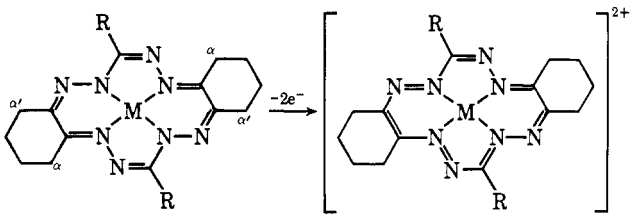
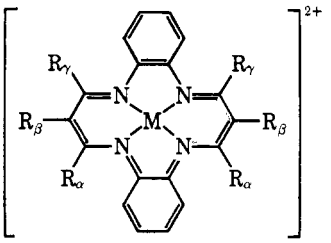
number of Ni(II) complexes are given in Table V.



26 27

Anodic processes are observed in each case. With



28

the exception of Ni(Me, COMe, H(phen)$_2$) these processes correspond to apparent two-electron oxidations, most of which are at best quasi-reversible as judged by wave slopes. The results do imply that the oxidations **26** → **27** and **1** → **28**, the possibility of which was recognized earlier by Jager,[6] can be effected. No chemical oxidations of **1** and **26** have been attempted. Unlike **14** each of these complexes undergoes a one-electron reduction at potentials somewhat less negative than those required for the Ni(II) → Ni(I) reduction of species **5** and **6**.

(c) M(MeHMe(en)$_2$) Complexes. For the purpose of comparison with the fully conjugated complexes **14**, the polarographic behavior of M(MeHMe(en)$_2$), M = Ni(II), Cu(II), and Zn(II), has been investigated. Results are given in Table V. These complexes do not reduce at potentials down to *ca.* −2.0 V but do undergo apparent one-electron oxidations at slightly positive potentials. No other anodic waves were observed. Due to the quite low potentials of these processes and their near-independence of metal ion, they are associated with oxidation of the ligand π system rather than with M(II) → M(III).[48] This interpretation is supported by the occurrence of similar slightly anodic oxidations with Ni(MeHMe(NH)$_2$)$_2$ (**19**, Table V) and [Ni(MeHMe(NCH$_2$CH$_2$NHMe)$_2$)]$^+$,[48a] which also contain delocalized β-iminoaminato chelate ring systems. The close correspondence of half-wave potentials between the oxidation of M(MeHMe(en)$_2$) and the first anodic process of M(MeHMe-2,9-diene) may indicate that they are related. In view of this, it should be emphasized that the representation **15** (Scheme I) for [M(MeHMe-2,9-diene)]$^+$ is only one of a number of simple formulations depicting the delocalized nature of the 15-π ligand system.

Further examples of the nontemplate synthesis of tetraaza macrocyles and additional results dealing with the preparation, reactivity, solution behavior, and electronic properties of complexes of the types **14**, **15**, and **16** will be reported subsequently.

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-15471) and the National Science Foundation (GP-18978X). The high-resolution mass spectra were provided by the facility supported by National Institutes of Health Grant RR00317 (Professor K. Biemann, Principal Investigator) from the Biotechnology Resources Branch, Division of Research Resources. Useful discussions with Professor A. Davison are acknowledged.

Phosphonitrilic Compounds. XIV.[1] Basic Hydrolysis of Aryloxy- and Spiroarylenedioxycyclophosphazenes[2]

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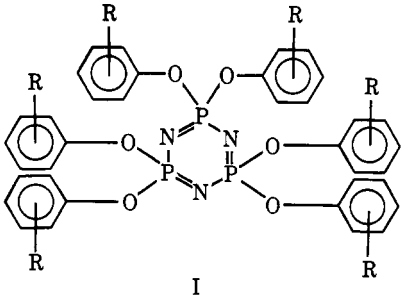
Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received July 28, 1971*

Abstract: Bis(aryloxy)cyclophosphazenes, [NP(OAr)$_2$]$_3$, and spirocyclic arylenedioxycyclophosphazenes, (NPO$_2$Ar)$_3$, have been hydrolyzed in basic 25 vol % water in diglyme. For the bis(aryloxy) derivatives, the ease of hydrolytic removal of the first aryloxy group in [NP(OR)$_2$]$_3$ from phosphorus is in the order OR = *p*-NO$_2$C$_6$H$_4$O− > *m*-NO$_2$C$_6$H$_4$O− > *o*-NO$_2$C$_6$H$_4$O− ≫ C$_6$H$_5$O− > *p*-CH$_3$C$_6$H$_4$O−. For the spirocyclic derivatives, the rate of cleavage of the first aryloxy–phosphorus bond is in the order [NP(O$_2$C$_6$H$_4$-1,2)]$_3$ > [NP(O$_2$C$_{10}$H$_6$-2,3)]$_3$ ≫ [NP(O$_2$C$_{12}$H$_8$-2,2′)]$_3$ and [NP(O$_2$C$_{12}$H$_6$-1,8)]$_3$. The mechanisms of these reactions are discussed, and comparisons are made with related phosphate ester hydrolyses.

Aryloxycyclo- and polyphosphazenes, [NP(OAr)$_2$]$_n$, and spirocyclic phosphazenes, [NP(O$_2$Ar)]$_3$ or [NP(O$_2$Ar)]$_4$, occupy an important place in phosphorus–nitrogen chemistry. Aryloxycyclophosphazenes, such as [NP(OAr)$_2$]$_3$ or [NP(OAr)$_2$]$_4$, are among the most thermally and oxidatively stable phosphorus

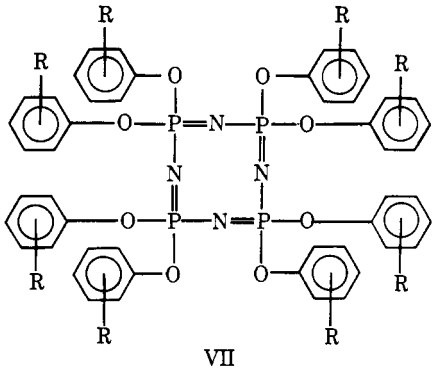
(1) Part XIII: H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, **11**, 1120 (1972).

(2) Preliminary report of parts of this work have appeared: H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, **91**, 3102 (1969); *Chem. Commun.*, 580 (1970).



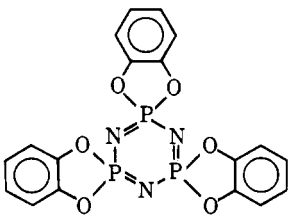
I

R = 2-NO_2 II
3-NO_2 III
4-NO_2 IV
H V
4-CH_3 VI

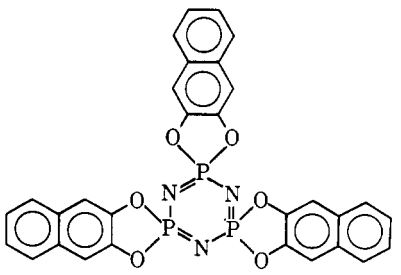


VII

R = 4-NO_2 VIII
H IX

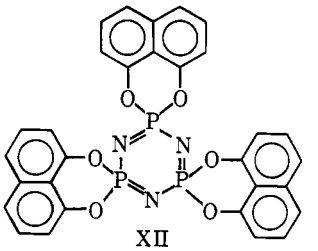


X

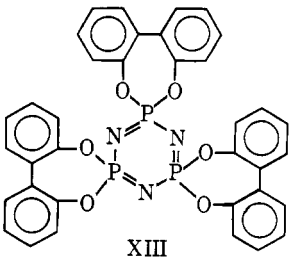


XI

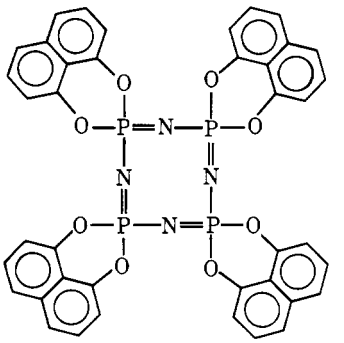
compounds known and, for this reason, many derivatives have been synthesized with technological uses in mind. The high polymer, $[NP(OC_6H_5)_2]_n$,[3,4] has attracted attention as the first member of an unusual new class of macromolecules, and spirocyclic phosphazenes are of considerable interest because of their unique clathration properties.[5] Yet the hydrolytic behavior of these compounds has not previously been investigated.



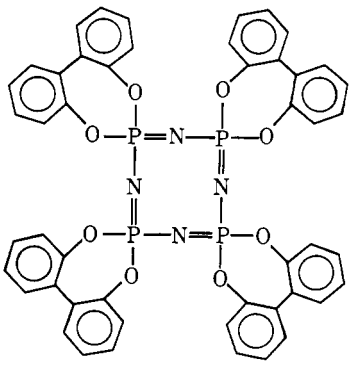
XII



XIII



XIV



XV

In this paper, we report product analysis and kinetic studies for the basic hydrolysis of a wide range of aryloxycyclophosphazenes. The compounds studied are depicted as I–XV. Compounds V and IX–XV were synthesized by techniques described previously.[6–9] Derivatives II, III, IV, and VIII were prepared by a new route which involved the interaction of nitrophenol with the appropriate chlorocyclophosphazene in tetrahydrofuran in the presence of anhydrous sodium carbonate.

$$(NPCl_2)_n + 2n NO_2C_6H_4OH + 2n Na_2CO_3 \longrightarrow [NP(OC_6H_4NO_2)_2]_n + 2n NaCl + 2n NaHCO_3$$

Compound VI was prepared by the interaction of

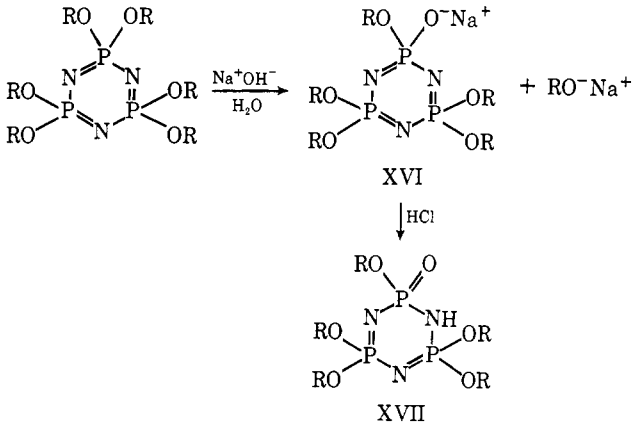
(3) H. R. Allcock, "Phosphorus–Nitrogen Compounds," Academic Press, New York, N. Y., 1972.
(4) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).
(5) H. R. Allcock and L. A. Siegel, *J. Amer. Chem. Soc.*, **86**, 5014 (1964).
(6) H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).
(7) H. R. Allcock, *J. Amer. Chem. Soc.*, **86**, 2591 (1964).
(8) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).
(9) H. R. Allcock and E. J. Walsh, *ibid.*, **10**, 1643 (1971).

sodium 4-methylphenoxide with hexachlorocyclotriphosphazene.

$$(NPCl_2)_3 + 6CH_3C_6H_4ONa \longrightarrow [NP(OC_6H_4CH_3)_2]_3 + 6NaCl$$

Results and Discussion

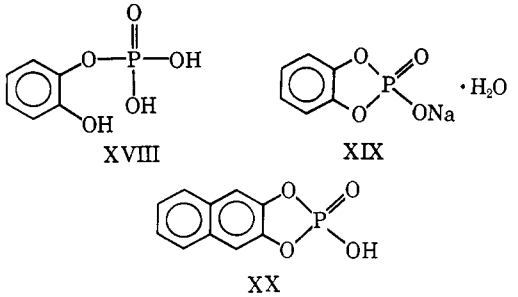
Products from the Hydrolysis of Bis(aryloxy)cyclophosphazenes, $[NP(OR)_2]_3$ or $[NP(OR)_2]_4$. The product scale hydrolysis of compounds I–IX in alkaline 25:75 water–diglyme medium showed that, under the conditions employed, the reaction products were the free phenoxide ion and the sodium salt of the pentakis(aryloxy)hydroxycyclotriphosphazene (XVI) or the appropriate tetramer. Treatment of XVI with acid yielded the 1,3,3,5,5-pentakis(aryloxy)-1-oxo-2-hydrocyclotriphosphazadiene (XVII). The identification of



these products is described in the Experimental Section. No products were detected in which more than one aryloxy group was displaced per molecule. For example, removal of the first nitrophenoxy group from IV is complete after 30 min at 80°, but no further hydrolysis is detected after 72 hr at the same temperature.

Attempts to hydrolyze poly[bis(phenoxy)phosphazene], $[NP(OC_6H_5)_2]_n$ ($n \sim 15{,}000$), in 25 vol % aqueous diglyme containing 4×10^{-2} M base in a heterogeneous system yielded no detectable phenoxide ion even after 500 hr at 80°. The hydrolysis of octakis(4-nitrophenoxy)cyclotetraphosphazene (VIII) was also carried out under heterogeneous conditions, but in this case the reaction was very rapid at 80° in 25 vol % aqueous diglyme.

Products from the Hydrolysis of Spirocyclic Arylenedioxyphosphazenes. The first product isolated from the hydrolysis of tris(*o*-phenylenedioxy)cyclotriphosphazene (X) in basic 25 vol % aqueous diglyme or basic 5–20 vol % aqueous dioxane was 2-hydroxyphenyl dihydrogen phosphate (XVIII) (or the sodium salt). However, in media which contained a lower proportion of water, such as in basic 1 vol % aqueous dioxane or 2 vol % aqueous diglyme, a white precipitate of the monohydrate of sodium *o*-phenylene phosphate (XIX) formed as the hydrolysis proceeded. Similarly, hydrolysis of tris(2,3-naphthalenedioxy)cyclotriphosphazene (XI) in basic 2 vol % aqueous diglyme yielded the cyclic phosphate XX. The identification of these products is discussed in the Experimental Section. The fact that cyclic species, such as XIX or XX, can be isolated from media with low water content is surprising in view of the fact that cyclic organo-phosphate esters with five-membered rings are known to undergo facile ring cleavage in aqueous–organic basic media.[10]



The spirophosphazenes with six- or seven-membered exocyclic units at phosphorus (XII–XV) showed no evidence of hydrolysis after 200 hr in 1×10^{-3} M basic 25% aqueous diglyme at 100°.

^{18}O Studies. Hydrolysis of hexakis(4-nitrophenoxy)cyclotriphosphazene (IV) in a 25:75 (vol) water–diglyme medium in which 1% of the water was $H_2{}^{18}O$ yielded 4-nitrophenol which contained no ^{18}O. Hydrolysis of tris(*o*-phenylenedioxy)cyclotriphosphazene (X) in the same medium yielded 2-hydroxyphenyl dihydrogen phosphate (XVIII). Cyclization of this compound to *o*-phenylene hydrogen phosphate occurred in the mass spectrometer with retention of some ^{18}O. Use of a higher ionization potential fragmented XVIII or the cyclized species to yield the 1,2-dioxyphenyl cation which contained no ^{18}O. This evidence indicates that the basic hydrolysis of both bisaryloxy- and spirocyclic arylenedioxyphosphazenes proceeds by cleavage of P–O rather than C–O bonds. In this respect, the reaction resembles the hydrolysis of fluoroalkoxycyclophosphazenes.[11]

Kinetic Results. Hexakis(aryloxy) Derivatives. Cleavage of the first aryloxy group from II, III, IV, V, and VI was studied kinetically in basic 25 vol % aqueous diglyme. Variations in base concentration, phosphazene concentration, and temperature were studied and the rates were found to follow the expression rate = k_2 [OH^-][phosphazene] over the range of conditions studied. The reactions were studied under pseudo-first-order conditions, with excellent straight line plots being obtained. However, it was also found that, at low base concentrations, the hydrolysis of IV was indeed second order with good second-order plots being maintained beyond 90% conversion. When a 6.30×10^{-6} M phosphazene solution was hydrolyzed in the presence of 1.07×10^{-5} M sodium hydroxide, the direct second-order rate constant obtained at 80° of 6.05×10^{-1} (l./mol sec) was in good agreement with the specific rate constant calculated from reactions in more basic media.

Table I lists pseudo-first-order rate constants (k_1) and specific rate constants (k_2), the latter obtained by division of the observed rate constants by the base concentration.

The hydrolysis rates were markedly dependent on the nature of the aryloxy substituents, with the rates for $[NP(OR)_2]_3$ decreasing in the order 4-$NO_2C_6H_4O^-$ > 3-$NO_2C_6H_4O^-$ > 2-$NO_2C_6H_4O^-$ ≫ C_6H_5O > 4-$CH_3C_6H_4O^-$. This overall sequence represents nearly a 10^6 times decrease in specific rate constant. The general trend in

(10) J. Kumamoto, J. R. Cox, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **78**, 4858 (1956).
(11) H. R. Allcock and E. J. Walsh, *ibid.*, **94**, 119 (1972).

Table I. Hydrolysis Rate Constants for Hexakis(aryloxy)cyclophosphazenes in 25 Vol % Aqueous Diglyme

Phosphazene (OR)	[Phosphazene], $\times 10^5$	[OH^-], $\times 10^2$	Temp, °C	$k_{1observed}$, sec^{-1}	$k_{2specific}$, l./ mol sec
II (2-$NO_2C_6H_4O$–)	1.54	0.65	80	1.42×10^{-4}	2.19×10^{-2}
II	1.75	2.13	80	4.25×10^{-4}	2.11×10^{-2}
II	1.03	2.70	80	5.90×10^{-4}	2.18×10^{-2}
II	0.50	2.65	80	5.65×10^{-4}	2.13×10^{-2}
II	1.54	1.02	55	2.01×10^{-5}	2.56×10^{-3}
III (3-$NO_2C_6H_4O$–)	4.97	0.69	80	8.68×10^{-4}	1.28×10^{-1}
III	4.97	0.34 (5)	80	4.32×10^{-4}	1.32×10^{-1}
III	2.49	0.69	80	8.62×10^{-4}	1.26×10^{-1}
III	4.50	0.98	55	8.80×10^{-4}	3.91×10^{-2}
IV (4-$NO_2C_6H_4O$–)	0.55	1.00	80	5.15×10^{-3}	5.16×10^{-1}
IV	0.40	0.96	35	5.71×10^{-4}	5.87×10^{-2}
IV	0.40	0.48	35	2.90×10^{-4}	5.92×10^{-2} [a]
IV	0.26	0.95	35	5.45×10^{-4}	5.75×10^{-2}
V (C_6H_5O–)	4.31	2.14	80	7.55×10^{-6}	3.53×10^{-6}
V	1.47	0.78	110	1.18×10^{-7}	1.52×10^{-7}
IX (C_6H_5O–) (tetramer)	2.29	1.96	80	1.21×10^{-7}	6.17×10^{-6}
VI (4-$CH_3C_6H_4O$–)	2.17	1.85	80	1.28×10^{-6}	6.93×10^{-7}
VI	1.27	0.78	110	1.40×10^{-6}	1.80×10^{-6}

[a] Hydrolysis of IV (3.05×10^{-6} *M*) with sodium hydroxide (5.61×10^{-3} *M*) at 35° in 15 vol % aqueous diglyme gave a specific rate constant of 2.07×10^{-1} (l./*M* sec).

reactivities parallels the decrease in acidity of the appropriate phenols. The reaction rates at two different temperatures were used to calculate the energies and entropies of activation shown in Table II. The reaction rates were increased by decreases in solvent polarity in the change from 25 to 15 vol % aqueous diglyme (Table I). It was also found that the cyclic tetramer, $[NP(OC_6H_5)_2]_4$ (IX), hydrolyzed nearly twice as fast as the trimer, $[NP(OC_6H_5)_3]_3$ (V), under the same conditions. This greater reactivity of the cyclic tetramer relative to the trimer is consistent with the results found for the hydrolysis of fluoroalkoxyphosphazenes.[11]

Table II. Activation Energies and Entropies for the Hydrolysis of Hexakis(aryloxy)cyclotriphosphazenes

Phosphazene	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu[a]
$[NP(OC_6H_4NO_2\text{-}4)_2]_3$ (IV)	10.25	−30.5
$[NP(OC_6H_4NO_2\text{-}3)_2]_3$ (III)	10.60	−32.0
$[NP(OC_6H_4NO_2\text{-}2)_2]_3$ (II)	18.20	−15.7
$[NP(OC_6H_5)_2]_3$ (V)	12.55	−48.2
$[NP(OC_6H_4CH_3\text{-}4)_2]_3$ (VI)	15.90	−40.5

[a] Calculated using k_2 specific at 80°.

Kinetic Results. Spirocyclophosphazenes. The rates of hydrolysis of tris(*o*-phenylenedioxy)cyclotriphosphazene (X) and tris(2,3-naphthalenedioxy)cyclotriphosphazene (XI) in solutions of sodium hydroxide in 25 vol % aqueous diglyme were too fast to be followed by the techniques used, even at 0°. However, the rates could be followed in neutral 25 vol % aqueous diglyme or in a buffer solution containing 6×10^{-7} *M* hydroxide ion in the same solvent. These results are summarized in Table III. The rates showed pseudo-first-order characteristics, as illustrated by straight-line ln A_t (ln absorbance at time *t*) against time plots. Activation energy values of 6.38 and 7.75 kcal/mol were calculated for X and XI, respectively, and the corresponding activation entropy values were −48.2 and −45.0 eu (the latter values calculated from the 0° rates). The *o*-phenylenedioxy derivative (X) hydrolyzed faster than the 2,3-naphthalenedioxy analog (XI).

Table III. Hydrolysis of Spirocyclophosphazenes in Neutral or Buffered 25 Vol % Aqueous Diglyme

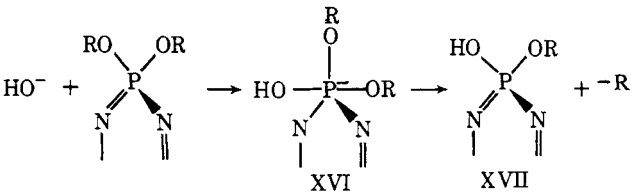
Phosphazene	[Phosphazene], $\times 10^5$	pH	Temp, °C	k_1,[a] sec^{-1}
X	1.30	7.79	0	8.52×10^{-3}
X	12.70	7.02	0	1.52×10^{-3}
X	1.33	7.02	32	5.23×10^{-3}
X	2.70	7.02	32	5.24×10^{-3}
XI	5.02	7.79	0	3.35×10^{-3}
XI	4.86	7.02	0	5.64×10^{-4}
XI	2.43	7.02	0	5.68×10^{-4}
XI	1.56	7.02	27.5	2.12×10^{-3}

[a] Graphical k_1 values.

Reaction Mechanism. The following are the principal mechanistic facts derived from these data. (a) The hydrolysis rates are first order in both phosphazene and hydroxide ion. (b) For hexakis(aryloxy)cyclotriphosphazene (I), removal of the first aryloxy group from phosphorus takes place very much faster than the removal of the second ligand or cleavage of the phosphazene ring. (c) In hexakis(aryloxy)cyclotriphosphazenes, electron-withdrawing ligands accelerate the hydrolysis rate and electron-supplying substituents retard it. (d) The hydrolysis rate is markedly accelerated by the presence of a five-membered exocyclic ring at phosphorus, but it is largely unaffected by a six- or seven-membered exocyclic system. (e) Hydrolysis of spirophosphazenes with a five-membered exocyclic ring results in *phosphazene* ring cleavage. In solvents with moderate concentrations of water the arylenedioxyphosphole ring is cleaved also, but at low water concentrations a cyclic phosphate ester (XIX or XX) is isolated. (f) The ^{18}O experiments indicate that P–O bonds are cleaved rather than C–O bonds. (g) Cyclic tetramers are hydrolyzed faster than cyclic trimers.

These characteristics (except item g) closely resemble those known for the hydrolysis of phosphate esters.[12-18]

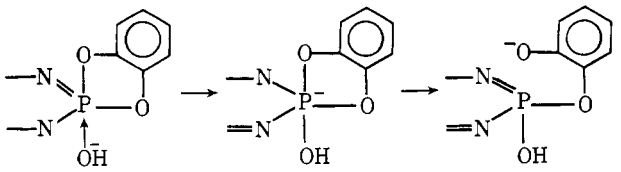
In particular, the reaction order, the ^{18}O results, and the rate-enhancing influence of electron-withdrawing ligands are consistent with an SN2-type mechanism in which hydroxide ion attacks phosphorus, and phenoxide ion is displaced. Implicit in this mechanism is the postulation of a pentacoordinate trigonal bipyramidal transition state (XVI). Thus, electron withdrawal by the



ligand from phosphorus facilitates attack by hydroxide ion at phosphorus, and electron supply to phosphorus retards this process. Ligands such as nitrophenoxy groups may also serve to stabilize the transition state by delocalization of the negative charge.

In these terms, the influence by 4-nitrophenoxy, 3-nitrophenoxy, phenoxy, and 4-methylphenoxy substituents can be readily understood. However, the high activation energy shown by the 2-nitrophenoxy derivative indicates the presence of a substantial steric hindrance factor, and yet the hydrolysis rate remains surprisingly high. This behavior also is reminescent of that reported for the hydrolysis of nitrophenylphosphate esters.[18] Presumably, the high entropy of activation for the hydrolysis of the 2-nitrophenoxyphosphazene (Table II) is responsible for the rapid reaction of this compound, and this may reflect either an increase in P–O bond length in the transition state or a decrease in solvation order because of poor delocalization.[12] The more rapid hydrolysis rates of the cyclic tetramers VIII and IX than of the respective trimers IV and V is consistent with the behavior of the chloro derivatives, $(NPCl_2)_3$ and $(NPCl_2)_4$, during hydrolysis, and with the degradation reactions of cyclophosphazenes to phosphoranes with catechol or *o*-aminophenol.[9,19] Cyclic tetramers react faster because the cyclotetraphosphazene ring is more flexible than the cyclotriphosphazene ring, and presumably the former can more easily accommodate the N–P–N bond angle changes which accompany the approach to the transition state in a nucleophilic substitution process. The phosphorus atoms in a puckered cyclic tetramer may also be more exposed to nucleophilic attack.

The exceedingly rapid hydrolysis of aryloxyphosphazenes which contain a five-membered exocyclic unit at phosphorus also reflects the behavior of related cyclic phosphate esters.[14,15] Cleavage of the exocyclic ring involves a release of steric strain and this clearly constitutes the driving force for the process. Spirophosphazenes with six- and seven-membered exocyclic rings are presumably unstrained and this driving force is absent. Thus, exocyclic ring cleavage follows the same mechanism as that discussed above for the aryloxy derivatives. Hydroxide ion attack at phosphorus can occur axially and an axial P–OAr bond is cleaved.



This mechanism is consistent with the low activation energies and very low activation entropies found for this particular system. Rapid cleavage of the phosphorus–nitrogen bond presumably occurs in a subsequent step (perhaps facilitated by the ortho oxyanion unit), although the rapidity of this secondary process is surprising in view of the stability of species such as XVII to subsequent attack.

The isolation of cyclic phosphates, such as XIX and XX, from hydrolysis reactions in media with low water content presents a mechanistic anomaly. If such species are formed by phosphazene ring cleavage, but without arylenedioxyphosphole ring cleavage, then pseudorotation[15] or equatorial P–N bond cleavage must be assumed. Pseudorotation would be inhibited in a molecule of this type because of the requirement that the N–P–N bond angle must approximate to 120° in a cyclic trimeric ring. Furthermore, there is no precedent for equatorial hydroxide ion attack or for axial attack followed by nonpseudorotatory, equatorial cleavage. A possible explanation is that an initial cleavage of the phenylenedioxyphosphole ring is followed first by cleavage of the phosphazene ring and *then* by recyclization to species such as XIX or XX. The known ability of dioxane and diglyme to complex strongly with water could provide a driving force for this last step. The facile cyclizations of XVIII and 2-hydroxy-3-naphthyl dihydrogen phosphate have been observed at elevated temperatures or in anhydrous media.

Experimental Section[20]

Materials. Hexachlorocyclotriphosphazene (Hooker Chemical Corp. or Millmaster Onyx) was recrystallized twice from *n*-heptane to yield material, mp 112–113°. Octachlorocyclotetraphosphazene (Alfa Inorganics), mp 121–123°, was used as received. 4-Nitrophenol (Aldrich) was recrystallized from toluene to yield material, mp 114°. 3-Nitrophenol (Aldrich) was recrystallized from a diethyl ether–petroleum ether mixture to give crystals, mp 96°. 2-Nitrophenol (Aldrich) was recrystallized from absolute ethanol to yield material, mp 44–45°. Phenol (Fisher) was distilled to yield a product, mp 42–43°. 4-Methylphenol (Aldrich) was vacuum distilled to yield material, mp 34–35°. Anhydrous sodium carbonate (Baker and Adamson) was used as received. Tetrahydrofuran and toluene (Fisher) were distilled from calcium hydride before use. Diethyl ether (Fisher) was dried over sodium and then filtered before use. The diglyme (bis-2-methoxyethyl ether) and water used for the kinetic runs were prepared as described previously.[11] Dioxane was purified by treatment with hydrochloric acid, sodium hydroxide pellets, and sodium metal, followed by distillation.[21] Analyses were by Schwarzkopf Microanalytical Laboratory or Midwest Microlabs.

Hexaphenoxycyclotriphosphazene (V), Octaphenoxycyclotetraphosphazene (IX), and Hexakis(4-methylphenoxy)cyclotriphosphazene (VI). All three compounds were prepared by the interaction

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(20) Ultraviolet and visible spectra were recorded on a Cary Model 15 spectrophotometer. Infrared spectra were obtained with the use of a Beckman IR-5 instrument, and mass spectra were obtained with an AEI MS9 spectrometer. Proton nmr spectra were obtained with the use of a Varian A-60 or A-60A spectrometer.

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of sodium aryloxide with the appropriate chlorocyclophosphazene in tetrahydrofuran solution by the general method described previously.[6] Compound V, mp 111.5–112°, was isolated in 50% yield. *Anal.* Calcd for $C_{36}H_{30}O_6P_3N_3$: C, 62.40; H, 4.33; N, 6.06. Found: C, 62.48; H, 4.50; N, 6.10. The tetramer (IX), mp 86°, was prepared in 80% yield. *Anal.* Calcd for $C_{48}H_{40}O_8P_4N_4$: C, 62.40; H, 4.33; N, 6.06. Found: C, 62.44; H, 4.55; N, 5.94. The 4-methylphenoxy derivative (VI), mp 118–119°, was isolated in 78.7% yield. *Anal.* Calcd for $C_{39}H_{36}O_6N_3P_3$: C, 64.86; H, 5.41; N, 5.41; Found: C, 64.79; H, 5.50; N, 5.40.

Nitrophenoxycyclophosphazenes. The following procedure, for the synthesis of hexakis(2-nitrophenoxy)cyclotriphosphazene (II), is typical. A mixture of hexachlorocyclotriphosphazene (24.4 g, 0.07 mol), 2-nitrophenol (58.7 g, 0.422 mol), and anhydrous sodium carbonate (45.0 g, 0.425 mol) was allowed to react for 72 hr in boiling tetrahydrofuran (500 ml). The mixture was then cooled to 25° and solvent was removed in a rotary evaporator. The solid residue was washed with 95% ethanol (2.5 l.), and the remaining solid was dissolved in dimethylformamide (50 ml) and then precipitated by the addition of distilled water (200 ml). The solid was removed by filtration, dried, and recrystallized from a cyclohexanone–ethanol mixture to yield **hexakis(2-nitrophenoxy)cyclotriphosphazene** (II) (53.4 g, 79%), mp 155–155.5°. *Anal.* Calcd for $C_{36}H_{24}O_{18}N_9P_3$: C, 44.86; H, 2.49; P, 9.69. Found: C, 44.74; H, 2.35; P, 9.72. A characteristic trimeric, infrared P–N ring stretching vibration was observed at 1185 cm^{-1}. Molecular weight from mass spectrum, 963 (theory, 963).

Similar procedures yielded **hexakis(3-nitrophenoxy)cyclotriphosphazene** (III), mp 141–141.5° (recrystallized from benzene–heptane), in 30% yield. *Anal.* Calcd for $C_{36}H_{24}O_{18}N_9P_3$: C, 44.87; H, 2.51; N, 13.08. Found: C, 44.62; H, 2.46; N, 12.82. Molecular weight from mass spectrum, 963 (theory, 963). **Hexakis(4-nitrophenoxy)cyclotriphosphazene** (IV), mp 258° (recrystallized from cyclohexanone) (lit.[22] 263–264°), was isolated in 80% yield. *Anal.* Calcd for $C_{36}H_{24}O_{18}N_0P_3$: C, 44.86; H, 2.51; N, 13.08. Found: C, 45.02; H, 2.66; N, 12.98. Molecular weight from mass spectrum, 963 (theory, 963). **Octakis(4-nitrophenoxy)cyclotetraphosphazene** (VIII), mp 296–297° (recrystallized from dimethylformamide) (lit.[22] 299°), was formed in 38% yield. *Anal.* Calcd for $C_{48}H_{32}O_{24}P_4N_{12}$: C, 44.86; H, 2.51; N, 13.08. Found: C, 45.00; H, 2.34; N, 13.10. All these compounds were pale yellow in color.

Pentakis(4-nitrophenoxy)chlorocyclotriphosphazene (XXI), mp 182–183° (lit.[22] 183°), was prepared by the 24-hr interaction of a 5:1 molar mixture of sodium 4-nitrophenolate and $(NPCl_2)_3$ in a boiling tetrahydrofuran–toluene medium. *Anal.* Calcd for $C_{30}H_{20}ClO_{15}N_9P_3$: C, 41.80; H, 2.35; Cl, 4.13. Found: C, 42.00; H, 2.30; Cl, 4.10. Hydrolysis of XXI (2.0 g, 2.15×10^{-3} mol) for 30 min in a boiling solution of potassium hydroxide (4.0 g), water (1 ml), and ethanol (50 ml) yielded **1,3,3,5,5-pentakis(4-nitrophenoxy)-1-oxo-2-hydrocyclotriphosphazadiene** (XVII, R = 4-nitrophenol), mp 223.°

Product from the Hydrolysis of Hexakis(4-nitrophenoxy)cyclotriphosphazene (IV). A solution of IV (0.4 g) in diglyme (600 ml) was mixed with a solution of sodium hydroxide (0.40 g) in distilled water (200 ml) and the resultant solution was boiled at reflux for 5 hr. The solvents were removed on a rotary evaporator, and the residue was dissolved in absolute ethanol (200 ml) and then acidified with concentrated hydrochloric acid (1.0 ml). The solution was heated to 50°, filtered, and cooled to give light yellow crystals of **1,3,3,5,5-pentakis(4-nitrophenoxy)-1-oxo-2-hydrocyclotriphosphazadiene** (XVII, R = 4-nitrophenoxy) (0.1 g), mp 223°. Proton nmr spectra showed two sets of phenyl proton peaks centered at δ 7.9 and 7.1, and an NH proton peak at δ 5.3, with an integrated ratio of 20:1. The infrared spectrum showed a characteristic P–N–H band at 2650 cm^{-1} and a P=O band at 1300 cm^{-1}, in addition to a characteristic P–N ring vibration at 1210 cm^{-1}.

Product from the Hydrolysis of Hexakis(2-nitrophenoxy)cyclotriphosphazene (II). A solution of II in basic aqueous diglyme, prepared as described above, was boiled for 10 hr. The reaction mixture was then acidified with concentrated hydrochloric acid (5 ml), and the solvents were removed on a rotary evaporator. The residue was extracted with warm ethanol (200 ml), filtered, and the filtrate was evaporated to yield the dark yellow **1,3,3,5,5-pentakis(2-nitrophenoxy)-1-oxo-2-hydrocyclotriphosphazadiene** (XVII, R = 2-NO_2 C_6H_4O–) (0.05 g, 15%), mp 130°. Infrared spectra showed a P–N–H band at 1300 cm^{-1}. The mass spectrum of this material showed a very strong peak at 841 amu, which corresponded to the expected molecular weight of XVII. The breakdown pattern was similar to that of the initial phosphazene (II), but the mass spectrum of II shows no peak at 841 amu.

Product from the Hydrolysis of Hexakis(3-nitrophenoxy)cyclotriphosphazene (III). A solution of III in basic aqueous diglyme, prepared as described above, was boiled for 12 hr, and the mixture was then cooled and acidified with concentrated hydrochloric acid (5 ml). Removal of the solvents left a yellow residue, which was recrystallized from absolute ethanol to yield the pale yellow solid, **1,3,-3,5,5-pentakis(3-nitrophenoxy)-1-oxo-2-hydrocyclotriphosphazadiene** (~0.05 g), mp 150–154°. The infrared spectrum of this solid showed a characteristic P–N–H band at 2655 cm^{-1} and a P=O band at 1305 cm^{-1}. A mass spectrum showed a parent peak at 841 amu, which corresponded to the expected molecular weight of the product.

Qualitative Hydrolysis of Octakis(4-nitrophenoxy)cyclotetraphosphazene (VIII). Quantitative data could not be obtained because of the insolubility of the phosphazene in the reaction medium. A slurry of octakis(4-nitrophenoxy)cyclotetraphosphazene (0.05 g), in 25 vol % aqueous diglyme (100 ml) containing 1.0×10^{-2} *M* sodium hydroxide, was heated for 1 hr at 55°. The solution became yellow and, after 1 hr, no solid remained. Visible spectroscopy at 405 mμ indicated 100% removal of the first 4-nitrophenoxy group. The reaction mixture was then stirred for an additional 12 hr at 55°, but no detectable increase in nitrophenoxide ion concentration was observed.

Hydrolysis of Hexakis(4-nitrophenoxy)cyclotriphosphazene in Diglyme–$H_2{}^{18}O$. A solution of hexakis(4-nitrophenoxy)cyclotriphosphazene (0.005 g, 5.2×10^{-6} mol) in diglyme (60 ml) was mixed with a 1% $H_2{}^{18}O$ solution which contained sodium hydroxide (8×10^{-3} g, 2.0×10^{-4} mol) in water (20 ml). The solution was boiled at reflux for 2 hr, the solvents were removed by evaporation, and the residue was dissolved in anhydrous ethanol (25 ml) and acidified with concentrated hydrochloric acid (0.1 ml). The solvent was again evaporated, and the residue was analyzed mass spectrometrically. The largest peak at 139 amu corresponded to 4-nitrophenol, but no peak was observed at 141 amu, which would have corresponded to the ^{18}O containing product. Thus, P–O bonds are cleaved rather than C–O bonds.

Product from the Hydrolysis of Hexaphenoxycyclotriphosphazene (V). A solution of hexaphenoxycyclotriphosphazene (4.3×10^{-5} *M*) and sodium hydroxide (2.14×10^{-2} *M*) in 25% aqueous diglyme (40 ml) was allowed to react at 80° for 400 hr. The solvents were then removed at reduced pressure and the residue was dissolved in absolute ethanol (25 ml) and treated with concentrated hydrochloric acid (0.1 ml). Filtration, followed by evaporation of the filtrate yielded a trace of solid material. A mass spectrum of this material showed a parent peak at 616 amu, which corresponded to the molecular weight of **1,3,3,5,5-pentaphenoxy-1-oxo-2-hydrocyclotriphosphazene.**

Attempted Hydrolysis of Poly[bis(phenoxy)phosphazene] $[NP(OC_6H_5)_2]_n$. Because of the insolubility of the high polymer in aqueous–organic media, a heterophase reaction was attempted. A mixture of poly[bis(phenoxy)phosphazene] (0.05 g), diglyme (60.0 ml), and 4×10^{-2} *M* sodium hydroxide solution (20.0 ml) was heated at 80° for 400 hr within a nitrogen filled sealed flask. No free phenol or phenoxide ion could be detected by an aminoantipyrine test.[23]

Tris(*o*-phenylenedioxy)cyclotriphosphazene (X), tris(2,3-naphthalenedioxy)cyclotriphosphazene (XI), tris(1,8-naphthalenedioxy)-cyclotriphosphazene (XII), tetrakis(1,8-naphthalenedioxy)cyclotetraphosphazene (XIV), tris(2,2′-dioxybiphenyl)cyclotriphosphazene (XIII), and tetrakis(2,2′-dioxybiphenyl)cyclotetraphosphazene (XV) were prepared by methods described previously.[7-9]

***o*-Phenylene Hydrogen Phosphate ($C_6H_4O_2P(O)OH$).** A mixture of phosphorus pentoxide (28.4 g, 0.2 mol) and 1,2-dihydroxybenzene (22.02 g, 0.2 mol) was heated in an erlenmeyer flask on a steam bath for 30 min. The unreacted 1,2-dihydroxybenzene was sublimed from the reaction mixture at 80° (3 mm), and the residue was then distilled at reduced pressure to yield a fraction which boiled at 236–238° (1 mm). The clear, liquid distillate was redistilled at 237–239° (1 mm) (lit.[24] 238–239° (1 mm)) to yield *o*-phenylene hydrogen phosphate (7.0 g, 20%), a clear liquid which solidified to a glass at room temperature.

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2-Hydroxyphenyl Dihydrogen Phosphate (XVIII). A solution of *o*-phenylene hydrogen phosphate (0.95 g, 5.5×10^{-3} mol) in water (10 ml) was heated on a steam bath for 30 min. The water was removed in a rotary evaporator, the residue was dissolved in acetonitrile (10 ml), and the solution was dried over anhydrous sodium sulfate. After filtration, acetonitrile was removed from the filtrate, and the residue was recrystallized from benzene to yield the white solid XVIII, mp 138° (lit.[24] mp 138–139°).

Sodium *o*-Phenylene Phosphate (XIX). A solution of *o*-phenylene hydrogen phosphate (0.285 g, 1.65×10^{-3} mol) in acetonitrile (8.0 ml) was neutralized with a stoichiometric amount of sodium hydroxide in water (2.0 ml). Removal of the solvents at 0.01 mm yielded a white residue of XIX. An infrared spectrum showed no hydroxyl peaks in the 3000-cm^{-1} region.

Product from the Hydrolysis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (X). A solution of X (0.194 g, 4.22×10^{-4} mol) in diglyme (150 ml) was mixed with aqueous 4.22×10^{-2} *M* sodium hydroxide solution (50 ml) and allowed to react at 25° for 10 min. An ultraviolet spectrum indicated the presence of sodium 2-hydroxyphenyl hydrogen phosphate (Na salt of XVIII) only. This same product, mp 137°, was recovered by evaporation of the solvent. Ammonia was detected during this evaporation procedure.

Product from the Hydrolysis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (X) in Basic 1% Aqueous Dioxane. A mixture of X (0.289 g, 6.30×10^{-4} mol) and sodium hydroxide (1.9×10^{-3} mol) in 1 vol % aqueous dioxane (200 ml) was stirred at 25° for 24 hr, during which time a white solid precipitated slowly from the reaction mixture. This solid showed identical infrared, ultraviolet, and mass spectra with an independently synthesized sample of sodium *o*-phenylene phosphate. Additional water (10 ml) was then added to the above reaction mixture, and the solution was boiled for 1 hr. Ammonia was evolved, orthophosphate was detected by precipitation with ammonium molybdate, and free 1,2-dihydroxybenzene was identified by ultraviolet spectroscopy.

Hydrolysis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (X) in Basic Dioxane–$H_2{}^{18}O$. A solution of X (0.285 g, 6.22×10^{-4} mol) in a solution of sodium hydroxide (1×10^{-2} *M*) in 25 vol % aqueous dioxane containing 1% of the water as $H_2{}^{18}O$ was stirred at 25° for 10 min, and the solvents were then removed in a rotary evaporator. The residue was examined by mass spectrometry. At 20 eV, the peak at 172 amu (from cyclic *o*-phenylene hydrogen phosphate) was accompanied by a peak at 174 amu and a weaker peak at 176 amu. The 70-eV spectrum showed 1,2-dioxyphenyl fragments at 108 amu, but no 110-amu peak. These results indicate that P–O bonds are cleaved rather than C–O bonds.

Product from the Hydrolysis of Tris(2,3-naphthalenedioxy)cyclotriphosphazene (XI). A solution of XI (0.25 g, 4.11×10^{-4} mol) and sodium hydroxide (0.4 g, 1×10^{-2} mol) in 1% aqueous diglyme was stirred at 25° for 25 hr, during which time a white precipitate formed. This solid was filtered off and dried at 25° for 24 hr. A mass spectrum of this solid showed a prominent parent peak at 224 amu which corresponded to the expected molecular weight of 2,3-naphthalene hydrogen phosphate (XX). An infrared spectrum suggested the presence of a phosphoric acid ester hydrate.

Attempted Basic Hydrolysis of Tris(1,8-naphthalenedioxy)cyclotriphosphazene (XII), Tetrakis(1,8-naphthalenedioxy)cyclotriphosphazene (XIV), Tris(2,2′-dioxybiphenyl)cyclotriphosphazene (XIII), and Tetrakis(2,2′-dioxybiphenyl)cyclotriphosphazene (XV). Homogeneous solutions of these phosphazenes (1.7×10^{-5} *M*) and sodium hydroxide (1.0×10^{-2} *M*) in 25 vol % aqueous diglyme were sealed in Pyrex tubes, and the tubes were heated at 110° in boiling toluene for 300 hr. After this time, no free phenolic or phenoxidic groups could be detected by ultraviolet spectroscopy or by the use of an aminoantipyrine test. A heterogeneous mixture of tris(1,8-naphthalenedioxy)cyclotriphosphazene (0.05 g) in 1×10^{-2} *M* sodium hydroxide in 25 vol % aqueous diglyme (15 ml) was heated in a sealed tube at 110° for 500 hr. When this mixture was tested with aminoantipyrine reagent, a faint pink color denoted the presence of a trace of phenolic-type species present.

Acidic Hydrolysis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (X). A solution of X (4×10^{-5} *M*) in diglyme (15 ml) was mixed with 5 ml of aqueous hydrochloric acid solution (4×10^{-2} *M*), and the solution was stirred at 25° for 1 hr. The solution was then diluted with water (30 ml) and the precipitated solid was filtered off. This unreacted phosphazene was dissolved in methylene chloride (50 ml) and the concentration was determined by ultraviolet spectroscopy. It was found that 95% of the starting material was recovered.

Kinetic Technique. (a) Nitrophenoxyphosphazenes. All the nitrophenoxyphosphazene kinetic runs were performed spectrophotometrically in stoppered quartz cells within the thermoregulated cell compartment of a Cary 15 spectrophotometer. The temperature was maintained within ±0.05° of the required value by the rapid circulation of water from a constant temperature bath through the cell housing. All reagent and solvent transfers were effected in a nitrogen-filled dry bag which contained a solution of pyrogallol to remove oxygen. A stock solution of the phosphazene ester in diglyme and stock aqueous sodium hydroxide solution were placed in a constant temperature bath at the reaction temperature for at least 20 min before samples were mixed. The quartz cell was also allowed to equilibrate to the thermoregulated housing temperature at least 1 hr before use.

Infinity values were determined from the absorbance values at 10 and 15 times the theoretical half-life, or until constant values were obtained over a 3-hr time span. The concentration of phosphazene in the stock solution was determined with the use of previously measured absorbance–concentration relationships. The base concentrations were measured by titration of a duplicate of the reaction mixture and also by titration of the reaction mixture itself after completion of the reaction.

Use of experimentally determined absorbance values, corrected for a small absorbance at time 0, gave calculated k_1 values which were in good agreement with the values obtained from the slope of the straight line plot of ln (absorbance$_\infty$ − absorbance$_t$) *vs.* time.

Kinetic Technique. (b) Phenoxy- and 4-Methylphenoxyphosphazenes. A different kinetic technique was used for the phenoxy and 4-methylphenoxy derivatives because of their slow rates of hydrolysis. A solution of the phosphazene (3×10^{-5} *M*) and sodium hydroxide (1×10^{-2} *M*) in 25 vol % aqueous diglyme (80.0 ml) was sealed in a nitrogen atmosphere within a glass flask fitted with a silicone rubber septum. The flask was then almost totally immersed in a constant temperature bath (80°) or in boiling toluene (110°), and the solution was sampled by means of a hypodermic syringe. After sampling, a 5-ml sample of the reaction mixture was pipetted into a 50-ml volumetric flask and 10.0 ml of a saturated aqueous sodium borate solution, 1.0 ml of an aqueous 3% aminoantipyrine solution, 1 ml of an aqueous 2% ammonium peroxydisulfate solution, and another 10.0-ml portion of saturated aqueous sodium borate solution were added. The color was allowed to develop for 10 min and the solution was then diluted to 50.0 ml with distilled water. This procedure provides a quantitative colorimetric test for aryloxide ions. The visible spectrum of each sample was compared with that of a control solution which contained all the reactants except the phosphazene. Pseudo-first-order rate constants were then calculated as discussed previously.

The base concentration of each sample was determined by titration with standardized hydrochloric acid. After 500 hr at 80° or 300 hr at 110°, significant changes in base concentration occurred due to a reaction with and etching of the glass reaction flasks.

Kinetic Technique. (c) Spirocyclophosphazenes. A typical procedure employed for the hydrolysis of tris(*o*-phenylenedioxy)cyclotriphosphazene or tris(2,3-naphthalenedioxy)cyclotriphosphazene was as follows. A stock solution of the phosphazene (2×10^{-5} *M*) in freshly distilled diglyme (150 ml) at the reaction temperature was mixed with either water (50 ml) or a buffer solution (50 ml) at the same temperature in a flask which was immersed in a constant temperature bath. The buffer solution employed was prepared from 25 ml of a solution of tris(hydroxymethyl)aminomethane (6.06 g, 0.05 mol) in distilled water (250 ml) with 25 ml of a solution of tris(hydroxymethyl)aminomethane (6.06 g, 0.05 mol) in 250 ml of 0.2 *M* hydrochloric acid. The pH of the buffer solution before mixing with the diglyme was 7.93. After mixing with diglyme, the pH was 7.79. The pH of the solution prepared with distilled water was found to be 7.02, with the pH values in all cases being determined with the use of a glass electrode and a Beckman pH meter.

Samples (25 ml) from the reaction mixture were diluted with distilled water (25 ml) to precipitate unreacted spirocyclophosphazene, and the latter was collected by filtration on a fine porosity sintered glass funnel and then dried for 1 hr at 25° *in vacuo*. The phosphazene was then redissolved in methylene chloride by washing of the glass funnel with three 10-ml aliquots of the solvent. The methylene chloride solution was then diluted quantitatively to 50 ml and the unreacted phosphazene concentration was determined by ultraviolet spectroscopy at 268 (for X) or 276 mμ (for XI). Control reactions yielded 98–99% recovery of the unreacted phosphazene after 20 sec at 0°. Pseudo-first-order rate constants were calculated from the slopes of the plots of ln A_t − (absorbance at time *t*) against time.

Ultraviolet Spectra. The following are λ_{max} values in mμ for compounds used in this study: $[NP(OC_6H_4NO_2\text{-}o)_2]_3$ (II), 254 sh;

$^{-}OC_6H_4NO_2$-*o*, 423; $[NP(OC_6H_4NO_2$-*m*$)_2]_3$ (III), 258 sh; $^{-}OC_6H_4NO_2$-*m*, 415; $[NP(OC_6H_4NO_2$-*p*$)_2]_3$ (IV), 264 (log ϵ 2.43); $[NP(OC_6H_4NO_2$-*p*$)_2]_4$, 265 (log ϵ 2.39); $^{-}OC_6H_4NO_2$-*p*, 405; $[NP(O_2C_{10}H_6$-1,8$)]_3$ (XII), 220, 225 sh, 269 sh, 280, 291 (log ϵ 4.37), 296 sh, 304 sh, 310, 318, 325; $[NP(O_2C_{10}H_6$-1,8$]_4$ (XIV), 220, 225 sh, 280, 291 (log ϵ 4.49), 296 sh, 305 sh, 310, 318, 325; and $[NP(O_2C_{12}H_8$-2,2′$)]_4$ (XV), 243 (log ϵ 4.81), 270 sh, 278 sh. The spectra of V, X, XI, and XII have been recorded previously.[7,8]

The kinetic runs were monitored at the following wavelengths: $[NP(OC_6H_4NO_2$-*o*$)_2]_3$ (II), 423 mμ; $[NP(OC_6H_4NO_2$-*m*$)_2]_3$ (III), 415 mμ; $[NP(OC_6H_4NO_2$-*p*$)_2]_3$, 405 mμ; $[NP(O_2C_6H_4$-1,2$)]_3$ (X), 268 mμ; and $NP(O_2C_{10}H_6$-1,2$)]_3$ (XI), 276 mμ.

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Stereochemically Nonrigid Six-Coordinate Molecules. II. Preparations and Reactions of Tetrakis(organophosphorus) Metal Dihydride Complexes

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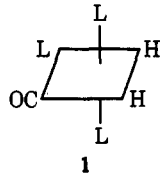
Abstract: A series of iron and ruthenium H_2ML_4 complexes were prepared with trivalent phosphorus (L) ligands. Synthesis of the iron complexes was greatly facilitated through a new and general procedure based on the reaction of bis(1,3,5,7-cyclooctatetraene)iron and a phosphorus(III) compound with hydrogen. The reaction chemistry of these coordinately saturated hydride complexes was explored. Reaction at the metal site required conditions where ligand dissociation was occurring at a reasonable rate. Consistent with this generalization, complexes possessing bulky ligands were found more reactive than those which have sterically less hindered ligands. Ostensibly, this reflects the greater propensity of the former class for ligand dissociation. Transesterification experiments using phosphites and methanol showed that metal-coordinated phosphites exchange with alcohol significantly slower than weakly coordinated or free phosphites.

Transition metal hydride complexes have attracted considerable interest during the past decade, especially in connection with catalytic processes[1] and structure elucidation.[2] We have recently communicated[3] on the stereochemical behavior of certain tetrakis(organophosphorus) metal dihydrides. These H_2FeL_4 complexes are stereochemically nonrigid on the nmr time scale and, because of ^1H–^{31}P couplings, are often amenable to detailed line-shape analyses yielding mechanistic information.[4] During these investigations, a substantial number of new iron and ruthenium complexes were prepared using synthetic methods of general utility. This paper describes the preparation and some reaction chemistry of metal dihydrides. A full discussion of the dynamic stereochemistry will be published in part III[5] of this series.

Structures of H_2ML_4 and H_2ML_3CO Complexes. Results of some nmr investigations of these hydride complexes and the structural implications have been reported;[3,4] the full analysis will be presented in part III.[5] Twelve of the fifteen H_2FeL_4 complexes exhibit evidence only for cis structures at $-50°$ in toluene solution as discerned by analysis of the nmr spectra. Two complexes, $H_2Fe[P(C_6H_5)(OC_2H_5)_2]_4$ and $H_2Fe[P(C_6H_5)(OCH_3)_2]_4$, populate significant amounts of the cis and trans forms in solution. The cis/trans ratio is lowest in *n*-hexane (0.95) and highest in methylene chloride (6.52) for the former in the more common organic solvents. One complex, $H_2Fe\{o\text{-}C_6H_4[P(C_2H_5)_2]_2\}_2$, detectibly (nmr) populates only the trans structure at $-50°$ in toluene, but exchange studies[5] showed that the cis form must be present in low concentration.[5] At higher temperatures, the limiting spectra of all iron compounds are quintets; relatively rapid intramolecular exchange is a characteristic feature of these molecules. This class of six-coordinate complexes is important because it provides the first unequivocal demonstration of intramolecular rearrangement in six-coordinate complexes.

The carbonyl complexes, H_2FeL_3CO [L = $P(C_6H_5)_2(CH_3)$, $P(C_6H_5)_2(C_2H_5)$], in toluene solution at $-50°$ exhibit hydride spectra consistent with the cis structure, **1**.



1

Above $-50°$, the proton nmr spectra broaden and finally emerge as regular quartets, indicating averaging of phosphorus environments. These iron complexes are thus stereochemically nonrigid like the $H_2M(PX_3)_4$ molecules. The cis structure **1** was proposed by Keim,

(1) C. A. Tolman in "Transition Metal Hydrides," Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 6.
(2) J. P. Jesson, *ibid.*, Chapter 4.
(3) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 1068 (1970); P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, **92**, 3482 (1970).
(4) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971).
(5) P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, in press.