ionize with difficulty but assist phosphorus-nitrogen bond cleavage will favor ring-ring equilibration.

SCHEME V **POLYMERIZATION AND RING-EXPANSION MECHANISMS**



POLYMER

7. EFFECT OF RING STRAIN INDUCED BY TRANSANNULAR STRUCTURES

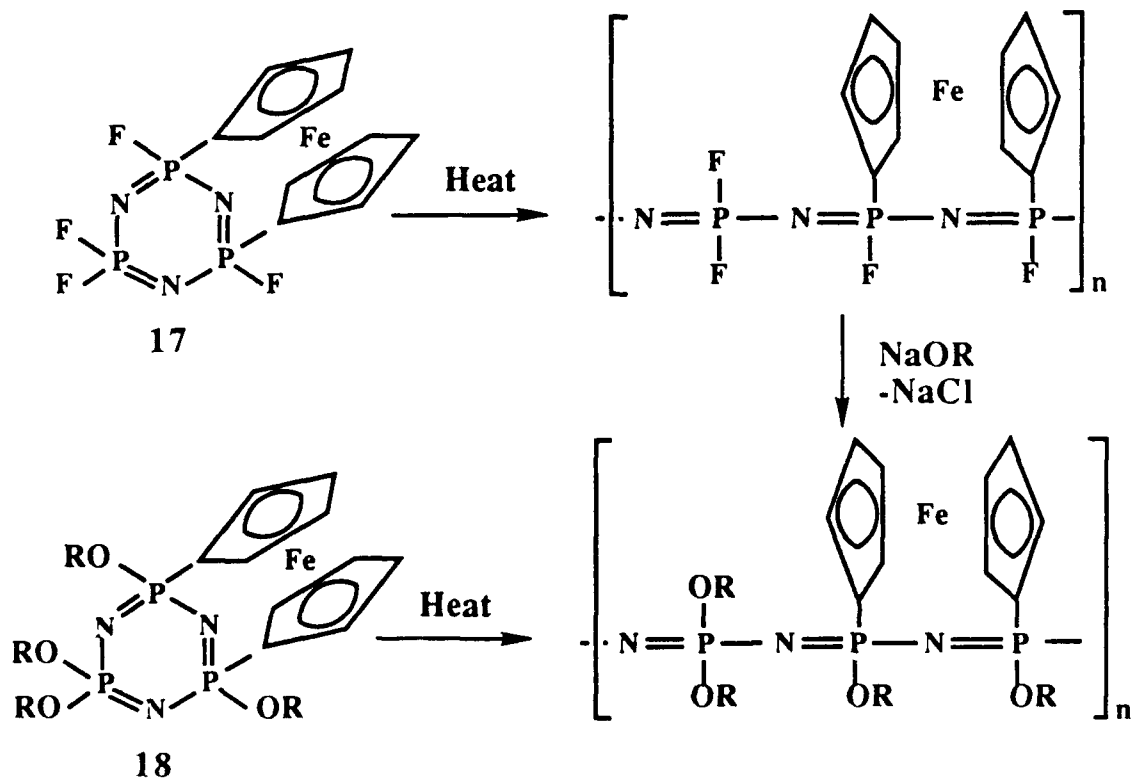
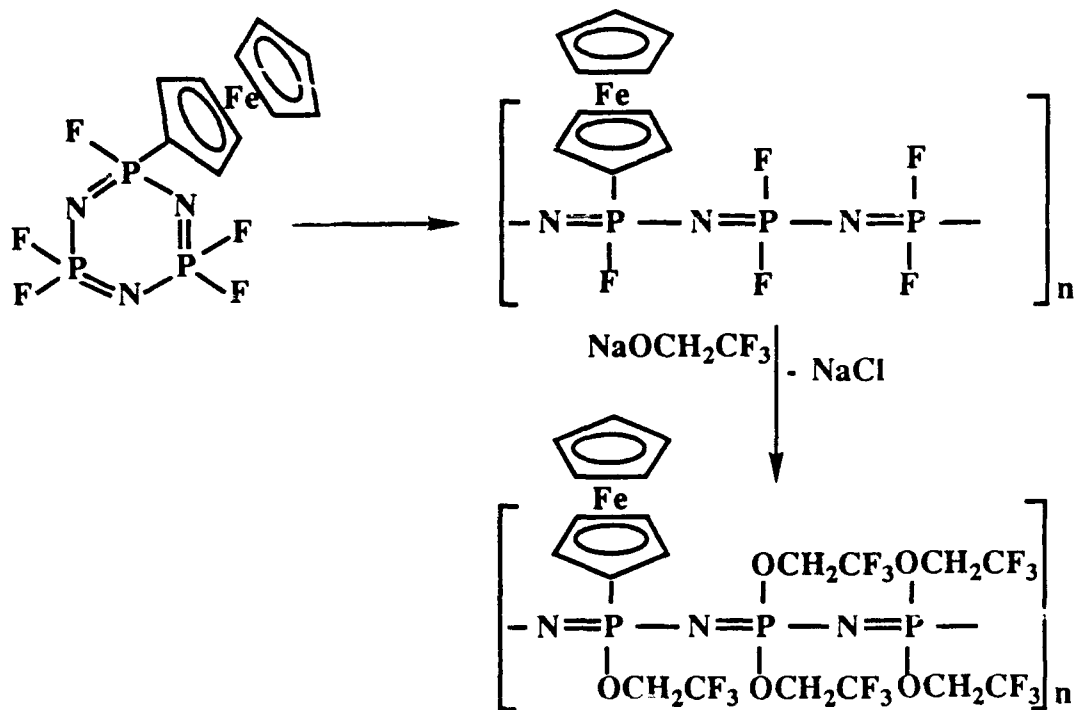
In recent years we have developed a number of organometallic reactions of phosphazenes that yield metallocenylphosphazenes, including derivatives that contain either pendent ferrocenyl or ruthenocenyl units or species in which the metallocene forms a transannular structure.¹⁰⁵⁻¹¹⁴ At the cyclic trimer level these compounds are interesting because they illustrate the strain-inducing properties of a transannular structure. For example, X-ray crystal structures show that the phosphazene ring in a compound such as 17 is severely puckered to accommodate to the structural requirements of the rigid metallocene unit. The metallocene is hardly distorted at all. Pendent metallocenyl units do not significantly affect the conformation of the phosphazene ring.

However, from the viewpoint of polymerization chemistry, the significant fact is that the transannular structure undergoes *phosphazene* ring opening polymerization and does so at a faster rate than the structure with pendent metallocenyl units. Thus, it appears that phosphazene polymerization can be assisted by a release of ring strain. The overall reaction pathway developed for this and related systems is illustrated in Scheme VI.

In addition, it has recently been found¹¹² that transannular metallocenyl cyclophosphazenes (18) that bear organic cosubstituents only, such as trifluoroethoxy groups, polymerize readily in the presence of traces of $(\text{NPCl}_2)_3$ used as an initiator. In a few cases the phosphazene undergoes ring-opening polymerization even in the absence of a halogen-containing initiator. Presumably this means that, if the ring strain inducement is sufficiently high, polymerization may occur via the ring fusion mechanism. Support for this idea came from the observation that transannular-linked trimers that bear bulky aryloxy cosubstituents do not polymerize, but instead ring-expand to the cyclic hexamer when heated. Clearly a balance of ring strain and side group steric hindrance allows a subtle control to be exercised over the reaction pathway. The presence of two transannular metallocene structures, as in the di-ruthenocenyl cyclic tetramer, $1,5,3,7\text{-N}_4\text{P}_4\text{F}_4[(n\text{-C}_5\text{H}_4)_2\text{Ru}]_2$, shown in Figure 1, not only prevents polymerization and ring-ring equilibration, but also inhibits replacement of the fluorine atoms by organic nucleophiles or hydroxide ion, since the backside attack mechanism at phosphorus is blocked.

Figure 1. Structure of $1,5,3,7\text{-N}_4\text{P}_4\text{F}_4[(n\text{-C}_5\text{H}_4)_2\text{Ru}]_2$

SCHEME VI
POLY(FERROCENYLPHOSHAZENES)



Metallocenylphosphazene polymers produced by these methods have a number of practical uses. One of the most interesting is their use as redox polymers and materials which, when coated on the surface of electrodes, function as electrode mediator catalysts. Since ferrocenylphosphazenes can be copolymerized with ruthenocenylphosphazenes, the possibility also exists that electron jumps can take place from one metallocene unit to another along the same chain, and this further increases the possibilities for catalytic processes.

8. RING STRAIN GENERATED BY THE PRESENCE OF HETEROELEMENTS

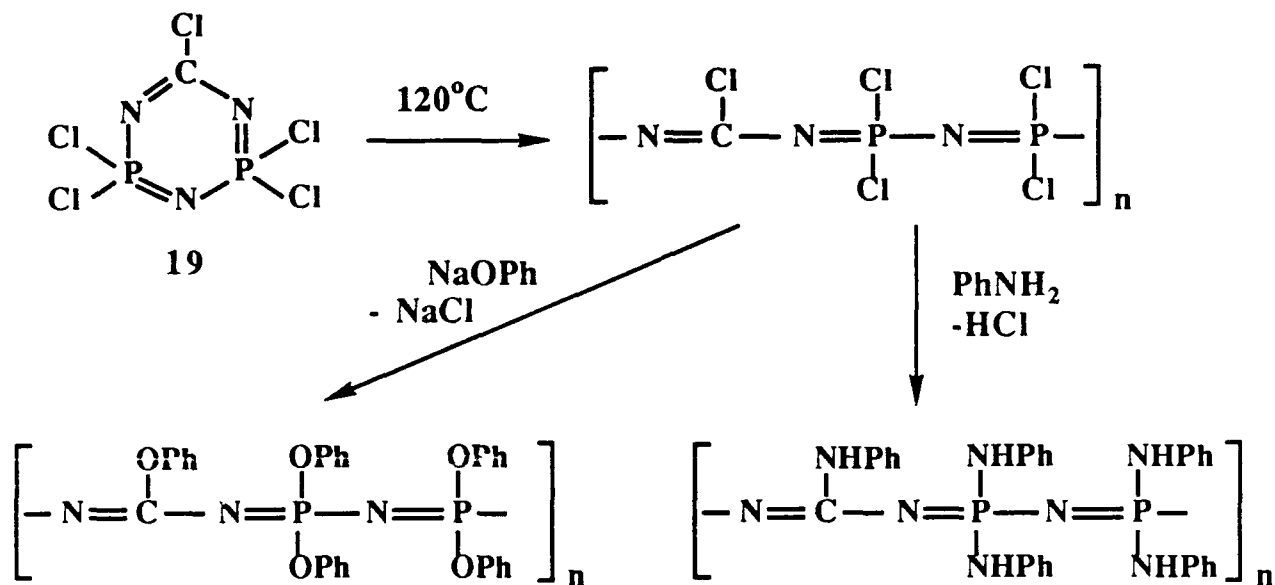
Our experience with the effects of ring strain on phosphazene ring-opening polymerization led to the possibility that strain could also be designed into the ring by another method - by the introduction of a heteroatom in place of phosphorus. Any differences in atomic size and bonding character might destabilize the ring to the extent that polymerization would occur under relatively mild conditions.

Cyclic heteroelementophosphazenes have been known for a number of years. For example, the cyclocarbophosphazene **19** was first reported by Fluck, Schmid, and Haubold in 1975,¹¹⁵ and the cyclothiophosphazene **20** was described by Roesky in 1972.¹¹⁶ Indeed, Schmidpeter and Schindler in 1968¹¹⁷ reported that the C-phenyl analogue of carbophosphazene **19** underwent an unusual ring-opening polymerization to poly(dichlorophosphazene) accompanied by extrusion of benzonitrile. In retrospect, this appears to be strong evidence for the release of ring strain.

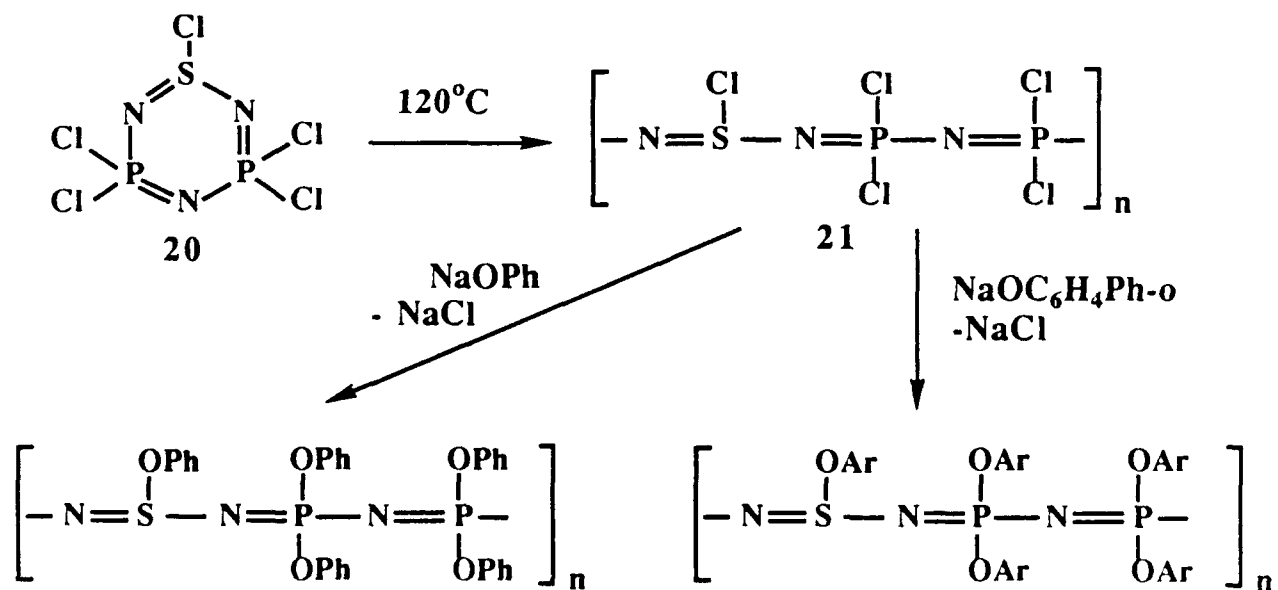
Our results show that carbophosphazene **19** behaves in a manner that is reminiscent of $(\text{NPCl}_2)_3$ in the sense that, when heated at temperatures above 150°C, compound **19** yields a crosslinked polymer. However, at temperatures between 120°C and 150°C, a clean, ring-opening polymerization occurs to give the uncrosslinked poly(carbophosphazene).^{118,119} This reaction, and the use of the polymer as a reactive macromolecular intermediate, are shown in Scheme VII. The unusually low temperature needed for this ring-opening polymerization probably reflects a release of ring strain. The presence of one carbon atom in each (trimeric) repeat unit raises the glass transition temperature (T_g) relative to the classical polyphosphazene counterparts with equivalent side groups. This is strong evidence that the carbon-nitrogen bonds raise the barrier to torsional motions, an effect that can be traced to the higher barrier of $p_\pi-p_\pi$ compared with $d_\pi-p_\pi$ bonds. This stiffening of the chain in carbophosphazenes offers additional opportunities for materials design.

A second illustration of these principles is shown in Scheme VIII. In recent work in our laboratory¹²⁰ it has been shown that the thiophosphazene cyclic trimer **20** polymerizes to poly(thiophosphazene) **21** at the surprisingly low temperature of 80-90°C, and that this polymer too undergoes halogen replacement by organic groups. The method has also been extended to the polymerization of a sulfur VI thiophosphazene,¹²¹ and the expectation exists that other heteroelemento-phosphazenes may provide a general route to a wide variety of new polymers.

SCHEME VII
POLY(CARBOPHOSPHAZENE) SYNTHESIS



SCHEME VIII
POLY(THIOPHOSPHAZENE) SYNTHESIS



9. GENERAL IMPLICATIONS FOR THE FUTURE

The synthesis of new polymers based on the inorganic elements promises to be a major area of research in the coming years. Polymers of this type bridge the gap between classical petrochemical polymers on the one hand and ceramics, metals, and semiconductors on the other. The objective of our research program has been to devise and synthesize polymers that can be "tuned" structurally to generate combinations of properties that are not available within the classical areas of materials science. This has required a broad approach to the subject, starting at the level of small-molecule reactions with inorganic rings,¹²² study of mechanisms, and X-ray, NMR, and other structural investigations, and then extending this information first to the level of individual polymer molecules, and later to the design and synthesis of solid materials and surfaces.^{46,123} It seems probable that this approach may prove to be the best one for the development of other macromolecular and materials systems in the future.

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