Macromolecules **1980,** *13,* 1345–1350

product (0.34 g). The molecular weight and spectroscopic properties of the polymer are listed in Table I. Ultraviolet spectroscopy was used to show that approximately 0.5% of the side groups were steroidoxy. The number of steroid units attached to XIV was less than the detectable limits of ^{31}P NMR methods.

Preparation of $[\mathrm{NP(OR)}_{0.036}(\mathrm{NHCH_3})_{1.964}]_n$, Where OR Is the Steroid Unit Derived from VIII. This polymer was prepared by a procedure similar to the one used for $[\mathrm{NP(OR)}_{0.1}(\mathrm{NHCH_3})_{1.9}]_n$, where OR is the steroid unit derived from VII (1.8%). The reaction conditions used for the synthesis are listed in Table III. The polymer was purified by dialysis as described previously. The molecular weight and spectroscopic properties of this polymer are listed in Table I. The number of steroid units attached to XIV was below the detectable limits of ^{31}P NMR methods. Thus, an elemental analysis was used to estimate the number of steroid units attached to XIV. Anal. Calcd for $[\mathrm{NP(OR)}_{0.036}(\mathrm{NHCH_3})_{1.964}]_n$, where OR is the steroid unit derived from VIII (1.8%): C, 27.82; H, 7.70; Cl, 0.0. Found: C, 27.82; H, 7.12; Cl, 4.60. (The presence of chlorine was attributed to salt formation with HCl).

Acidic Hydrolysis of $[\mathrm{NP(OR)}_{0.036}(\mathrm{NHCH_3})_{1.964}]_n$ (XIV), Where OR Is the Steroid Unit Derived from VIII. Several high molecular weight fractions of this polymer in ethanol were collected by gel permeation chromatography and combined. A concentrate of this solution was heated (<50 °C) in 3 N hydrochloric acid for 15 min. The solution was then neutralized with sodium hydroxide and reseparated by gel permeation chromatography. An absorbance in the ultraviolet spectrum of the acid-treated high molecular weight fraction appeared at 243 nm (vs. 241 nm for testosterone; see Table I). The 1,4-dihydro ring of the steroid unit VIII had hydrolyzed to an α,β-unsaturated ketone.[8] However, the molecular weight of the polymer had decreased from 10^6 to 10^4–10^5. This molecular weight decrease may have resulted from a thermal elimination of the steroidal units from XIV in acid or to a hydrolytic chain-cleavage process.

Acknowledgment. This work was supported by a grant from the Public Health Service (Grant 5RO1HL11418-09). We thank P. J. Harris and A. J. Freyer for the NMR analyses.

References and Notes

(1) For an earlier, related paper in this series see: Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980,** *13,* 1325.

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(9) In earlier work[7] it was shown that when an estrone residue was present, the formation of XI was complicated by the formation of a 17-methylimino group and water. In the high-polymeric system this liberation of water was expected to induce cross-linking reactions. Hence, for this steroid, the reaction was terminated at a stage corresponding to XIII, and this species was examined by ^{31}P NMR techniques only.

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(11) In fact, the homopolymer $[\mathrm{NP(NHCH_3)_2}]_n$ can be prepared by the interaction of XII with methylamine at −6 to 25 °C.[10]

(12) These reactions involve dehydration reactions of the steroid,[7] a process that is accelerated by heat or the presence of hydrochloric acid.

(13) A conservative estimate of the limit of detection of P–Cl bonds was less than 5% (or 5 P–Cl residues for every 100 substituent groups or 50 P=N repeat units).

(14) Cholesterol and mestranol (the 3-methyl ether of VI) underwent dehydration reactions with XII or IX[7] at elevated temperatures to form hydroxyphosphazenes. The reaction occurred even when sodium hydride was present. Cholesteryl chloride was one of the products formed by the reaction between cholesterol and XII.

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(19) The Magnedrive autoclave was manufactured by Autoclave Engineers, Inc. The autoclave unit (1-L capacity) and stirrer assembly were made of Hastalloy B. The unit was externally cooled (−50 °C), and methylamine (Linde) was condensed into the vessel through stainless steel tubing.

(20) A final separation of cyclic, trimeric, and tetrameric species not removed by dialysis was effected by a reprecipitation from ethanol (or an ethanol–water mixture) into an organic solvent such as benzene, tetrahydrofuran, or heptane.

(21) The percent of a substituent group is for the formula $[\mathrm{NP(OR)}_x(\mathrm{NHR})_{2-x}]_n$.

Thermal Rearrangement of $[\mathrm{NP(OCH_3)_2}]_3$ and $[\mathrm{NP(OCH_3)_2}]_4$[1]

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ABSTRACT: The thermal rearrangements of $[\mathrm{NP(OCH_3)_2}]_3$, $[\mathrm{NP(OCD_3)_2}]_3$, and $[\mathrm{NP(OCH_3)_2}]_4$ in the molten state or in *o*-dichlorobenzene to yield $[\mathrm{RNP(O)OR}]_{3\ \mathrm{or}\ 4}$ have been studied. The rearrangement reaction is accelerated by the formation of the products. Moreover, evidence was obtained that the rearrangement is *inter*molecular since the reaction rates are concentration dependent and "cross alkylation" products were detected from the interaction of $[\mathrm{NP(OCH_3)_2}]_3$ with $[\mathrm{NP(OCD_3)_2}]_3$. The rearrangement of the tetramer, $[\mathrm{NP(OCH_3)_2}]_4$, yields first a kinetically preferred geometric isomer of $[\mathrm{CH_3NP(O)OCH_3}]_4$ (VII) which is subsequently converted to the thermodynamically preferred isomer (VIII). The ^{1}H, ^{31}P, and ^{13}C NMR spectra of the starting materials and products are discussed.

Cyclic and high polymeric phosphazenes that contain alkoxy groups attached to phosphorus (I) have been known for many years.[2–6] It has also been recognized since the early 1960s[7–9] that alkoxyphosphazene cyclic trimers and tetramers which contain methoxy, ethoxy, propoxy, or benzyloxy side groups attached to phosphorus can undergo a thermal-rearrangement reaction in which alkyl groups migrate from oxygen to skeletal nitrogen to yield cyclophosphaz*a*nes (II). The sensitivity of the high polymers of formula $[\mathrm{NP(OCH_3)_2}]_n$ or $[\mathrm{NP(OC_2H_5)_2}]_n$ to high-temperature or high-energy decomposition processes[6,10] has been ascribed to such a rearrangement reaction. The value

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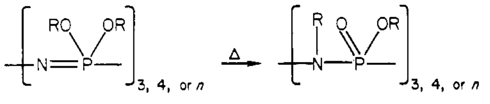
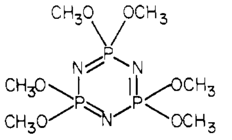


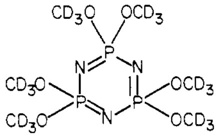
I II

of ^{13}C NMR spectroscopy as a tool for monitoring the course of the rearrangement of $[NP(OCH_3)_2]_n$ has been reported.[11] This rearrangement process does not occur in either cyclic or high polymeric phosphazenes if the side group is a fluoroalkoxy or aryloxy unit.

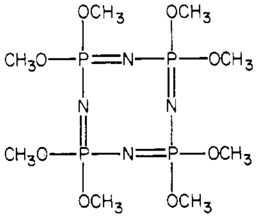
In this paper we explore some unusual features of this rearrangement for the three closely related cyclic species, III, IV, and V.



III



IV



V

The methoxy or trideuteriomethoxy derivatives were selected as representative alkoxy derivatives for the following reasons. First, a series of preliminary experiments showed that the rearrangement of the methoxy derivatives was initiated at a lower temperature (140 °C) than was needed for the rearrangement of the ethoxy or propoxy analogues. The use of this temperature reduced the possibility of complications from side reactions and also facilitated comparisons of the molten-state and solution-state reactions. Second, the methoxy derivatives could be obtained in a high state of purity by the use of recrystallization techniques, whereas the ethoxy and propoxy derivatives could not. Finally, the use of the methoxy derivatives allowed a detailed analysis of the reaction products by NMR techniques and permitted the identification of intermediates that could have been detected only with difficulty for the ethoxy or propoxy systems.

Species III–V are considered as small-molecule models for the high polymer $[NP(OCH_3)_2]_n$. It is stressed that, because of the sensitivity of the rearrangement to the presence of impurities, III–V were prepared and used in a highly purified form. ^{31}P NMR spectroscopy was employed as the main tool for monitoring the rearrangements.

Results and Discussion

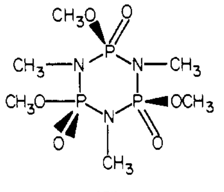
Identification of the Products. Cyclic Trimers. Heating of molten III or V at 140–152 °C leads to the formation of the fully rearranged products, $[CH_3NP(O)OCH_3]_{3\text{ or }4}$, in 6 or 10 h, respectively. In the case of the tetrameric system, the resultant cyclophosphazane crystallizes from the reaction mixture as the rearrangement proceeds. As 0.7 M solutions in *o*-dichlorobenzene at 152 °C, III or V rearranged completely in 12 or 24 h, respectively. The solution reactions were homogeneous throughout the course of the rearrangement, and the products were recovered by crystallization only when the solutions were cooled to 25 °C or below.

The authenticity of the products, $[CH_3NP(O)OCH_3]_{3\text{ or }4}$, was confirmed by their melting points,[8] infrared spectra (particularly by the appearance of a P=O band at 1250 cm^{-1}), mass spectral parent ions, elemental microanalysis, and ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. Partially rearranged species were detected as transient intermediates by the use of ^{1}H or ^{31}P NMR spectroscopy. One specific isomer, *trans*-$[CH_3NP(O)OCH_3]_3$ (VI), was detected as the reaction product from the rearrangement of III, both in the melt[12] and in solution. Two isomers (VII and VIII) were detected as products from V.[13,14] As will be discussed, the preponderance of VII or VIII depends on the reaction conditions.

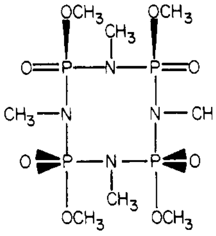
Table I
NMR Chemical Shifts (ppm)

	^{1}H	^{31}P	^{13}C
$[NP(OCH_3)_2]_3$ (III)	3.69	20.6	52.5
$[N(CH_3)P(O)(OCH_3)]_3$ (VI)	3.85	r_1 9.6 (J = 20 Hz)	53.8
	3.10	r_2 6.8	33.6
			31.2
$[NP(OCH_3)_2]_4$ (V)	3.67	3.8	52.9
$[N(CH_3)P(O)(OCH_3)]_4$			
isomer VIII	3.85	8.03	53.8
	3.10		33.8
isomer VII	3.85	7.47	53.8
	3.10		34.1

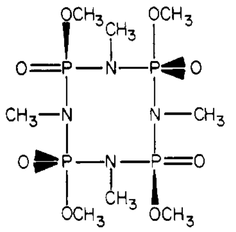
Because the course of these reactions was monitored by NMR spectroscopy, it was first necessary to understand fully the NMR spectra of the starting materials and products. The ^{1}H NMR spectra of methoxycyclophosphazenes are complicated by "virtual long-range coupling" phenomena that involve the phosphorus atoms of the ring.[15-17] This can be demonstrated by heteroatom decoupling techniques in the following example.



VI



VII



VIII

The ^{1}H NMR spectrum of $[NP(OCH_3)_2]_3$ (III) consists of a multiplet of four major lines centered at δ 3.69 (Figure 1). Decoupling of the phosphorus nuclei brought about a collapse of the spectrum to a singlet. The ^{31}P NMR spectrum of III consisted of a septet, a consequence of coupling to the protons of the methoxy groups attached to the *adjacent* phosphorus atoms. This splitting pattern was understandable in terms of the usual spin-multiplicity rule, $2nI + 1$, where n corresponds to the six neighboring methoxy protons. The proton-decoupled ^{31}P NMR spectrum was a singlet at 20.6 ppm. The simplicity of the NMR spectra of III verified the absence of impurities.

The conversion of III to VI was accompanied by marked changes in the NMR spectra. Specifically, the 100-MHz ^{1}H spectrum of VI consisted of a doublet of doublets centered at δ 3.85 and a multiplet centered at δ 3.10 (Figure 2). The downfield peaks represented the methoxy pro-

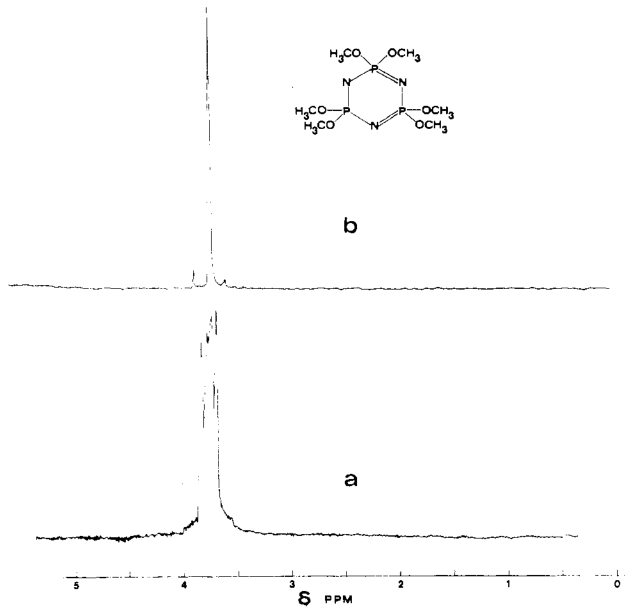


Figure 1. (a) ^{1}H NMR spectrum of III in chloroform. (b) ^{31}P-decoupled ^{1}H NMR spectrum of III in chloroform.

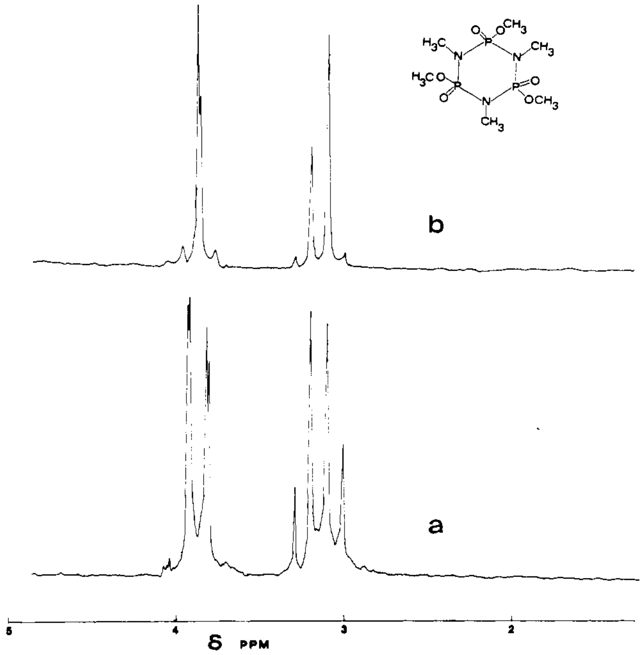


Figure 2. (a) ^{1}H NMR spectrum of VI in chloroform. (b) ^{31}P-decoupled ^{1}H NMR spectrum of VI in chloroform. The difference in environments for the methoxy and methyl protons reflects the geometry of an isomer with two methoxy groups above the ring and one below.

tons, and the upfield multiplet was associated with the protons of the NCH_3 units. Within the doublet of doublets, the larger (12 Hz) coupling arose from interactions of the methoxy protons with the nearby phosphorus nucleus, since this splitting was lost after decoupling of the phosphorus nuclei. However, the smaller splitting persisted after phosphorus decoupling, and this suggested that the compound was the trans isomer (VI),[12] especially since the two peaks were present in a 2:1 ratio. The ^{31}P decoupling also simplified the NCH_3 proton signal at 3.1 ppm from a multiplet to a doublet. The complexity of the original multiplet at 3.1 ppm was ascribed to long-range virtual coupling that involved the phosphorus atoms. Some confirmation for this view was obtained by the enhanced complexity of the multiplet which followed changes in the primary frequency from 100 to 60 or 200 MHz.

The proton-decoupled ^{31}P NMR spectrum of VI consisted of an AB_2 pattern, with A centered at 9.6 ppm and B at 6.8 ppm. This was consistent with the structure of a trans isomer. The peaks in the proton-coupled spectrum were broader. Finally, the proton-decoupled ^{13}C spectrum of VI consisted of a complex peak centered at 53.8 ppm (CH_3OP) and two peaks at 33.6 and 31.2 (CH_3N) in a 1:2 ratio.

The isomer VI identified in this work corresponds to the one studied by Ansell and Bullen[18] by X-ray diffraction techniques. However, some tentative evidence exists that a transformation to the other geometric isomer may occur at elevated temperatures. Variable-temperature proton-decoupled ^{31}P NMR examination of VI in *o*-dichlorobenzene showed a reversible increase in complexity in the spectrum as the temperature was raised from 35 to 155 °C.

Identification of the Products. Cyclic Tetramers. The undecoupled ^{1}H NMR spectrum of V was a complex multiplet centered at δ 3.67 ppm. The complexity was attributed to long-range coupling with distant phosphorus nuclei around the ring. Decoupling of the phosphorus atoms led to a simplification of the spectrum to yield a singlet. The proton-coupled ^{31}P spectrum consisted of one broad peak centered at 3.8 ppm. This peak contracted to a sharp singlet on proton decoupling. The proton-decoupled ^{13}C spectrum of V consisted of a broad singlet at 52.9 ppm. An X-ray crystal structure of this compound has been reported.[19]

The rearrangement of V yielded two isomers of the phosphazane, $[CH_3NP(O)OCH_3]_4$. These are distinguishable by proton-decoupled ^{31}P NMR spectroscopy. One isomer shows a singlet chemical shift of 8.03 ppm (VIII) and the other a singlet at 7.47 ppm (VII). The ^{1}H NMR spectrum consists of two sets of multiplets with chemical shifts of δ 3.85 and 3.10. The downfield peaks result from the methoxy groups and the upfield peaks from the CH_3N units.[12]

The formation of these two isomers depends on the reaction conditions. It has been reported[12] that both isomers are formed if molten V is heated for less than 7 h. Our results show that only one isomer (VIII) is formed when V is heated at 152 °C for 18 h in the molten state. In solution in *o*-dichlorobenzene at 152 °C, V is converted to a mixture of VII and VIII, with isomer VIII predominating. The present results suggest that isomer VII is the kinetically favored product of the rearrangement but that isomer VIII is formed from it and is the thermodynamically favored form. These results explain several of the anomalies present in the literature.[11] This conclusion was reinforced by the results of the kinetic experiments discussed in the following section.

Autoaccelerating Characteristic of the Rearrangement. The speed of the rearrangement of III and V in *o*-dichlorobenzene solvent was followed by proton-decoupled ^{31}P NMR techniques (Figures 3 and 4). The cyclic trimer (III) rearranged faster than the cyclic tetramer (V). Indeed, at 152 °C the trimer underwent a more than 90% conversion to VI within 6 h (Figure 3), whereas the tetramer V underwent no detectable rearrangement during this period.

However, it was found that the rearrangements of both III and V accelerated as larger quantities of the rearranged species (VI or VII–VIII) were formed (Figure 5) or were deliberately added. Moreover, although no rearrangement of pure V took place at 145 °C in chlorobenzene solution, the reaction took place readily after VIII was added. Plots of the disappearance of V as a function of time showed

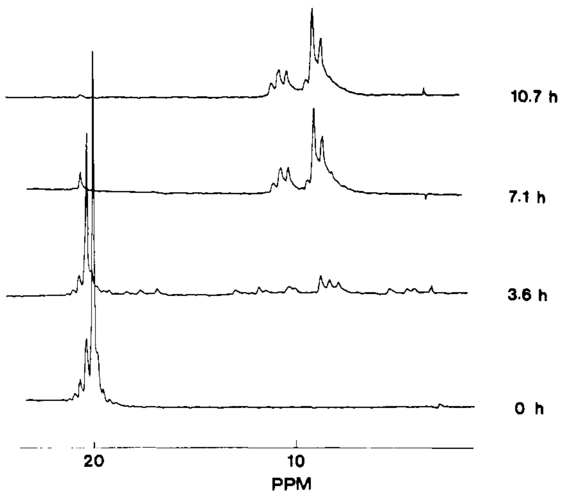


Figure 3. ^{1}H-decoupled ^{31}P NMR spectra obtained during the thermal conversion of III to VI in *o*-dichlorobenzene at 152 °C. The large number of peaks generated at 3.6 h was indicative of partially rearranged species. The fully rearranged product yielded an AB_2 spin pattern. The spectra are offset for clarity.

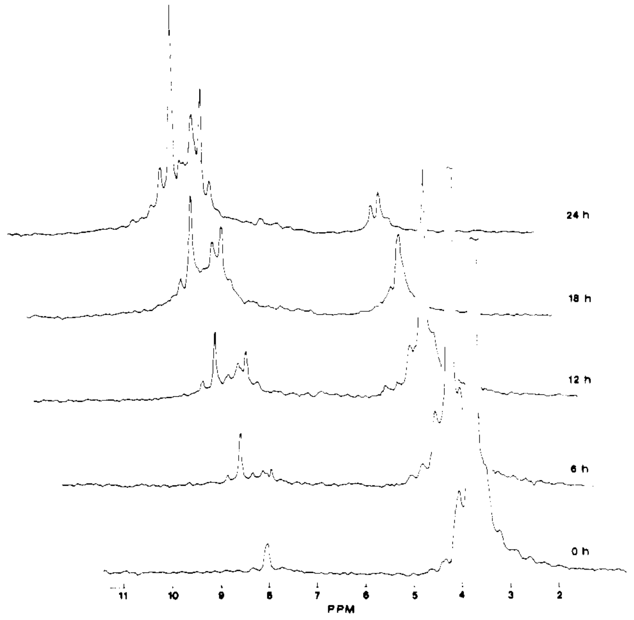


Figure 4. ^{1}H-decoupled ^{31}P NMR spectra obtained during the thermal conversion of V to VIII in *o*-dichlorobenzene at 152 °C in the presence of an initial 10% of added VIII. The spectra are offset for clarity.

zero-order characteristics in V when an excess of VIII was present (Figure 6). The zero-order characteristics were not evident when a deficiency of VIII was present and, in such circumstances, an initial acceleration was still evident. Thus, it was concluded that either VIII or a product derived from it is an accelerator for the rearrangement. The detailed nature of the catalytic pathway is not yet understood. However, such catalysis, if it also occurs with the high polymer, would have a catastrophic effect on the stability of each macromolecule.

Information was also obtained about the relative rates of formation of the two isomers VII and VIII in *o*-dichlorobenzene at 152 °C. The rearrangement of V in the presence of VIII (in a 10:1 deficiency) initially resulted in the formation of isomer VII as the only new product. Subsequently, additional isomer VIII was detected. At the point where all of V had reacted, the ratio of VII to VIII was roughly 1:2. Further thermolysis led to a decrease in the concentration of VII and an increase in the concentration of VIII. However, a solution of isomer VIII in *o*-dichlorobenzene did not yield VII when heated at 150 °C. Hence, the equilibrium lies well over to the side of isomer VIII.

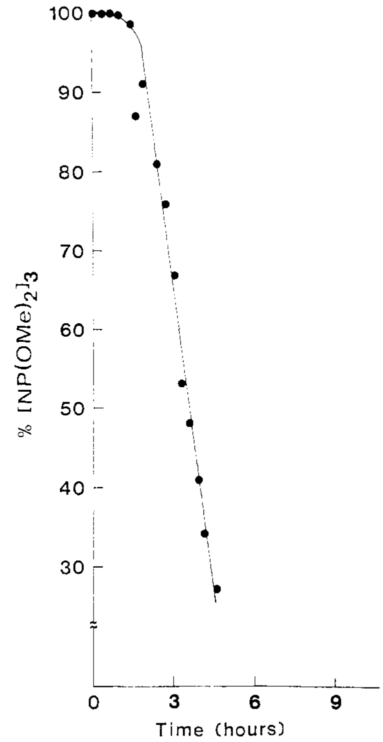


Figure 5. Disappearance of III vs. time for the thermal conversion of III to VI at 152 °C following the initial induction period.

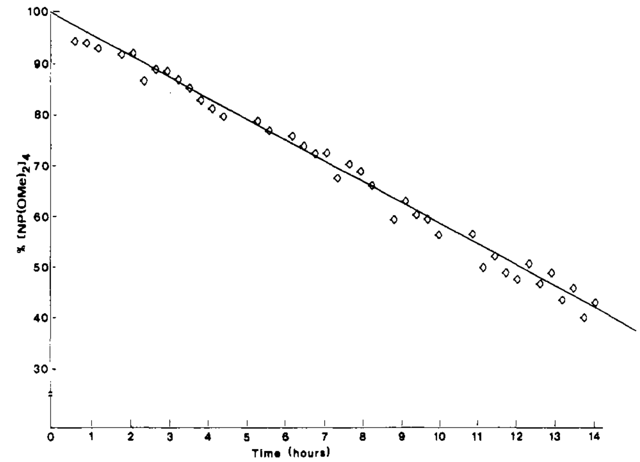


Figure 6. Disappearance of V vs. time during the catalyzed conversion of V to VIII at 145 °C in *o*-dichlorobenzene. The product, VIII, was initially present in a V:VIII ratio of 1:6. It was inferred from the plot that the rearrangement was zero order when a large excess of VIII was present.

Intermolecular Migration of CH_3 and CD_3 Groups. As discussed, the rate of rearrangement was dependent on the concentration of the phosphazane product. This suggested that the rearrangement could proceed via an *inter*molecular pathway that might involve scrambling or "crossing" of the methyl group from the methoxy unit on one phosphazene molecule to the skeletal nitrogen atom of another molecule. Thus, the two phosphazenes $[NP(OCH_3)_2]_3$ (III) and $[NP(OCD_3)_2]_3$ (IV) were allowed to react under conditions that were known to bring about the rearrangement of III (in the molten state at 145 °C). The products contained cyclophosphazanes that contained *both* methyl and deuteriomethyl units connected to the skeletal nitrogen atoms. These products were detected by mass spectrometry. Molecular ions were detected unambiguously for all eight of the possible permutations of CH_3 and CD_3 units in the cyclotriphosphazane products. The Gaussian distribution of molecular ions indicated scrambling of the methyl and the trideuteriomethyl group between rearranged trimer rings. However, no exchange of methyl and trideuteriomethyl groups was detected between the phosphazene rings (III and IV) at temperatures below those necessary for rearrangement (for example, at 95 °C).

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and octachlorocyclotetraphosphazene, $(NPCl_2)_4$, were obtained from Ethyl Corp. and from the Firestone Tire and Rubber Co. The commercial trimer-tetramer mixtures were purified first by vacuum sublimation at 60 °C and then by recrystallization from heptane, followed by another vacuum sublimation. Methanol (Fisher) was dried by boiling at reflux over barium oxide and was then distilled onto activated 3- and 4-Å molecular sieves. Benzene was dried before use by boiling at reflux over calcium hydride, followed by distillation from the same reagent. *o*-Dichlorobenzene (Baker) was distilled. Sodium spheres (MC/B) were cleaned with methanol. All syntheses were conducted with the reaction mixture under a nitrogen atmosphere. Glass ampules (10-mL total volume) were fitted with ground-glass joints that allowed evacuation of the ampules. Analytical data were obtained from Galbraith Laboratories.

Hexamethoxycyclotriphosphazene, $[NP(OCH_3)_2]_3$. This compound was prepared from hexachlorocyclotriphosphazene (60 g, 0.17 mol) and sodium methoxide in benzene (400 mL).[8] The sodium methoxide was prepared from methanol (300 mL) with the use of sodium spheres (47 g, 2.0 mol) in benzene (200 mL). Purification was effected by four recrystallizations from diethyl ether-hexane mixtures to yield a white crystalline solid, mp 45-46 °C. Anal. Calcd for $N_3P_3O_6C_6H_{18}$: C, 22.44; H, 5.65; N, 13.08; P, 28.93; O, 29.89; Cl, 0. Found: C, 22.44; H, 5.72; N, 13.01; P, 28.70; O, 29.89; Cl, 0.11.

Hexakis(trideuteriomethoxy)cyclotriphosphazene, $[NP(OCD_3)_2]_3$. This compound was prepared by a modification of the synthesis described above. A solution of sodium trideuteriomethoxide was prepared by the addition of a solution of methanol-d_4 (15.0 g, 0.42 mol) in tetrahydrofuran (15 mL) to sodium spheres (3.6 g, 0.15 mol) in tetrahydrofuran (15 mL). A solution of hexachlorocyclotriphosphazene (4.8 g, 0.014 mol) in tetrahydrofuran (20 mL) was added dropwise to the stirred sodium methoxide solution cooled in an ice bath. The reaction was stirred at 25 °C for 72 h. The solvent was removed on a rotary evaporator, water was added (200 mL), and the product was extracted three times with methylene chloride (40 mL). A white solid remained after removal of the solvent. Further purification was effected by filtration of a diethyl ether solution, followed by removal of the solvent to yield a white, crystalline material, mp 46.5-47.5 °C. The yield was 70%. An electron-impact mass spectrum showed a parent ion at 339 amu (from IV). No ion at 321 amu (III) was detected.

Octamethoxycyclotetraphosphazene, $[NP(OCH_3)_2]_4$. This compound was prepared from octachlorocyclotetraphosphazene (51 g, 0.11 mol) and sodium methoxide, itself prepared from sodium spheres (50 g, 2.2 mol) and methanol (300 mL) in benzene (200 mL). Purification was effected by four recrystallizations from toluene-hexane mixtures to yield a white, crystalline solid, mp 41-42 °C. Anal. Calcd for $N_4P_4O_8C_8H_{24}$: C, 22.44; H, 5.65; N, 13.08; P, 28.93; O, 29.89; Cl, 0. Found: C, 22.48; H, 5.68; N, 13.03; P, 29.08; O (by difference), 29.73; Cl, <0.01.

Sealed-Tube Melt Reactions. In a typical experiment, the starting material (III or V) was placed in a glass ampule, the air was removed, and the ampule was cooled in liquid nitrogen and sealed. The ampule was then heated for 3-24 h in an oven that was operated at 152 °C.

Cothermolysis of $[NP(OCH_3)_2]_3$ (III) and $[NP(OCD_3)_2]_3$ (IV). Equal amounts of (III) (0.127 g, 0.396 mmol) and its deuterated analogue (IV) (0.134 g, 0.395 mmol) were placed in a glass ampule and heated for 1.5 h at 145 °C. A standard that contained only $[NP(OCH_3)_2]_3$ was treated similarly. The reaction products were analyzed by mass spectrometry. A strong parent peak was observed at *m/e* 321 in the standard, but no other high *m/e* peaks were detected in this region. The mixture yielded two strong peaks at *m/e* 321 and 339 of equal intensity plus five other peaks at intervals of three amu between the two intense molecular ions. The five peaks were present in a Gaussian distribution. The same sample was sealed in another glass ampule and was heated at 145 °C for 17 h. The mass spectrum of the product yielded seven peaks between *m/e* 321 and 339 in a Gaussian distribution.

A separate experiment utilized equal amounts of III (0.114 g, 0.355 mmol) and IV (0.114 g, 0.336 mmol). The mixture was sealed in a glass ampule and was heated for 2 h at 95 °C. Peaks were detected at 321 and 339 amu only.

These experiments provide further evidence for an intermolecular exchange of methyl groups among the components of the reaction mixture. However, this exchange occurred only in the presence of the phosphazane.

NMR Techniques and Kinetic Experiments. ^1H NMR data were collected with the use of a Varian A-60 spectrometer operated at 60 MHz, a JEOL PFT 100 Fourier transform NMR spectrometer operated at 100 MHz and linked to a Nicolet computer, or a Bruker 200-MHz Fourier transform NMR spectrometer operated at 200 MHz. ^{13}C NMR data were collected with the use of a Varian-CFT-20 Fourier transform NMR spectrometer operated at 20 MHz. The JEOL PFT 100 spectrometer operated at 40 MHz was also used to collect ^{31}P NMR spectra, and for all heteroatom decoupling experiments. Positive ^1H and ^{13}C NMR chemical shift values were downfield relative to Me_4Si. ^{31}P NMR chemical shifts were relative to external phosphoric acid with positive values downfield.

Kinetic experiments were performed with the reaction sample contained within the ^{31}P probe of the JEOL PFT 100 spectrometer. The spectrometer was equipped with a variable-temperature controller that maintained the temperature of the probe to within ±0.5 °C. The deuterium lock was maintained by the use of a dimethyl-d_6 sulfoxide capillary. Data were collected with five scans which lasted for a total of 20 s.

Two experiments were conducted in which equal amounts of the product were placed in two separate NMR tubes along with different amounts of V. One tube contained V (0.0755 g, 0.176 mmol) and VIII (0.6650 g, 1.55 mmol) before the rearrangement was initiated; the other tube contained V (0.2050 g, 0.479 mmol) and VIII (0.6636 g, 1.55 mmol). Both thermolyses took place in 2.0 mL of *o*-dichlorobenzene at 145 °C. Compound VIII had been prepared previously by heating pure V in a sealed, evacuated glass ampule for 18 h at 152 °C. The exact amount of VIII in solution at 145 °C was not known because VIII was only partially soluble in hot *o*-dichlorobenzene. However, the ratio of the amount of V to VIII in solution could be determined at 145 °C. This amount was estimated in both experiments to be 0.40 g (0.93 mmol). No rearrangement was detected in the absence of VIII after 20 h at 145 °C.

Two experiments were conducted in which equal amounts of V were placed in two separate NMR tubes along with different amounts of VIII. Thus, one tube contained both V (0.6626 g, 1.55 mmol) and VIII (0.0686 g, 0.160 mmol) before the rearrangement was initiated. The other tube initially contained V (0.6670 g, 1.56 mmol) and VIII (0.2050 g, 0.479 mmol). Both thermolyses took place in 2.0 mL of *o*-dichlorobenzene at 152 °C. Compound VIII had been prepared previously by the heating of pure V in a sealed, evacuated ampule for 18 h at 152 °C. No rearrangement was detected in the absence of VIII after 20 h at 152 °C. An additional experiment was carried out in which III (0.6635 g, 2.06 mmol) was placed in an NMR tube. The reaction was conducted in 2.0 mL of *o*-dichlorobenzene at 152 °C.

Sealed-Tube Solution Reactions. Two identical solutions of V (0.33 g, 0.77 M) in *o*-dichlorobenzene (1 mL) were placed in glass ampules. Freshly prepared phosphazane VIII (0.16 g) was added to one of the tubes and both were evacuated and sealed. Both tubes were placed in an oven at 145 °C and were heated for 22 h. At this point the reaction mixtures were homogeneous. The samples were then allowed to cool to room temperature. The sample which originally contained the phosphazane VIII solidified from the precipitation of additional VIII. ^1H and ^{31}P NMR spectra showed a complete conversion of V to VIII. By contrast, the ampule which was not initiated with VIII contained no precipitate after cooling. This indicated that appreciable rearrangement had not occurred in this sample. This same tube was reheated at 145 °C for an additional 18 h. After the tube cooled, a large amount of VIII precipitated.

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Synthesis of Linear Poly(divinylbenzene) through Proton-Transfer Polyaddition by Oxo Acids

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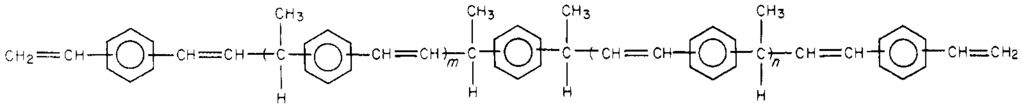
ABSTRACT: Polymerization of *p*- and *m*-divinylbenzenes to linear polymer took place without cross-linking with cationic oxygen-containing acid (oxo acid) catalysts such as CF_3SO_3H and $AcClO_4$ in nonpolar solvents above room temperature and at low monomer concentrations. The polymer was soluble in aromatic and halogenated hydrocarbons and consisted of trans olefinic and phenyl groups in the main chain with vinyl groups at both ends, that is



The molecular weight of the polymer increased with increasing conversion and further increased on sequential addition of monomer to the reaction mixture. The molecular weight of the polymer could be controlled in the range of about 10^2–10^4. A stepwise reaction mechanism is proposed for this linear divinylbenzene polymerization, in which the terminal vinyl group is protonated, the carbocation formed adds to another vinyl group, and a proton is immediately released to give an unsaturated linear backbone.

Linear polymers with carbon–carbon double bonds in the backbone and/or at chain ends are attractive as macromers because of the potential reactivity of the olefinic double bonds in the polymer chain and the end groups. Few examples have been reported which form unsaturated linear polymers from divinyl compounds with the exception of anionic and coordinative polymerization of conjugated 1,3-dienes (butadiene[1] and isoprene[2]). Polymers obtained from these monomers do not have terminal double bonds because the polymerizations are regular 1,4-addition reactions.

Divinylbenzene (DVB; diethenylbenzene) yields usually insoluble, cross-linked polymers in radical[3] and anionic[4] polymerizations. The cationic polymerization of DVB and its derivatives can give, under specific conditions, soluble polymers without cross-linking. In polymerizations of *o*-DVB,[5] the two vinyl groups in the monomer cannot propagate independently and cyclopolymerization occurs. Another example of a polymerization of divinylbenzene derivatives is the proton-transfer polyaddition of *p*-diisopropenylbenzene[6] and its derivatives,[7] forming cyclic structures with indan units in the main chain. The propagation of the sterically hindered isopropenyl group to form an indan structure proceeds no further than the dimer stage.[8] Polymerizations of α,ω-bis(4-vinylphenyl)alkenes also produce linear polymers.[9] However, no linear, unsaturated polymer has yet been prepared from DVB with cationic catalysts.

We have recently found that an unsaturated linear dimer (I) of styrene can be obtained in a very selective reaction with oxo acid catalysts, such as CF_3SO_3H and $AcClO_4$, via the reaction sequence shown in eq 1.[10–12]

It might be visualized that each vinyl group of DVB is capable of repeating the same reaction; if this type of reaction occurs instead of the conventional cationic addition polymerization, a linear unsaturated polymer III would be formed. (Scheme I; illustrated for *p*-DVB only for simplicity. The possible reactions of the cationic species are also omitted for simplicity.) The first process is the dimerization of DVB, analogous to eq 1, which yields a linear dimer II with two terminal vinyl groups. The dimer II can subsequently be protonated at either of the terminal vinyl groups, add to another DVB monomer, and release a proton to give a linear DVB trimer. Repetition