(27) P. A. Yeats, B. F. E. Ford, J. R. Sams, and F. Aubke, *Chem. Commun.*, 791 (1969).
(28) B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Inorg. Nucl. Chem.*, **33**, 23 (1971).
(29) T. H. Tan, J. R. Dalziel, P. A. Yeats, J. R. Sams, R. C. Thompson, and F. Aubke, *Can. J. Chem.*, **50**, 1843 (1972).
(30) B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, **8**, 1120 (1969).
(31) P. J. Smith, *Organomet. Chem. Rev.*, **5**, 373 (1970).

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

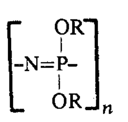
Ring-Ring and Ring-Chain Equilibration of Dimethylphosphazenes. Relationship to Phosphazene Polymerization[1,2]

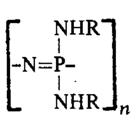
H. R. ALLCOCK* and D. B. PATTERSON

Received September 20, 1976 AIC60699R

Hexamethylcyclotriphosphazene, $[NP(CH_3)_2]_3$, and octamethylcyclotetraphosphazene, $[NP(CH_3)_2]_4$, participate in a ring-ring equilibration between 200 and 350 °C, but they do not polymerize. A ΔH value of 10.2 kcal and a ΔS value of 14.3 eu were determined for the tetramer-trimer interconversion. The equilibration is inhibited by base. Acids accelerate equilibration and also yield linear low molecular weight compounds: these species cyclize to III and IV when heated. The results are compared with the ring-high polymer and ring-ring interconversions in the halogenophosphazene, dimethylsiloxane, dimethylsilthiane, and polysulfur series.

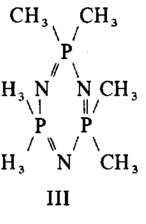
The synthesis of high molecular weight poly(organophosphazenes) (I) and (II) by the nucleophilic replacement of halogen in poly(dichlorophosphazene) has been described in earlier papers.[3-11] This earlier work[11] suggested that a marked increase in thermal stability might be anticipated if the substituent groups could be restricted to alkyl or aryl residues bonded directly to phosphorus. This viewpoint was based on the observation that bulky substituent groups (such as phenoxy) destabilized the polymer thermodynamically and favored depolymerization at high temperatures to cyclic oligomers. Moreover, the mechanisms of depolymerization and decomposition were believed to be connected with the presence of ionizable or displaceable groups such as alkoxy or aryloxy. Thus, a prime objective in phosphazene chemistry is the synthesis of high polymers that contain short alkyl or aryl residues as side units.


$$\left[-N{=}P(OR)_2-\right]_n$$
I


$$\left[-N{=}P(NHR)_2-\right]_n$$
II

In an earlier paper we reported the synthesis of polymers that contained both phenyl *and* halogeno, alkoxy, or amino substituents.[12] However, up to the present no authentic linear high polymers have been reported which contain *only* alkyl or aryl substituent groups. The most definitive attempt was by Sisler, Frazier, Rice, and Sanchez,[13] who reported the formation of oligomers or low polymers of dimethylphosphazene by the pyrolysis of dimethyldiaminophosphonium chloride.

Our interest in methylphosphazenes was prompted by the realization that the small steric size of the methyl group and the high bond strength of P—C bonds ($Me_3P{=}O$ can be heated without decomposition to 700 °C[14]) offered the prospect that the cyclic phosphazenes, $[NP(CH_3)_2]_{3\text{ and }4}$ (III and IV), might be polymerizable to thermally stable linear high polymers. Earlier work had suggested that the polymerizability of $(NPF_2)_3$, $(NPCl_2)_3$, and $(NPBr_2)_3$ was connected with the presence of small, ionizable (or hydrolyzable) halogen substituents, while the nonpolymerizability of $[NP(OC_6H_5)_2]_3$ and $[NP(C_6H_5)_2]_4$ was connected with the relatively large steric size of the substituent groups.[12] On the other hand, it was thought possible that, although thermal ionization or hydrolysis of methyl groups from phosphorus was unlikely, the steric inhibition to polymerization would be far less than that found for alkoxy, aryloxy, or aryl groups.


III

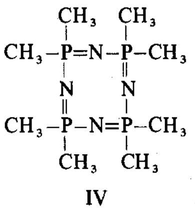

IV

Table I. Equilibration of $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$[a]

Temp, °C	Starting material	Reaction time, days	Final compn, mol % $[NP(CH_3)_2]_3$	$[NP(CH_3)_2]_4$
346.5	$[NP(CH_3)_2]_3$	4	48.6	51.4
346.5	$[NP(CH_3)_2]_4$	4	45.4	54.6
250.0	$[NP(CH_3)_2]_3$[b]	11	36.3	63.7
250.0	$[NP(CH_3)_2]_4$[b]	11	37.1	62.9

[a] In the molten bulk phase. [b] 1 wt % $[NP(CH_3)_2]_4 \cdot 2HCl$ added. Other reactions carried out in the absence of this reagent gave essentially the same result.

Results and Discussion

Ring-Ring Equilibration. When pure $[NP(CH_3)_2]_3$ or $[NP(CH_3)_2]_4$ was heated, equilibration occurred to yield mixtures of the two. In no case was more than a trace (<1%) of higher cyclic oligomers formed during this process. As the temperature was raised from 200 to 349.5 °C (Table I), the proportion of trimer in the equilibrate increased markedly. For the equilibration system

$$3[NP(CH_3)_2]_4 \rightleftharpoons 4[NP(CH_3)_2]_3$$

it was calculated that $\Delta H = +10.2$ kcal and $\Delta S = +14.3$ eu. Thus, the trimer is destabilized by about 1 kcal/monomer unit.

This large value of ΔH could be explained in three ways. First, it is possible that the cyclic tetramer is in some way electronically stabilized to a greater degree than is the trimer. This explanation is difficult to accept because (a) the tetramer is known to be puckered (at least in the solid state)[15] and (b) little or no evidence has been produced to suggest that the tetramer is electronically stabilized more than the trimer when

Table II

System[a]	ΔH/ monomer unit, kcal	Ref
$4[NP(CH_3)_2]_3 \rightleftharpoons 3[NP(CH_3)_2]_4$	0.9	This work
$4[OSi(CH_3)_2]_3 \rightleftharpoons 3[OSi(CH_3)_2]_4$	1–4[b]	16
$3[SSi(CH_3)_2]_2 \rightleftharpoons 2[SSi(CH_3)_2]_3$	3	17
$4(S\text{–}S)_3 \rightleftharpoons 3(S\text{–}S)_4$	1.75[c]	18

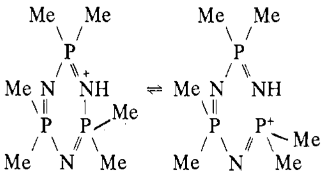
[a] The more stable cyclic species is shown on the right. [b] The value of 4 kcal/monomer unit is considered to be the least accurate of this range. [c] For the purposes of comparison, an S_2 residue is considered as a monomer unit in this system.

other substituent groups (e.g., Cl, C_6H_5, etc.) are present. Second, the possibility exists that the side group interactions are more severe in the trimer than in the tetramer, but again no structural analogy for this argument can be found elsewhere in phosphazene chemistry. Finally, it is possible that the trimer is destabilized by ~1 kcal/monomer unit by ring strain.

Ring strain is undoubtedly a factor in the destabilization of $[OSi(CH_2)_2]_3$ and $(S\text{–}S)_3$ relative to their cyclic tetramers and in the destabilization of $[SSi(CH_3)_2]_2$ relative to its cyclic trimer (Table II). However, high polymer is also a product from the equilibration of dimethylsiloxane and sulfur cyclic oligomers whereas, in the dimethylphosphazene series, no polymer is formed.

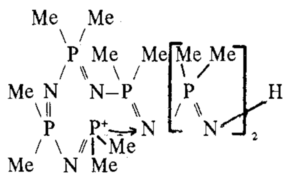
The mechanism of dimethylphosphazene ring–ring equilibration has not been elucidated in detail. However, mechanisms based on dissociation to the monomer, ionization of methyl groups from phosphorus, ring cleavage to yield zwitterions, or homolytic ring cleavage to yield diradicals seem unlikely in view of the known chemistry of other cyclic phosphazenes.[11] The possibility of ring–ring coalescence reactions (by the concerted nucleophilic attack of a ring nitrogen atom on the phosphorus of another ring) cannot be conclusively eliminated.

The most plausible mechanism is one that requires protonation of a ring nitrogen (V) followed by ring cleavage (VI).



V VI

Such a phosphazenium cation could then attack another ring to lengthen the chain. Cyclic trimer or tetramer could be re-formed by a backbiting mechanism (VII). Evidence in favor of this mechanism includes the fact that bases, such as sodium amide or sodium methoxide, totally inhibit ring–ring equilibration. Moreover, acids accelerate the reaction (see a later section). In a presumed neutral system, protons could be acquired from hydroxy groups on the surface of the glass reaction vessels or from traces of water in the system.



VII

Thermal Decomposition. All equilibration reactions, in both neutral and acidic systems, were accompanied by the formation of small amounts of volatile side products. These products had a phosphinelike odor and were shown by mass spectral analysis to include trimethylphosphine, dimethylphosphine, trimethyldiphosphine, and tetramethyldiphosphine.

However, one significant point should be noted—even at 350 °C, the amount of irreversible decomposition was less than 2%/week. Thus, it can be inferred that, if the high polymer could be synthesized and if cyclization–depolymerization could be inhibited, the polymer would show a very high resistance to random thermal degradation to phosphines at this temperature.

Pyrolysis of Dimethyldiaminophosphonium Chloride. The earlier literature report[13] that dimethylphosphazene polymers could be formed by the pyrolysis of dimethyldiaminophosphonium chloride, $(CH_3)_2P(NH_2)_2Cl$, led us to reinvestigate this reaction. Heating of this reagent in a vacuum sublimator at elevated temperatures resulted in no reaction between 25 and 180 °C. At 200 °C, melting and a concurrent reaction accompanied by sublimation occurred during 1 h to yield mainly ammonium chloride and ammonia, together with a trace of the phosphazenes III and IV. Continued pyrolysis for longer times (5–6 h) yielded little additional ammonium chloride, but it did provide a high-yield sublimate of III and IV. Only a trace of an unsublimable, organic-insoluble residue remained. Its infrared spectrum contained a peak at 1555 cm^{-1} that closely resembled a peak found in the spectrum of $Ph_2(P(NH_2)\overset{\cdots}{-}N\overset{\cdots}{-}P(NH_2)Ph_2]^+Cl^-$.

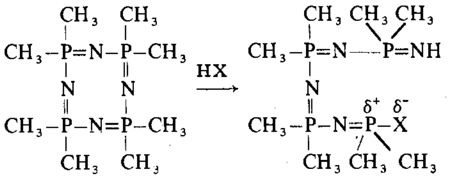
If 10 wt % of ammonium chloride was added to the phosphonium salt before pyrolysis, the system behaved in a similar manner to that described above, but the final unsublimable residue now comprised 10 wt % or less of the total reaction product. From these results we conclude that the initial pyrolysis product (formed within the first hour at 200 °C) is a short-chain linear phosphazene, probably with a structure of the type $H_2N[P(Me_2){=}N]_nP(Me_2)Cl$. The degree of polymerization, n, is very small, since gel permeation chromatography of chloroform solutions showed that no high or even medium molecular weight polymers were present. Mass spectrometric analysis of this product showed species with masses up to ~1500 amu, with a fragmentation pattern consistent with the release of $NPMe_2$ monomer and pentamer residues. The short, linear, end-capped species cyclize to trimer and tetramer during the subsequent extended pyrolysis. The ring–ring equilibration work described here strongly suggests that high polymer cannot be formed directly from cyclic species such as III or IV.

Reaction with Acids. In view of the suspicion that the ring–ring equilibration reaction was acid catalyzed, the system was investigated further for mixtures of $[NP(CH_3)_2]_4$ with various acids. The acids used included hydrogen chloride, ammonium chloride, an $HCl{\cdot}AlCl_3$ complex, aluminum chloride, $[NP(CH_3)_2]_4{\cdot}2HCl$, fluorosulfonic acid ($FSO_3H$), "magic acid" ($SbF_5{\cdot}FSO_3H$), and methanesulfonic acid (CH_3SO_3H). The reaction conditions involved temperature variations over the range 175–350 °C, with reaction times of 1–14 days at 350 °C and 36 days at 175 and 250 °C. The ratios of acid to phosphazene were varied from 2.9×10^{-3} mol of acid:1 mol of tetramer to 0.16 mol of acid:1 mol of tetramer.

With the exception of methanesulfonic acid, all of the acids induced similar changes in the phosphazene system. These influences were as follows. Phase separation occurred when more than 0.1 mol % of acid was present to give a colorless upper layer and a yellowish heavier phase. Phase separation was not evident at 350 °C, but cooling to 250 °C caused two layers to appear. The amount of the lower phase increased as the amount of acid was increased but was virtually independent of the type of acid added. As each reaction proceeded, the lower phase grew (after an apparent induction period of about 1 h at 350 °C) at the expense of the upper phase until a limiting ratio of the two was reached. Methanesulfonic acid did not induce phase separation.

Analysis of the two layers indicated that both phases contained $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$ together with a third material which proved to be nonvolatile and, hence, unsublimable. The denser phase in each case was richer in this nonvolatile component. The ratios of the three components appeared to approach that of an equilibrium. However, it was observed that the amount of the heavier phase could be markedly increased by temperature increases (for example, from 300 to 350 °C) but that cooling to 300 °C did not decrease the amount of the denser phase. The addition of the acid accelerated the equilibration of $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$.

This phase separation behavior is remarkably similar to that observed when mixtures of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and phoshorus pentachloride are heated. In that system, the heavier (yellow) phase has been shown to contain mainly short, linear phosphazene chains end-capped by the elements of PCl_5.[19] In the methylphosphazene system also, the unsublimable product appears to be a linear phosphazene (VIII) formed by an acid-induced cleavage of the phosphazene ring. A peak in the infrared spectrum of VIII at 2660 cm^{-1} was attributed to an NH end group or to a protonated middle unit.



VIII

Relationship to Polymer Synthesis. The direct conversion of the dimethylphosphazene trimer or tetramer to high polymer in either the absence or the presence of acidic catalyst did not take place under the reaction conditions employed in this work. In view of the well-known polymerization behavior of halocyclophosphazenes, dimethylsiloxanes, and cyclic sulfur or sulfur–nitrogen compounds, some explanation for this difference is needed.

First, it seems clear from the present work that a mechanism of *equilibration* is accessible to the dimethylphosphazene system, in both the absence and the presence of acidic catalysts within the 200–350 °C temperature range. It appears that high-polymer formation is inhibited by both thermodynamic and mechanistic factors. First, the cyclic tetramer appears to be an "energy trap" that effectively prevents the establishment of a broad polymeric series by the acid-catalyzed mechanism. The question remains as to why the dimethylphosphazene cyclic oligomers are apparently more effectively stabilized against polymerization than are the difluoro-, dichloro-, and dibromophosphazene[11] analogues. Indeed, it has been reported[20] that the nongeminal methylchlorophosphazene trimer, $[NP(CH_3)Cl]_3$, polymerizes thermally. Even methyl substituent groups may be sufficiently bulky to generate intramolecular steric repulsions in the high polymer. Calculations have shown[21] that the intramolecular repulsions are probably more serious in the dimethylphosphazene high polymer than in poly(dimethylsiloxane). Nevertheless, the inability of methylcyclophosphazenes to polymerize is surprising if steric factors alone inhibit chain propagation; the bromine atom has roughly the same steric size as a methyl group, and $(NPBr_2)_3$ polymerizes readily. Hence, mechanistic factors must be important. Conceivably, the mechanisms of ring–ring equilibration and polymerization are different. Polymerization may require the presence of an ionizable substituent group or a hydroxy substituent as well as methyl.[19] If so, the conversion of $[NP(CH_3)_2]_3$ or $[NP(CH_3)_2]_4$ to a linear high polymer may only be possible by the intermediate generation of a high-energy species that can by-pass the tetramer in a rapid chain-propagation process.

Experimental Section

Materials. Tetramethyldiphosphine disulfide, $[(CH_3)_2PS]_2$, was obtained from Orgmet Inc. and was used as received. Carbon tetrachloride (Baker) was used as received. Chlorobenzene (Fisher) was dried over P_4O_{10} and distilled before use. Chlorine gas was dried by passage through concentrated sulfuric acid. Hydrogen chloride gas (Matheson) was used as received. Anhydrous aluminum chloride (Fisher) was sublimed before use. The antimony pentafluoride–fluorosulfuric acid complex ("magic acid") was used as received from Aldrich. Sodium amide and sodium methoxide (Fisher) were used from freshly opened bottles and were handled in a dry nitrogen atmosphere. Ammonium chloride was converted to a finely divided form by precipitation from water into acetone, followed by vacuum-drying.

Analytical Techniques. Vapor-phase chromatography (VPC) was performed with a Hewlett-Packard HP5750 research chromatograph fitted with a 6-ft OV17 column. The temperature scan was from 100 to 250 °C at a 10°/min temperature rise following a 2-min post-injection phase. The thermal conductivity detector was calibrated for the phosphazene trimer and tetramer. Peak areas were measured by planimetry.

Gel permeation chromatography (GPC) was carried out with use of Waters Associates ALC-201 and ALC-GPC 501 instruments. Two column arrangements were employed: a 4 ft × $^3/_8$ in. 10^6 Styragel packing with tetrahydrofuran solvent and an 8 ft × $^3/_8$ in. column comprised of four 2-ft sections of 75-, 175-, 700-, and 2000-Å controlled pore glass used with either chloroform or water. When water was employed as an eluent, a distortion to the retention times was noted which erroneously implied that medium molecular weight polymer ($\bar{M}_n \approx 10000$) was formed from the "acid-catalyzed" reactions. These values were not confirmed by subsequent analyses in which chloroform was used as the eluent.

Infrared spectra were obtained with a Perkin-Elmer 621 unit with samples examined in KBr pellets or as films on silver chloride plates. NMR spectra were measured with Varian A-60 and Jeol PS-100 FT instruments. Mass spectra were obtained with the use of an AE1 MS 902 or a Finnigan 3200 instrument.[22]

Synthesis of $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$ (Method 1). The following synthesis was adapted from those reported in the literature.[23-25] Tetramethyldiphosphine disulfide, $[(CH_3)_2PS]_2$, (64.8 g, 0.35 mol) was suspended in 1500 ml of reagent grade carbon tetrachloride, with protection from atmospheric moisture. The suspension was then chilled in an ice bath and stirred vigorously as chlorine gas was bubbled through it.[24,26] Chlorine was introduced for 6 h, until the carbon tetrachloride was saturated with chlorine. The reaction mixture was then stirred for 6 h at 25 °C and, finally, was brought briefly to reflux in order to expel excess chlorine.

Under an atmosphere of dry nitrogen, the orange-red solution of sulfur chlorides in carbon tetrachloride was filtered from the suspended dimethyltrichlorophosphorane. The phosphorane was allowed to remain in the original reaction flask and was washed with two 300-ml portions of chlorobenzene before being suspended in 1200 ml of chlorobenzene. Ammonium chloride, 58 g (1.1 mol) was added to the phosphorane–chlorobenzene suspension. The reaction mixture was then brought to reflux. (*Caution*! On first coming to reflux, or shortly thereafter, the reaction mixture usually foams vigorously with rapid evolution of hydrogen chloride. The reaction should be monitored closely at this stage and heating stopped if necessary. Also, the use of a foam trap between the flask and the reflux condenser is recommended. After the initial vigorous reaction has subsided, refluxing may be continued safely.) The reaction mixture was allowed to boil at reflux for several hours and then allowed to cool to room temperature.

The reaction mixture was multiply extracted with water and the combined aqueous extracts were brought to near saturation with potassium hydroxide.[24] The precipitated product was recovered by multiple extraction of the aqueous extracts with benzene after the addition of potassium hydroxide. The combined benzene extracts were evaporated to dryness to give 37.0 g (70.8% based on $[(Me_2)_2PS]_2$) of crude product. This material was doubly sublimed at 100 °C (0.1 Torr) and analyzed by vapor-phase chromatography. The mixture consisted of approximately 90% $[NP(CH_3)_2]_4$ and 10% $[NP(CH_3)_2]_3$.

Pure $[NP(CH_3)_2]_4$ could be obtained readily from the sublimed product by recrystallization from heptane. Pure $[NP(CH_3)_2]_3$ was best obtained by enrichment of the product in trimer by equilibration at elevated temperatures (see below) followed by multiple fractional sublimation and, finally, by recrystallization from heptane. Recrystallized samples of both $[NP(CH_3)_2]_4$ and $[NP(CH_3)_2]_3$ were freed of solvent by sublimation. Subsequent purification by multiple sublimation within a glass high-vacuum system had no perceptible influence on the equilibration behavior.

Alternative Synthesis of $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$ (Method 2). This method was first reported by Sisler and co-workers[13] and was modified by Cotton.[25] It involves a pyrolytic sublimation of $(CH_3)_2P(NH_2)_2Cl$, which is conveniently prepared by the reaction of $(CH_3)_2PCl_3$ with ammonia.[25] This method has been used to prepare high yields of $[NP(CH_3)_2]_3$[25] or short linear dimethylphosphazene chains.[13] Our experience was that method 1 was more convenient for the preparation of trimer and tetramer, especially on a larger scale.

Preparation of $[NP(CH_3)_2]_4 \cdot 2HCl$ This hydrochloride was used in order to accurately introduce small quantities of hydrogen chloride into the thermolysis tubes. Two synthetic routes to the bis(hydrochloride) were employed: that of Cotton[25] (method 1) in which $[NP(CH_3)_2]_4$ in ethanol was allowed to react with aqueous hydrochloric acid and that of Paddock[27] (method 2) in which gaseous hydrogen chloride was passed into a solution of $[NP(CH_3)_2]_4$ in an inert organic solvent. Similar results were obtained from the thermolysis with the bis(hydrochloride) prepared by either route. In method 1 $[NP(CH_3)_2]_4$, 0.25 g, was dissolved in 10 ml of ethanol and 4 ml of concentrated hydrochloric acid was added. The mixture was allowed to evaporate to dryness, and the remaining solid was vacuum-dried over phosphorus pentoxide. In method 2 $[NP(CH_3)_2]_4$, 0.5 g, was dissolved in 8 ml of benzene and gaseous hydrogen chloride was bubbled into the benzene solution. An exothermic reaction was accompanied by the formation of a white precipitate. After the reaction appeared to be complete, the precipitate was filtered off, washed thoroughly with benzene, and dried under vacuum.

Equilibration Technique. Thermal equilibrations of $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$ were carried out in evacuated, sealed Pyrex glass ampules. Before filling, each ampule was washed with 5% hydrofluoric acid, then with deionized water, and with acetone and was subsequently dried at 135 °C in an oven. Each tube was charged with 0.15–5.5 g of trimer or tetramer, and the tube was then evacuated and sealed. The molten trimer or tetramer normally occupied half of the tube volume. When acids or bases were to be added, the evacuated tube was first charged with trimer or tetramer, then filled with dry nitrogen, and charged with a measured volume or weighed amount of acid or base. All vacuum-line connections were of glass.

Following sealing of the tubes, each was heated in a Freas thermoregulated oven at 175–350 °C for periods of time ranging from 1 to 35 days. Several reactions were performed in a tube furnace at 450 °C, but these exploded after several hours due to the buildup of internal gas pressure. When more than traces of acids were also present, separation into two phases took place. Neither phase consisted of a pure product.

After the completion of each reaction, the tip of each tube was cooled in liquid nitrogen to condense out any volatile products, and the tube was opened. Either the solid products were analyzed directly by vapor-phase chromatography, infrared, or mass spectral techniques or the product was placed in a vacuum sublimator and the volatile cyclic oligomers were removed at 80–100 °C (0.1 Torr). In all cases an unsublimable residue remained. However, this constituted only a trace amount of product when acid additives had not been used.

Isolation Procedures from Acid-Induced Reactions. The unsublimable residue that remained after vacuum sublimation was treated in a number of different ways. In some experiments the hygroscopic residue was dissolved in chloroform and analyzed directly by gel permeation chromatography or infrared spectrometry. Alternatively, the product was dissolved in water and either subjected directly to gel permeation analysis or precipitated by addition to tetrahydrofuran to yield an adhesive conglomerate. In other cases, the unsublimable residue was dissolved in water, and the solution was saturated with potassium carbonate and then extracted with benzene. This procedure was designed to remove or modify the terminal groups and to render the material soluble in nonpolar media. Invariably, this procedure brought about changes in the infrared spectrum.

γ-Ray Irradiation. A 0.25-g sample of $[NP(CH_3)_2]_4$ was sealed in an evacuated glass tube and was subjected to γ irradiation from a ^{60}Co source at 30 °C for 72 h for a total dose of 6.26×10^7 rads. Following irradiation, the tube contents were shown by VPC analysis to consist of unchanged cyclic tetramer, together with a trace of unsublimable but tetrahydrofuran-soluble material. Gel permeation chromatography analysis of this solution showed no evidence of high polymer.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

Registry No. $[NP(CH_3)_2]_3$, 6607-30-3; $[NP(CH_3)_2]_4$, 4299-49-4; $[NP(CH_3)_2]_4 \cdot 2HCl$, 34478-57-4; $[(CH_3)_2PS]_2$, 3676-97-9; ammonium chloride, 12125-02-9.

References and Notes

(1) This paper is part 27 in a series on phosphorus–nitrogen compounds.
(2) Part 26: H. R. Allcock, R. W. Allen, E. Bissell, and L. A. Smeltz, *J. Am. Chem. Soc.*, **98**, 5120 (1976).
(3) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965).
(4) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).
(5) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1716 (1966).
(6) H. R. Allcock, W. J. Cook, and D. P. Mack, *Inorg. Chem.*, **11**, 2584 (1972).
(7) H. R. Allcock and G. Y. Moore, *Macromolecules*, **5**, 231 (1972).
(8) S. H. Rose, *J. Polym. Sci., Polym. Lett. Ed.*, **6**, 837 (1968).
(9) R. E. Singler, G. L. Hagnauer, G. L. Schneider, N. S. LaLiberte, B. R. Sacher, and R. E. Matton, *J. Polymer Sci., Polym. Chem. Ed.*, **12**, 433 (1974).
(10) D. P. Tate, *J. Polym. Sci., Polym. Symp.*, **No. 48**, 33 (1974).
(11) (a) H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972; (b) *Chem. Rev.*, **72**, 315 (1972); (c) *Chem. Technol.*, **5**, 552 (1975); (d) *Science*, **193**, 1214 (1976).
(12) H. R. Allcock and G. Y. Moore, *Macromolecules*, **8**, 377 (1975).
(13) H. H. Sisler, S. E. Frazier, R. G. Rice, and M. G. Sanchez, *Inorg. Chem.*, **5**, 326 (1966).
(14) W. J. Bailey, W. M. Muir, and F. Marktscheffel, *J. Org. Chem.*, **27**, 4404 (1962).
(15) M. W. Dougill, *J. Chem. Soc.*, 5471 (1961).
(16) W. A. Piccoli, G. G. Haberland, and R. L. Merker, *J. Am. Chem. Soc.*, **82**, 1883 (1960).
(17) K. Moedritzer, J. R. Van Wazer, and C. H. Dungan, *J. Chem. Phys.*, **42**, 2478 (1965).
(18) H. Braune, S. Peter, and V. Neveling, *Z. Naturforsch., A*, **6**, 32 (1951).
(19) H. R. Allcock, J. E. Gardner, and K. M. Smeltz, *Macromolecules*, **8**, 36 (1975).
(20) V. N. Prons, M. P. Grinblat, and A. L. Klebanskii, *Zh. Obshch. Khim.*, **41**, 482 (1971).
(21) R. W. Allen and H. R. Allcock, results to be submitted for publication.
(22) The GC–mass spectrometric results were kindly provided by Dr. L. B. Hendry.
(23) H. T. Searle, *Proc. Chem. Soc., London*, 7 (1959).
(24) J. Dyson, Ph.D. Thesis, Victoria University at Manchester, 1964.
(25) F. A. Cotton and A. Shaver, *Inorg. Chem.*, **10**, 2362 (1971).
(26) R. Baumgartner, W. Sawodny, and J. Coubeau, *Z. Anorg. Allg. Chem.*, **333**, 171 (1964).
(27) H. T. Searle, J. Dyson, T. N. Ranganathan, and N. L. Paddock, *J. Chem. Soc., Dalton Trans.*, 203 (1975).