monium zeolite A, in an attempt to prepare the hydrogen form, causes a complete collapse of the crystal structure. As shown above, the structure of high-silica acid ZK-22 is thermally stable. Table XV contains $\alpha$

TABLE XV
CRACKING ACTIVITY OF HYDROGEN ZEOLITE ZK-22

| Expt | SiO$_2$/ Al$_2$O$_3$ | Residual Na, wt % | $\alpha$ | n-Hexane sorption, g/100 g of zeolite |
|------|------|------|------|------|
| 19 | 3.94 | 0.21 | 160 | Nd |
| 24 | 5.66 | 0.39 | 850 | 11.9 |
| 32 | 5.70 | 0.14 | 55,000 | 13.5 |
| | After steaming | | 200 | ⋯ |

values of hydrogen zeolite ZK-22. It is evident that the activity increases with the silica content and with decreasing sodium content. After severe steam treatment, the material was still 200 times as active as fresh silica–alumina compared with 20 for steamed Ce, La, H faujasite.[18] The highest activity sample gave only

0.1% conversion of methylpentane, thus proving shape-selectivity of the zeolite.

Table XVI shows the activities of lanthanum hydro-

TABLE XVI
CRACKING ACTIVITY OF LANTHANUM HYDROGEN ZEOLITE ZK-22

| Expt | SiO$_2$/ Al$_2$O$_3$ | Residual Na, wt % | Equiv of La$^{3+}$/Al | $\alpha$ | n-Hexane sorption, g/100 g of zeolite |
|------|------|------|------|------|------|
| 19 | 3.94 | 1.1 | 0.71 | 46 | 11.6 |
| 21 | 4.06 | 0.79 | 0.87 | 26 | 14.5 |
| 32 | 5.70 | 0.18 | 0.47 | 4100 | 12.6 |

gen forms of zeolites ZK-21 and ZK-22. Again the most siliceous sample with the lowest percentage of residual sodium shows the highest activity.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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# Phosphonitrilic Compounds. XI.[1] Electroreduction and Electron Spin Resonance Spectra of Phosphazenes[2]
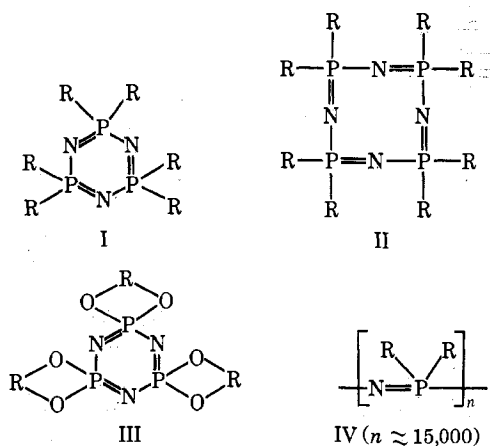
BY H. R. ALLCOCK* AND W. J. BIRDSALL

Electrolytic reduction of several organocyclophosphazenes in nonaqueous media has generated phosphazene radical anions, and electron spin resonance spectra of these species have been observed. The data suggest that the organic ligands are the primary reduction sites.
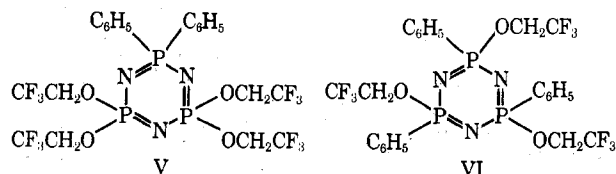
## Introduction

The reduction of organic aromatic compounds to radical anions has been widely investigated, and the reduction potentials and electron spin resonance spectra of the products have provided valuable structural information. Considerably less information is available about inorganic "pseudoaromatic" systems. Reduction potentials have been reported for borazines,[3] and radical anions have been obtained from tetrasulfur tetranitride,[4] but no prior electrolytic reduction studies have been described for cyclo- and polyphosphazenes (phosphonitriles).

We have undertaken an electrolytic reduction and electron spin resonance examination of a number of phosphazene derivatives. The compounds studied included cyclic trimers of general structure I where R is C$_6$H$_5$, OC$_6$H$_5$, p-OC$_6$H$_4$NO$_2$, OCH$_2$CF$_3$, OCH$_3$, NHC$_6$H$_5$, F, Cl, and Br, cyclic tetramers of structure II where R is C$_6$H$_5$, OC$_6$H$_5$, and OCH$_2$CF$_3$, spirocyclic trimers of structure III where O$_2$R is 2,3-O$_2$C$_{10}$H$_6$ (dioxynaphthyl), 1,8-O$_2$C$_{10}$H$_6$ (dioxynaphthyl), 1,2-O$_2$C$_6$H$_4$ (o-dioxyphenyl), and 2,2'-O$_2$C$_{12}$H$_8$ (dioxybiphenyl), and linear

(1) Part X: H. R. Allcock and E. J. Walsh, *Inorg. Chem.*, **10**, 1643 (1971).
(2) A preliminary report on this work has appeared: H. R. Allcock and W. J. Birdsall, *J. Amer. Chem. Soc.*, **91**, 7541 (1969).
(3) D. F. Shriver, D. E. Smith, and P. Smith, *ibid.*, **86**, 5153 (1964).
(4) D. Chapman and A. G. Massey, *Trans. Faraday Soc.*, **58**, 1291 (1962).



high polymers of structure IV where R is OC$_6$H$_5$ and OCH$_2$CF$_3$. The mixed-substituent cyclic trimers, V and VI, were also examined.

The only electron spin resonance measurements reported previously with phosphazenes were by Chapman, Glarum, and Massey,[5] who described the formation of the biphenyl radical anion spectrum when $[NP(C_6H_5)_2]_3$ was treated with metallic sodium.

## Results and Discussion

**Electrochemical Results.**—A number of phosphazenes were reduced electrolytically at a dropping mercury electrode in dimethylformamide in the presence of 0.1 *M* tetra-*n*-butylammonium iodide as the supporting electrolyte. Half-wave potentials $(E_{1/2})$ are shown in Table I. The following compounds did not reduce at

TABLE I
HALF-WAVE REDUCTION POTENTIALS
AND ESR BEHAVIOR OF PHOSPHAZENES

| Compound | $E_{1/2}$ vs. sce, V | No. of esr lines |
|---|---|---|
| $[NP(C_6H_5)_2]_3$ (VII) | -2.65 | 1 |
| $[NP(C_6H_5)_2]_4$ (VIII) | -2.67 | 1 |
| $[NP(OCH_2CF_3)(C_6H_5)]_3$ (VI) | -2.45 | 0 |
| $N_3P_3(C_6H_5)_2(OCH_2CF_3)_4$ (V) | -2.57 | 1 |
| $[NP(OC_6H_4NO_2)_2]_3$ (IX) | -1.24$^a$ | 13 |
| $[NP(2,3-O_2C_{10}H_6)]_3$ (X) | -1.83 | 5 |
| $[NP(1,8-O_2C_{10}H_6)]_3$ (XI) | -2.15 | 15-20 |
| $[NP(2,2'-O_2C_{12}H_8)]_3$ (XII) | -2.33 | 0 |

$^a$ Electroreduction was accompanied by a color change from colorless to blue-green. The other solutions remained colorless during reduction.

potentials more positive than $-3$ V: $(NPCl_2)_3$ (XIII), $(NPCl_2)_4$ (XIV), $(NPCl_2)_n$ (XV), $(NPF_2)_3$ (XVI), $(NPBr_2)_3$ (XVII), $(NPClC_6H_5)_3$ (XVIII), $N_3P_3Cl_4(C_6H_5)_2$ (XIX), $[NP(OC_6H_5)_2]_3$ (XX), $[NP(OC_6H_5)_2]_4$ (XXI), $[NP(OC_6H_5)_2]_n$ (XXII), $[NP(OCH_2CF_3)_2]_3$ (XXIII), $[NP(OCH_2CF_3)_2]_4$ (XXIV), $[NP(OCH_2CF_3)_2]_n$ (XXV), $[NP(OCH_3)_2]_3$ (XXVI), $(NPO_2C_6H_4)_3$ (XXVII), and $[NP(NHC_6H_5)_2]_3$ (XXVIII). Those compounds which contained halogen atoms bonded directly to phosphorus (XIII, XIV, XV, XVI, XVII, XVIII, and XIX) showed spurious polarographic behavior which was attributed to ligand ionization or decomposition.

All but two of the compounds which did reduce showed well-defined reduction waves which were indicative of one-electron transfers. The two exceptions were hexakis(4-nitrophenoxy)cyclotriphosphazene, [NP-$(OC_6H_4NO_2)_2]_3$ (IX), which showed a highly irreversible charge transfer, and tris(2,3-dioxynaphthyl)cyclotriphosphazene, $(NPO_2C_{10}H_6)_3$ (X), which exhibited a maximum of the first kind. This indicates that the reduced species from IX decomposes rapidly, a fact which is confirmed by an observable rapid color change from colorless to blue-green. The polarographic behavior of X may reflect a cleavage of the five-membered exocyclic ring at phosphorus immediately following reduction of the naphthyl unit. For all the reducible phosphazenes, the primary reduction wave was accompanied by an ill-defined wave at more negative potentials near the breakdown point, which presumably reflects the addition of a second electron. A typical polarogram of $[NP(C_6H_5)_2]_3$ (VII) is shown in Figure 1. Coulometric experiments performed with $[NP(C_6H_5)_2]_3$ (VII) on the reduction plateau showed a catalytic reaction which appeared to regenerate $[NP(C_6H_5)_2]_3$. The reaction product had the same half-wave potential

(5) D. Chapman, S. H. Glarum, and A. G. Massey, *J. Chem. Soc.*, 3140 (1963).



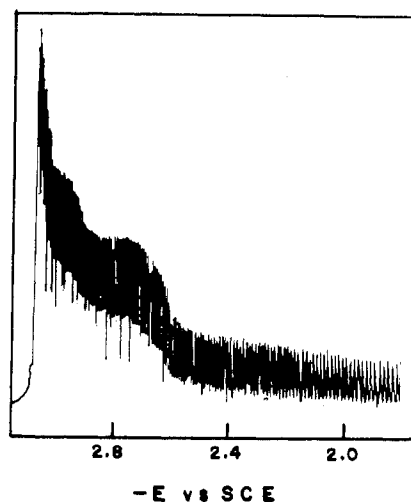Figure 1.—Polarogram for the reduction of $[NP(C_6H_5)_2]_3$ (VII) (0.001 *M*) with tetrabutylammonium iodide (0.1 *M*) in dimethylformamide.

and cyclic voltammogram as a freshly prepared sample. The coulometric experiments with $[NP(C_6H_5)_2]_3$ and the cyclic voltammograms for the other compounds suggested that the primary process was a one-electron reduction in each case.

Qualitative information about the stability of the radicals was provided by the variations in reoxidation peak height for cyclic voltammetry at different sweep frequencies. The radicals formed from phenyl-substituted phosphazenes, such as $[NP(C_6H_5)_2]_3$ (VII), $[NP(C_6H_5)_2]_4$ (VIII), $[NP(C_6H_5)OCH_2CF_3]_3$ (VI), and $N_3P_3(C_6H_5)_2(OCH_2CF_3)_4$ (V), were unstable at slow sweep rates (<0.05 cps) and did not show reoxidation peaks; reoxidation waves occurred only when the sweep rate exceeded ~1 cps. The radicals could decompose by a rapid chemical reaction, or they may relax faster than the sweep rate employed. Since no decomposition products were detected from these particular electrolyses, the second explanation is preferred. For the remaining reducible phosphazenes, such as IX, X, XI, and XII, stable cyclic voltammograms were observed at all sweep rates between 0.01 and 60 cps.

**Electron Spin Resonance Results.**—Those phosphazenes which could be reduced polarographically were subjected to combined reduction and electron spin resonance examination. As shown in Table I, six of the eight reducible phosphazenes yielded esr spectra. All the observed esr signals occurred at the free-electron value $(g = 2)$ and were 20–30 G in width, these values being consistent with the presence of radical-anion type species.

Three of the compounds studied (VII, VIII, and V) yielded singlets as esr spectra[6] (Figure 2). In all cases, cessation of electrolysis was followed by a slow decay of the spectrum without change in line shape over a period of 1–2 min. This was evidence in favor of a single radical species which was stable on an esr time scale. It should

(6) For these compounds, a series of experiments were conducted to vary the phosphazene concentration over the range 0.001–0.01 *M*, the supporting electrolyte concentration over the range 0.1–1.0 *M*, and the temperature over the range $-30$ to $+35°$. The supporting electrolyte was also changed from tetra-*n*-butylammonium iodide to the bromide or chloride and to tetra-*n*-pentyl-, tetra-*n*-hexyl-, and tetra-*n*-heptylammonium iodides. The solvent was varied from dimethylformamide to dimethylacetamide or dimethyl sulfoxide. Variations in the klystron power level were also investigated. None of these changes brought about resolution of the singlet into a finer structure spectrum.
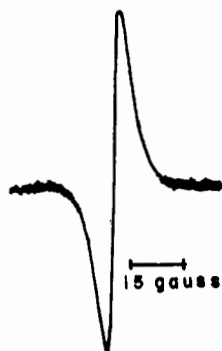
Figure 2.—Electron spin resonance singlet observed for $[NP(C_6H_5)_2]_3$ (VII) and $[NP(C_6H_5)_2]_4$ (VIII).

be noted that we did not detect the radical anion of biphenyl in any of our electrochemical esr experiments.[7] However, the addition of small amounts of biphenyl to the reducing phosphazene solution yielded the characteristic color and esr spectrum of the biphenyl radical anion, thus confirming that the observed singlet spectrum of the phenylphosphazenes cannot be attributed to this decomposition product.

**Implications of the Data.**—The experimental results indicate that phosphazenes which contain phenyl, *p*-nitrophenoxy, 2,3-dioxynaphthyl, 1,8-dioxynaphthyl, or 2,2′-dioxybiphenyl side groups can be reduced at potentials more positive than $-3$ V, whereas compounds with trifluoroethoxy, phenoxy, methoxy, *o*-dioxyphenyl, or phenylamino side groups cannot. On the basis of the half-wave potential values, the ease of reduction decreases in the order $p$-$NO_2C_6H_4O > 2,3$-$O_2$-$C_{10}H_6 > 1,8$-$O_2C_{10}H_6 > 2,2′$-$O_2C_{12}H_8 > (OCH_2CF_3)$-$(C_6H_5)$ in VI > $1,1$-$C_6H_5$-$2,2,4,4$-$OCH_2CF_3$ in V > $C_6H_5$ in VII or VIII.

The following observations are important. (1) Phosphazenes which contain only the most electronegative ligands, such as $OCH_2CF_3$, cannot be reduced in this potential range. (2) Phosphazenes which contain an unsubstituted phenyl group linked through oxygen or nitrogen to phosphorus cannot be reduced under these conditions, but those with phenyl groups linked directly to phosphorus can. (3) Reduction of phenylphosphazenes is facilitated by the presence of trifluoroethoxy groups either on the same phosphorus atom as the phenyl group or on adjacent phosphorus atoms. (4) Reduction is possible if an aromatic unit is linked to phosphorus through oxygen only if the aromatic group itself is independently reducible in this potential range.

For those compounds which fall into this latter category, such as $[NP(OC_6H_4NO_2)_2]_3$, $[NP(2,3$-$O_2C_{10}H_6)]_3$, $[NP(1,8$-$O_2C_{10}H_6)]_3$, and $[NP(2,2′$-$O_2C_{12}H_8)]_3$, it seems clear that the aromatic side units are the primary reduction sites. The half-wave reduction potential for each compound corresponds closely to those of derivatives of the free side groups. In addition, the esr spectra of $[NP(OC_6H_4NO_2)_2]_3$, $[NP(2,3$-$O_2C_{10}H_6)]_3$, and $[NP(1,8$-$O_2C_{19}H_6)]_3$ can be rationalized in terms of radicals of the side group units or their decomposition products. Thus, for these compounds, the evidence sug-

gests that the side groups function as separate moieties, electronically insulated from the skeleton. Further confirmation of this fact is provided by the nonreducibility of $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2CF_3)_2]_4$, and $[NP(OCH_2CF_3)_2]_n$, under the experimental conditions employed, which suggests that the phosphazene skeleton has antibonding $\pi$ levels that are higher in energy than those of organic aromatic units, even when strongly electron-withdrawing substituents are present.

The polarographic data for the phenyl- and phenoxy-substituted phosphazenes are particularly revealing. The reducibility of a phosphazene is markedly enhanced when a phenyl group is directly bonded to phosphorus, compared to the situation when an oxygen (or nitrogen) atom intervenes. Benzene or anisole cannot be reduced in this potential range, and it appears that simple reduction of phenyl group cannot explain the data. Instead, it must be assumed that the reducibility of a phenylphosphazene is a function of lowered antibonding orbital levels in the $C_6H_5$–P unit, in a $C_6H_5$–P–$C_6H_5$ segment, or over larger sections of the molecule. The second alternative appears less likely since the reduction potential of $[NP(C_6H_5)(OCH_2CF_3)]_3$ (VI) is actually more positive than that of $N_3P_3$-$1,1$-$(C_6H_5)_2$-$3,3,5,5$-$(OCH_2CF_3)_4$ (V) or $[NP(C_6H_5)_2]_3$ (VII). It is important to note that a trifluoroethoxy group enhances the reducibility of a phosphazene, both when it is attached to the same phosphorus atom as a phenyl group and when present on adjacent phosphorus atoms, although the effect is greatest in the former situation. This constitutes evidence for both short- and long-range inductive influences by the electronegative trifluoroethoxy group.

Polarographic experiments with phosphazenes having different degrees of polymerization suggest that increasing ring size or chain length does not enhance the reducibility of the molecule. For example, the reduction potentials of $[NP(C_6H_5)_2]_3$ and $[NP(C_6H_5)_2]_4$ are almost identical, and the increasing degree of polymerization along the series $[NP(OC_6H_5)_2]_3$, $[NP(OC_6H_5)_2]_{15,000}$, and $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2CF_3)_2]_4$, $[NP(OCH_2CF_3)_2]_{15,000}$ is not accompanied by a lowering of the reduction potential into the measurable range. Thus, there is no evidence that the degree of $\pi$-electron delocalization in the antibonding orbital varies with ring size or chain length, and this provides an argument against a broadly delocalized $\pi$-electron model.

The esr spectra observed for the reduced species derived from $[NP(OC_6H_4NO_2)_2]_3$, $[NP(2,3$-$O_2C_{10}H_6)]_3$, and $[NP(1,8$-$O_2C_{10}H_6)]_3$ all showed hyperfine splitting (Table I). The 13-line spectrum observed for the blue-green species obtained by reduction of $[NP(OC_6H_4NO_2)]_3$ has a very similar appearance to the one reported by Santhanam, Wheeler, and Bard[9] from the electroreduction of tris(*p*-nitrophenyl)phosphate. These authors attributed the observed signal to a decomposition to the 4,4′-dinitrobiphenyl radical anion. Since the electrochemical results for $[NP(OC_6H_4NO_2)_2]_3$ show a highly irreversible electron transfer, it is possible that a similar decomposition reaction takes place here.

However, there is no evidence that the 5- and 15–20-line spectra observed from $[NP(2,3$-$O_2C_{10}H_6)]_3$ and $[NP(1,8$-$O_2C_{10}H_6)]_3$, respectively, are due to decomposition products. The results suggest that the hyperfine-

(7) The biphenyl radical anion esr spectrum has been reported by Santhanam and Bard[8] from the electrolytic reduction of triphenylphosphine. We have independently confirmed this result.

(8) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 1118 (1968).

(9) K. S. V. Santhanam, L. O. Wheeler, and A. J. Bard, *ibid.*, **89**, 3386 (1967).

splitting scheme results from spin density within the aryl or arylenedioxy units only and that no interaction occurs with the phosphorus atoms or the phosphazene ring. Thus, as implied by the polarographic data, bridging oxygen atoms appear to insulate the phosphazene from the arylene rings. The 2,2'-dioxybiphenyl derivative $[NP(O_2C_{12}H_8)]_3$ (XII) can be reduced at $-2.33$ V, but no esr spectrum was detected. Crystal structure studies[10] have shown that the aryl groups within each biphenyl unit in XII are twisted 41° about the 1,1 carbon–carbon bond. Thus, the delocalization stability is probably insufficient for the radical anion to be observed on the esr time scale.

The singlet esr spectra obtained from $[NP(C_6H_5)_2]_3$, $[NP(C_6H_5)_2]_4$, and $N_3P_3$-1,1-$(C_6H_5)_2$-3,3,5,5-$(OCH_2CF_3)_4$ (V) are identical in shape and width. However, $[NP(C_6H_5)(OCH_2CF_3)]_3$ (VI) gave no detectable esr spectrum when reduced, a fact which suggests that two phenyl groups are required on each phosphorus before a stable radical can be formed. It is presumed that the observed singlet represents an unresolved multiplet from hyperfine interactions within a $C_6H_5$–P–$C_6H_5$ unit or a larger molecular fragment. Spin delocalization probably extends beyond a single $C_6H_5$–P unit, since the 36 lines expected for this situation should have been readily resolvable. Delocalization within a $C_6H_5$–P–$C_6H_5$ segment could give rise to 150 lines, or 648 lines if the phenyl groups are nonequivalent, and this is probably beyond the resolution limit of the spectrometer. It is also possible that the lack of hyperfine splitting results from rapid electron exchange.

Finally it should be noted that the half-wave reduction potentials of $[NP(C_6H_5)_2]_{3\text{ and }4}$ are comparable to those of phenylphosphines and phenylphosphine oxides.[11] The fact that both triphenylphosphine oxide and diphenylvinylphosphine oxide are easier to reduce than the phenylcyclophosphazenes provides an additional argument against a broad delocalization interaction between the phenylphosphorus units and the $\pi$ electrons of the phosphazene ring. It is also noteworthy that neither triphenyl phosphate nor $[NP(OC_6H_5)_2]_{3,4,\text{ or }n}$ can be reduced at potentials more positive than $-3$ V but that tris($p$-nitrophenyl) phosphate[7] and $[NP(OC_6H_5NO_2)_2]_3$ can. These comparisons further confirm the view that organophosphazenes are reduced through the side groups and that the combined $\pi$ electrons of the phosphazene ring or chain exert little influence on this process.

## Experimental Section

**Synthesis of Phosphazenes.**—Hexachlorocyclotriphosphazene (XIII) (Hooker Chemical Corp.) was recrystallized twice from $n$-heptane to yield material of mp 112–112.5°. Hexafluorocyclotriphosphazene (XVI), mp 26–27°, was prepared by a metathetical reaction between XIII and sodium fluoride.[13] Hexabromocyclotriphosphazene (XVII), mp 189.5–191°, was synthesized by the reaction of ammonium bromide with phosphorus tribromide and bromine.[14] Octachlorocyclotetraphosphazene (XIV) (Hooker Chemical Corp.) was recrystallized from $n$-heptane before use to give material of mp 121–123°. Poly(dichlorophosphazene) (XV) was prepared by the thermal polymerization of XIII,[15] and poly[bis(trifluoroethoxy)phosphazene] (XXV) and

poly[bis(phenoxy)phosphazene] (XXII) were synthesized by the reaction of XV with sodium trifluoroethoxide or sodium phenoxide.[15]

Hexaphenylcyclotriphosphazene (VII), mp 226–228°, and octaphenylcyclotetraphosphazene (VIII), mp 314–316°, were prepared by the reaction of diphenylchlorophosphine with sodium azide.[16] *trans*-Tris-1,3,5-trichlorotris-1,3,5-triphenylcyclotriphosphazene (XVIII), mp 155–156°, was synthesized by the reaction between phenyldichlorophosphine, chlorine, and ammonium chloride.[17] 1,1-Diphenyl-3,3,5,5-tetrachlorocyclotriphosphazene (XIX), mp 91–92°, was obtained by the reaction of XIII with boiling benzene in the presence of anhydrous aluminum chloride for 7 days.[18]

Tris(2,3-dioxynaphthyl)cyclotriphosphazene (X), tris-(1,8-dioxynaphthyl)cyclotriphosphazene (XI), tris(2,2'-dioxybiphenyl)-cyclotriphosphazene (XII), and tris($o$-phenylenedioxy)cyclotriphosphazene (XXVII) were obtained by the interaction of XIII with 2,3-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,2'-dihydroxybiphenyl, or catechol by methods described previously.[19–21] Hexakis(4-nitrophenoxy)cyclotriphosphazene (IX), mp 258°, was prepared from XIII and 4-nitrophenol,[22] and hexaphenoxycyclotriphosphazene (XX),[23] mp 111.5–112°, octaphenoxycyclotetraphosphazene (XXI), mp 86°, hexakis-(trifluoroethoxy)cyclotriphosphazene (XXIII), mp 49°, octakis-(trifluoroethoxy)cyclotetraphosphazene (XXIV), mp 65°, and hexamethoxycyclotriphosphazene (XXVI), mp 46–48°, were prepared by the reaction of XIII or XIV with the appropriate sodium aroxide or alkoxide in tetrahydrofuran or diethyl ether.[24] Hexakis($N$-phenylamino)cyclotriphosphazene (XXVIII) was prepared by the interaction of aniline with XIII.[25]

1,1-Diphenyl-3,3,5,5-tetrakis(trifluoroethoxy)cyclotriphosphazene (V) was prepared as follows. 1,1-Diphenyl-3,3,5,5-tetrachlorocyclotriphosphazene (XIX) (6.0 g, 0.0139 mol) in anhydrous diethyl ether (50 ml) was added dropwise to a solution prepared from 2,2,2-trifluoroethanol (8.31 g, 0.0831 mol) and sodium (1.7 g, 0.0735 g-atom) in diethyl ether (50 ml). The mixture was boiled at reflux for 24 hr during which time a white precipitate formed. After cooling, the mixture was washed three times with water (100 ml) and the ethereal layer was dried over sodium sulfate. White crystals (square plates) were obtained by slow evaporation of the ethereal layer. These were purified by sublimation at 70° (1 mm) to yield **1,1-diphenyl-3,3,5,5-tetrakis(trifluoroethoxy)cyclotriphosphazene (V)** (7.5 g, 79%), mp 50–51°. The identity of this compound was confirmed by infrared and proton nmr techniques. Thus, the proton spectrum consisted of two peaks with an integrated intensity of 4:5, from eight equivalent trifluoroethoxy hydrogens and ten equivalent phenyl protons. Thin layer chromatography confirmed the presence of only one compound.

A similar reaction between XVIII (7.2 g, 0.0154 mol) and the product from sodium (2.0 g, 0.087 g-atom) and 2,2,2-trifluoroethanol (9.83 g, 0.0983 mol) in ether (50 ml) yielded *trans*-**1,3,5-triphenyl-tris(trifluoroethoxy)cyclotriphosphazene (VI)** (8.15 g, 80%), mp 78–80°. The structure of this compound was confirmed by infrared and nmr techniques. For example, the aliphatic to aromatic proton ratio was 6:15. The purity of the compound was confirmed by thin layer chromatography.

**Polarographic Solvents.**—Dimethylformamide (DMF) (Fisher Certified reagent) was dried over calcium hydride and then fractionated through a 90-cm, helix-packed Todd column at 735 mm before storage in a helium atmosphere. The solutions were purged with helium before electrolysis, and a helium atmosphere was maintained over the solutions during each experiment. Consistently good polarographic base lines were obtained when this technique was used. Dimethylacetamide, dimethyl sulfoxide, and acetonitrile (all Fisher Certified reagent) were dried over calcium hydride and then distilled at reduced pressure. Tetrahydrofuran (THF) (Fisher Certified reagent) was dried over sodium amalgam and then fractionated from calcium hydride

(10) H. R. Allcock, M. T. Stein, and J. A. Stanko, *J. Amer. Chem. Soc.*, **93**, 3173 (1971).

(11) $(C_5H_5)_3P$, $-2.70$ V;[8] $(C_6H_5)_3P{=}O$, $-2.51$ V;[8] $(C_6H_5)_2(CH_2{=}CH)$-$P{=}O$, $-2.40$ V.[12]

(12) H. R. Allcock and R. L. Kugel, *J. Polym. Sci.*, **1**, 3627 (1963).

(13) T. Moeller, K. John, and F. Tsang, *Chem. Ind. (London)*, **37** (1961).

(14) T. Moeller and K. John, *J. Inorg. Nucl. Chem.*, **22**, 199 (1961).

(15) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).

(16) D. L. Herring and C. M. Douglas, *ibid.*, **4**, 1012 (1965).

(17) B. G. Grushkin, M. G. Sanchez, and R. G. Rice, *ibid.*, **3**, 623 (1964).

(18) K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 121 (1964).

(19) H. R. Allcock, *J. Amer. Chem. Soc.*, **85**, 4050 (1963).

(20) H. R. Allcock, *ibid.*, **86**, 2591 (1964).

(21) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).

(22) H. R. Allcock and E. J. Walsh, unpublished work.

(23) H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).

(24) B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1935 (1964).

(25) A. W. Hofmann, *Chem. Ber.*, **17**, 1909 (1884).

through a 90-cm Todd column. It should be noted that, unless a rigorous purification technique is followed, tetrahydrofuran solutions yield a spurious triplet esr spectrum when electrolyzed.

**Supporting Electrolytes.**—For most experiments, tetra-*n*-butylammonium iodide (Southwestern Analytical Chemicals) was used as the supporting electrolyte at a concentration of 0.1 *M*. A few experiments were carried out with tetra-*n*-pentyl-, tetra-*n*-hexyl-, or tetra-*n*-heptylammonium iodide (Eastman Polarographic grade) or with tetra-*n*-butylammonium perchlorate[26] (Matheson Coleman and Bell) as supporting electrolytes.

**Equipment for Polarography and Voltammetry.**—Polarograms and cyclic voltammograms were obtained with a Heath multipurpose instrument, employing operational amplifier circuiting with a three-electrode configuration. A Sargent Model SR recorder was used for polarograms, and a standard X-Y recorder and oscilloscope for cyclic voltammograms. The triangular-wave potential source was a Hewlett-Packard Model 202-A low-frequency function generator. Controlled-potential electrolysis was performed with a Wenking potentiostat equipped with an operational amplifier difference integrator to integrate the electrolysis current. The electrolysis cell was a Sargent S-29390 vessel. A silver–silver iodide electrode, calibrated to a saturated calomel electrode, was used as the reference electrode, and a dropping mercury electrode formed the working electrode. Direct use was made of a saturated calomel electrode during preliminary experiments, but the high resistance between the reference and working electrodes and the prospect of contamination of the solvent system by water prompted its replacement by a silver–silver iodide electrode. For cyclic voltammetry, a platinum disk replaced the dropping mercury electrode, and a mercury pool was the counter electrode.

**Polarographic and Cyclic Voltammetric Technique.**—In a typical polarographic experiment, a freshly prepared solution of tetra-*n*-butylammonium iodide (0.1 *M*) and phosphazene (0.001 *M*) in dimethylformamide (10 ml) was transferred to the electrolysis cell and the three electrodes were introduced. The solution was then purged for 10 min with helium which had previously been bubbled through pure dimethylformamide. This minimized loss of solvent from the cell. An atmosphere of helium was then maintained over the solution as the polarogram was recorded. Purging with helium was also carried out prior to each repeat run on the same solution. The reduction potential values obtained were derived from at least three measurements on different solutions of each compound with five runs being conducted on every individual solution sample. The silver–silver iodide electrode was calibrated against a saturated calomel electrode at the end of each experiment.

In a typical cyclic voltammetric experiment, freshly prepared solutions were used, identical with those employed in polar-

ography. The same cell as used for polarography was employed except for the use of a solid platinum disk working electrode. After each solution was purged with helium, the potential range was swept back and forth by means of the triangular-wave generator connected to the operational amplifier. The frequency range of 0.01–60 cps was usually investigated, with the voltammograms being recorded either on an X-Y recorder (<1 cps) or by photography from the oscilloscope for the higher sweep rates.

**Coulometric Technique.**—Coulometric experiments were conducted with $[NP(C_6H_5)_2]_3$ with the use of the techniques described by DiGregorio and Morris.[27] The first reduction wave corresponded to a one-electron transfer, and a catalytic wave was observed similar to that reported by Santhanam and Bard[8] for triphenylphosphine oxide reduction.

**Electron Spin Resonance Technique.**—Electron spin resonance experiments were performed with the use of a Varian V 4500 spectrometer with 100-kc field modulation. A Varian quartz flat cell with a three-electrode system was used for this work. The radicals were generated directly within the esr cavity on a mercury working electrode surface which half-filled the flat section of the cell. The silver–silver iodide reference electrode and the platinum counter electrode entered the solution at the top of the cell and extended to within 10 cm of the mercury surface. The same reagent concentrations, supporting electrolyte, and solvent were used as in the polarographic experiments, and each solution was purged with helium prior to introduction into the cell. The potential across the solution was adjusted by the same operational amplifier as used in the polarography experiments. For each compound, the applied potential corresponded to the plateau of the polarographic reduction wave, and the signal was recorded when the radical concentration reached a detectable concentration (probably $>10^{-6}$ *M*). For experiments at low temperatures, nitrogen gas, cooled through a coil immersed in Dry Ice–acetone or liquid nitrogen, was blown down the wave guide onto the sample.

**Electrolytic Oxidations.**—Attempts were made to generate radical cations by electrolytic oxidation of all the phosphazenes described in this paper. With dimethylformamide used as a solvent and tetra-*n*-butylammonium perchlorate as a supporting electrolyte, the limiting potential was that of mercury oxidation near +0.6 V. The compounds $(NPCl_2)_3$, $(NPCl_2)_4$, and $(NPF_2)_3$ were the only phosphazenes studied which exhibited oxidation waves below this potential. The oxidation waves for $(NPCl_2)_3$ and 4 were identical, each showing two waves at +0.1 and +0.4 V. However, no esr spectra were detected for the oxidized species when a mercury pool working electrode was used. Other experiments were conducted with the use of a platinum wire microelectrode as the working electrode. No electron spin resonance signals were detected for any of the phosphazenes under these conditions, only the characteristic quartet of the perchlorate radical being observed.[28]

(26) Tetra-*n*-butylammonium perchlorate was the only supporting electrolyte examined which was soluble enough in tetrahydrofuran to permit electrochemical work. However, electrolysis of 0.001 *M* phosphazene or anthracene in tetrahydrofuran in the presence of 0.1 *M* tetra-*n*-butylammonium perchlorate gave no radical species detectable by electron spin resonance. Presumably, this reflects the lower polarity of tetrahydrofuran and the higher resistance of solutions in this medium. The addition of 5% dimethylformamide to the mixture allowed esr spectra of $[NP(C_6H_5)_2]_3$ to be detected. These were identical with those obtained in pure dimethylformamide.

(27) J. S. DiGregorio and M. D. Morris, *Anal. Chem.*, **40**, 1286 (1968).
(28) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959).