It is also possible to isolate unsolvated Zintl phases from the aqueous extraction of certain ternary alloys. Aqueous extraction of the ternary Zintl phase, obtained from the high-temperature reaction of KSn with Te, gives a bright red-orange solution. Filtration and evaporation to near dryness, followed by treatment with DMF or acetone, gives nearly quantitative yields of K_4SnTe_4. The tetrapotassium tetratellurastannate[40] was identified by elemental analysis[41] and ^{125}Te and ^{119}Sn NMR spectroscopies.[42] A solvate of Na_4SnTe_4 was previously isolated,[43] but no analytical data were reported.

In summary, the results presented here show that a very large number of novel materials can be obtained by extraction of various Zintl phases. The isolation of Zintl anions in large amounts, in high yields, and without the use of amine solvents and expensive cryptates should greatly facilitate the study of the chemistry of these polyanions.

Experimental Section

General Considerations. The preparation of the alloys and subsequent reactions are all performed under an argon atmosphere (<1 ppm O_2). The nonaqueous solvents are dried by standard techniques, and all solvents are degassed before use. Ethylenediamine is distilled from a red solution of K_4Sn_9. Raman spectra were obtained in sealed 5-mm Pyrex tubes with 514.5-nm excitation.

$[K(HMPA)_2]_4Sn_9$. An alloy of nominal composition K_4Sn_9 is prepared by fusion of the elements under Ar in quartz vessels. The alloy (1 g) is dissolved in 10 mL of a 1:1 (v:v) mixture of en/HMPA. Slow removal of the en under vacuum gives >90% yield of black-red crystals of $[K(HMPA)_2]_4Sn_9$, which were identified as described in the text. This material decomposes slowly at 25 °C and should be stored at -78 °C.

$[(CH_3)_4N]_4Sn_9$. The alloy K_4Sn_9 is added to excess $(CH_3)_4NB(C_6H_5)_4$[44] in DMF. The red-brown precipitate (identified as described in the text) is filtered and dried briefly under vacuum to give a quantitative yield of $[(CH_3)_4N]_4Sn_9$. This material should be stored at -78 °C.

Polychalcogenides $(Bu_4N)_2M_x$ (M = Te, x = 5; M = Se, x = 6; M = S, x = 6). The preparations of these materials are essentially identical. Typically, 1-3 g of the binary compounds K_2Te_3 (from K + Te), Na_2Se_6 (from Na_2Se + Se) and "Na_2S_3" (from Na_2S + S) are dissolved in 5-10 mL of water containing a twofold excess of Bu_4NBr (recrystallized twice from ethyl acetate). The reactions are stirred overnight at 25 °C and filtered. Drying under vacuum followed by slow cooling of concentrated acetone solutions to -40 °C gives high yields (ca. 60% for Te_5^{2-} and >90% for Se_6^{2-} and S_6^{2-}) of the polychalcogenides.

K_4SnTe_4. The alloy KSn (prepared from the fusion of K + Sn) is melted with 1 equiv of Te under argon. After cooling, the material is crushed and the plug of Sn removed. The finely powdered ternary K/Sn/Te alloy is extracted with water (~5 mL of H_2O/g of alloy for 30 min), filtered, and evaporated until the solution is saturated. Treatment of the deep red-orange solution with DMF gives a bright orange-red solid. The solid is stirred with acetone, filtered, and dried briefly under vacuum to give >80% yield of analytically pure K_4SnTe_4 as a dark black-red powder.

Acknowledgment. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38. We are grateful to the groups of Drs. J. M. Williams and W. M. Butler for the use of the diffractometers and many helpful discussions. We thank Drs. J. P. Haushalter and R. P. Van Duyne for the Raman spectra, and Dr. J. Hunt for the use of the variable-temperature visible absorption spectrometer.

Registry No. $[K(HMPA)_2]_4Sn_9$, 85533-98-8; $[(CH_3)_4N]_4Sn_9$, 85533-92-2; $(Bu_4N)_2Te_5$, 85533-94-4; $(Bu_4N)_2Se_6$, 85533-95-5; $(Bu_4N)_2S_6$, 85533-96-6; K_4SnTe_4, 85533-99-9.

Supplementary Material Available: Listings of atomic positions and thermal parameters, observed and calculated structure factors, and distances and angles within the Bu_4N^+ cation (27 pages). Ordering information is given on any current masthead page.

(40) A Raman and Mössbauer study of $SnTe_4^{4-}$ and its metal complexes will be published elsewhere.
(41) Anal (Schwarzkopf Microanalytical Laboratories, Woodside, NY). Calcd for K_4SnTe_4: K, 19.87; Sn, 15.16; Te, 64.97. Found: K, 19.56; Sn, 15.43; Te, 64.52.
(42) ^{119}Sn NMR: three peaks in the ratio 0.136:1.000:0.133; (calculated for Sn:Te (1:4) 0.140:1.000:0.140) with $J(^{125}Te-^{119}Sn)$ = 2860 Hz. ^{125}Te NMR: five peaks in the ratio 0.054:0.047:1.000:0.047:0.054 (calculated 0.043:0.038:1.000:0.038:0.043) with $J(^{125}Te-^{117}Sn)$ = 2740 Hz. These compare favorably with literature values for Na_4SnTe_4[43] in solution.
(43) Rudolph, R.; Wilson, R.; Taylor, R. *J. Am. Chem. Soc.* **1981**, *103*, 2481.
(44) Prepared from $(CH_3)_4NBr$ and $NaB(C_6H_5)_4$ in water.

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Phosphazenes. 2. Synthesis of Ketone- and Enol-Substituted Cyclotriphosphazenes

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The reactions of the enolate anions of acetaldehyde, acetone, and acetophenone with hexachlorocyclotriphosphazene and methylpentachlorocyclotriphosphazene have been investigated. These reactions led exclusively to enol-substituted phosphazene compounds. Acetonyl-substituted phosphazene compounds were synthesized via the reaction of 2-methoxyallyl bromide with a metallophosphazene followed by hydrolysis. The 2-methoxyallyl-substituted phosphazene product was found to undergo a rapid migration of the double bond prior to the hydrolysis step. The mechanistic aspects of the various reactions are discussed as well as the factors that affect the migration of the allylic double bond.

Introduction

Studies of the chemistry of cyclic phosphazene compounds are important for a variety of reasons. Small-ring phosphazenes are ideal "models" for the reactions of high-polymeric phosphazenes,[2] while other interests lie in the use of cyclic compounds as mechanistic probes[3] or in studies related to the bonding within the phosphazene skeleton.[4]

In recent years, the reactions of phosphazenes with lithium,[5,6] Grignard[3,7] or organocopper reagents[8] have been investigated as a means of binding organic substituents directly

(1) NSF-URP Scholar, Summer 1981.
(2) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(3) Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1981**, 852.
(4) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.
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(6) Harris, P. J.; Fadeley, C. L. *Inorg. Chem.* **1983**, *22*, 561.
(7) Allcock, H. R.; Chu, C. T. W. *Macromolecules* **1979**, *12*, 551.
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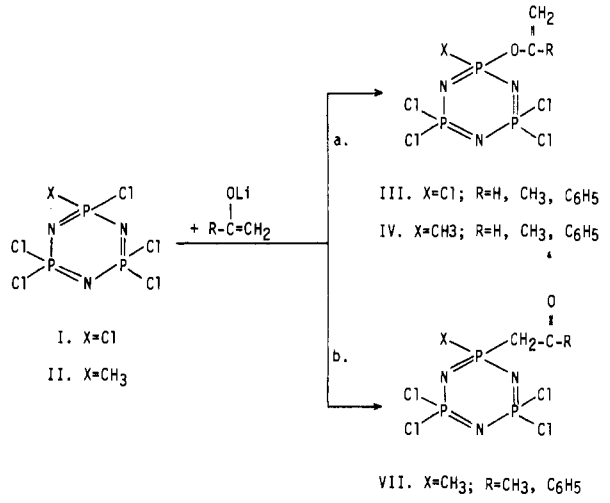
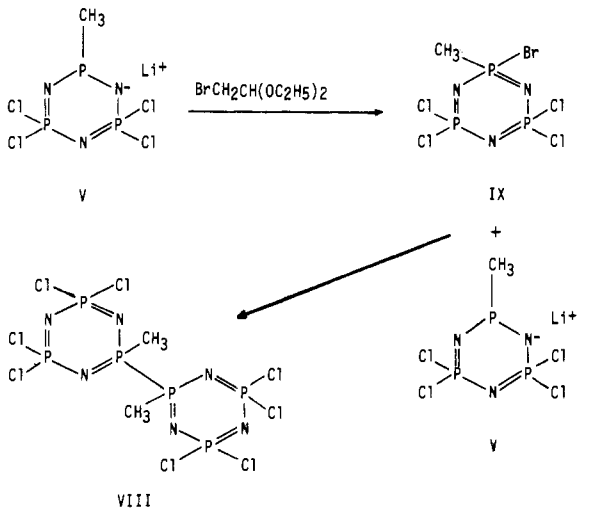
0020-1669/83/1322-1812$01.50/0

Scheme I



Scheme II



to the phosphazene skeleton through phosphorus–carbon bonds. Although some of these reactions are, in part, successful in producing the desired products, the reaction mechanisms are extremely complex and in some cases proceed via a metal–halogen exchange pathway[3] or ring cleavage[6] rather than substitution. In an attempt to circumvent the metal–halogen exchange or ring cleavage problems, we initially undertook an exploration of the reactions of enolate anions[9] with cyclic chlorophosphazenes. These reactions were directed toward the synthesis of phosphazene compounds with a ketone function on the exocyclic group. Compounds of this type could be important precursors to a wide variety of new products derived from reactions of the carbonyl group. Only one synthetic route for the formation of ketone-substituted phosphazenes has previously been reported. However, these reactions require the use of the relatively inaccessible, fully alkylated phosphazenes $N_3P_3Me_6$ or $N_4P_4Me_8$ as starting materials.[10]

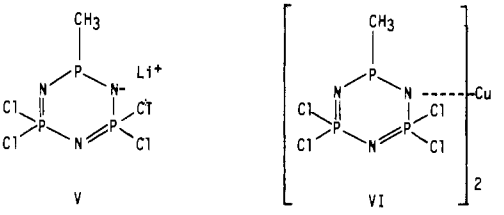
The principal objectives of this present work were to answer the following questions: (1) How would enolate anions react with halophosphazenes? (2) If ketone-substituted phosphazenes were not available by this route, could they be synthesized by other routes? (3) How would the phosphazene ring affect the chemistry of the resultant products?

Results and Discussion

The enolate anions used for this work were derived from acetaldehyde,[9] acetone, and acetophenone. Clearly, there are two possible routes by which these anions could react with a halophosphazene as shown in Scheme I. These are either an "O" alkylation pathway (a) or a "C" alkylation pathway (b). Often, in carbon chemistry, both routes are observed to occur in competition.[11]

Reactions of the enolate anions of acetaldehyde, acetone, and acetophenone were carried out with both hexachlorocyclotriphosphazene (I) and methylpentachlorocyclotriphosphazene (II). Compound II was examined as a substrate because earlier work[12,13] had shown that the halogen geminal to the methyl group in this compound was readily, and exclusively, replaced by a variety of nucleophiles. Thus, it was reasoned that compound II would be the best substrate with which to observe the "C" alkylation reaction of the enolate anions. However, in all cases, the reactions were found to proceed exclusively by the "O" alkylation pathway. This led to the isolation of compounds III and IV in high yield. Compound III (R = H) has previously been reported.[9] These compounds were readily identified as enol-substituted phosphazenes by means of their IR, NMR (^1H and ^{31}P), and mass spectral data and elemental analysis. These data are listed in Tables I and II .

Clearly then, aldehyde- and ketone-substituted phosphazenes were not available by these direct synthesis routes, and alternative methods toward their synthesis were sought. The first series of reactions investigated involved the interaction of α-bromoacetophenone or bromoacetone with the phosphazene anion V[14] or VI.[8,15] In each case these reactions were



found to be extremely complex and led to a variety of unidentified products, many of which appeared to result from attack at the carbonyl carbon of the haloketone. Only in the reaction between the lithiophosphazene (V) and α-bromoacetophenone was any significant amount (~5%) of the acetophenone-substituted phosphazene (VII, R = C_6H_5) isolated. Spectroscopically, this compound appeared to be quite different from the enol-substituted phosphazenes III and IV (R = C_6H_5). The presence of the ketone group was readily confirmed by IR, NMR (^1H and ^{31}P), and mass spectral data and elemental analysis. These data are also listed in Tables I and II.

A procedure for the synthesis of the acetaldehyde-substituted phosphazene was designed that involved the reactions of the lithiophosphazene (V) with 2-bromo-1,1-diethoxyethane, followed by subsequent hydrolysis of the resultant acetal to the aldehyde. Interestingly, this reaction did not yield the desired products but led to the formation of the bis(cyclotriphosphazene) complex VIII.[3] This compound had previously been observed as the major product from the reaction of

(9) While this work was in progress, the reactions of hexachlorocyclotriphosphazene with the enolate anion of acetaldehyde were reported: Allen, C. W.; Ramachandran, K.; Bright, R. P.; Shaw, J. C. *Inorg. Chim. Acta* **1982**, *64*, L109.
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(11) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977.
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(13) Harris, P. J.; Williams, K. B.; Fisher, B. J., manuscript in preparation.
(14) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256.
(15) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.

Table I. Selected NMR Data for Ketone- and Enol-Substituted Phosphazenes

compd	^{31}P NMR[a,b]		^{1}H NMR[b,c]			
	PRR'	PCl_2	R	δ	coupling const[d]	*J* value, Hz
III (X = Cl, R = H)	13.2 t	23.4 d	$P^{V}OCH=CH$	5.16 m	J_{PNP}	64.7
					J_{HCH}	2.5
			$P^{V}OCH=CH$	4.89 m	$J_{HCCH(cis)}$	5.8
					$J_{HCCH(trans)}$	13.4
			$P^{V}OCH=CH$	6.55 m	J_{POCH}	7.6
					$J_{POCCH(cis)}$	2.7
					$J_{POCCH(trans)}$	2.6
III (X = Cl, R = CH_3)	10.2 t	22.3 d	$P^{V}OCCH_3$	4.95 d, d	J_{PNP}	62.4
					J_{HCH}	2.0
			$P^{V}OCCH_3$	4.76 m	$J_{POCCH(cis)}$	2.7
					$J_{POCCH(trans)}$	2.6
			$P^{V}OCCH_3$	2.03 d	$J_{HCCCH(trans)}$	3.1
III (X = Cl, R = C_6H_5)	12.4 t	23.0 d	$P^{V}OCC_6H_5$	5.44 d, d	J_{PNP}	62.0
					J_{HCH}	2.5
			$P^{V}OCC_6H_5$	5.29 d, d	$J_{POCCH(cis)}$	2.7
					$J_{POCCH(trans)}$	2.6
			$P^{V}OCC_6H_5$	7.6 br m		
IV (X = CH_3, R = H)	29.6 t	21.6 d	$P^{V}CH_3$	1.62 d, t	J_{PNP}	21.9
			$P^{V}OCH=CH$	4.91 m	J_{PCH}	17.7
					J_{PNPCH}	1.8
			$P^{V}OCH=CH$	4.66 m	J_{HCH}	2.6
					$J_{HCCH(cis)}$	5.7
			$P^{V}OCH=CH$	6.34 m	$J_{HCCH(trans)}$	13.5
					J_{POCH}	7.5
					$J_{POCCH(cis)}$	2.8
					$J_{POCCH(trans)}$	2.7
IV (X = CH_3, R = CH_3)	30.0 t	21.2 d	$P^{V}CH_3$	1.74 d, t	J_{PNP}	20.8
			$P^{V}OCCH_3$	4.87 m	J_{PCH}	17.5
					J_{PNPCH}	2.0
			$P^{V}OCCH_3$	4.70 m	J_{HCH}	2.6
					$J_{POCCH(methyl)}$	1.2
			$P^{V}OCCH_3$	1.91 d	$J_{POCCH(cis)}$	2.8
					$J_{POCCH(trans)}$	2.7
IV (X = CH_3, R = C_6H_5)	32.8 t	23.4 d	$P^{V}CH_3$	1.74 d, t	J_{PNP}	21.0
			$P^{V}OCC_6H_5$	5.37 d, d	J_{PCH}	18.0
					J_{PNPCH}	1.7
			$P^{V}OCC_6H_5$	5.14 d, d	J_{HCH}	2.0
					$J_{POCCH(cis)}$	2.8
			$P^{V}OCC_6H_5$	7.14 br m	$J_{POCCH(trans)}$	2.8
VII (X = CH_3, R = CH_3)	31.4 t	19.2 d	$P^{V}CH_3$	1.60 d, t	J_{PNP}	9.7
			$P^{V}CH_2CCH_3$	3.13 d, t	$J_{PCH(methyl)}$	15.0
					$J_{PCH(methylene)}$	16.2
			$P^{V}CH_2CCH_3$	2.34 s	$J_{PNPCH(methyl)}$	1.8
					$J_{PNPCH(methylene)}$	1.4
VII (X = CH_3, R = C_6H_5)	32.4 t	19.3 d	$P^{V}CH_3$	1.82 d, t	J_{PNP}	9.7
			$P^{V}CH_2C$(C$_6$H$_5$)	3.66 d, t	$J_{PCH(methyl)}$	15.0
					$J_{PCH(methylene)}$	17.5
			$P^{V}CH_2C$(C$_6$H$_5$)	7.98 d, d	$J_{PNPCH(methyl)}$	2.0
					$J_{PNPCH(methylene)}$	1.5
			$P^{V}CH_2C$(C$_6$H$_5$)	7.50 m	J_{HCCH}	8.0
					J_{HCCCH}	2.5

Table I (*Continued*)

compd	^{31}P NMR[a,b] PRR′	PCl_2	^1H NMR[b,c] R	δ	coupling const[d]	*J* value, Hz
X	37.4 t	18.3 d	$P^V CH_3$	1.66 d, t	J_{PNP}	4.1
			$P^V CH_2C(OCH_3)=CH_2$	3.21 s	$J_{PCH(methyl)}$	14.8
					$J_{PCH(methylene)}$	15.0
			$P^V CH_2C(OCH_3)=CH_2$	3.40 d, t	$J_{PNPCH(methyl)}$	2.0
					$J_{PNPCH(methylene)}$	1.3
			$P^V CH_2C(OCH_3)=CH_2$	5.40 m		
XI	27.0 t	18.1 d	$P^V CH_3$	1.71 d, t	J_{PNP}	12.2
			$P^V CH=C(OCH_3)CH_3$	3.60 s	$J_{PCH(methyl)}$	14.8
					$J_{PCH(methylene)}$	15.1
			$P^V CH=C(OCH_3)CH_3$	4.54 d, t	$J_{PNPCH(methyl)}$	2.1
					$J_{PNPCH(methylene)}$	1.5
			$P^V CH=C(OCH_3)CH_3$	2.21 s		

[a] All ^{31}P NMR chemical shifts (in ppm units) are referenced to a capillary tube of 85% phosphoric acid placed into the sample. Positive chemical shift values are downfield from this reference. All compounds were dissolved in chloroform-*d*. [b] s = singlet, d = doublet, t = triplet, br = broad, m = multiplet. [c] All ^1H NMR chemical shifts are referenced to tetramethylsilane. All compounds were dissolved in chloroform-*d*. [d] Coupling constants were determined from spectral simulations using a local version of the program LAOCOON III. Coupling constants not listed were not resolved.

Table II. Characterization Data for Ketone- and Enol-Substituted Phosphazenes

compd	mp or bp	% yield	ν(C=C) or ν(C=O)[a]	ν(P=N)[a]	*m/s* (calcd/found)[b]	anal.[c] (calcd/found) % C	% H	% N
III (X = Cl, R = H)	bp 110 °C (0.1 mm)	60	1650 m	1220 vs	353/353[d]	6.75/6.73	0.84/0.96	11.81/11.91
III (X = Cl, R = CH_3)	bp 115 °C (0.1 mm)	62	1665 mw	1185 vs 1210 s 1220 s	367/367[d]	9.74/9.40	1.35/1.18	11.36/11.16
III (X = Cl, R = C_6H_5)	bp 150 °C (0.1 mm)	85	1635 w	1205 vs	429/429[d]	22.25/22.29	1.62/1.64	9.73/9.72
IV (X = CH_3, R = H)	bp 110 °C (0.1 mm)	34	1645 m	1180 vs 1215 vs	333/333[e]	10.75/10.73	1.79/2.30	12.54/12.31
IV (X = CH_3, R = CH_3)	bp 120 °C (0.1 mm)	48	1660 mw	1180 vs 1205 sh 1230 s	347/347[e]	13.75/13.81	2.29/3.34	12.03/11.86
IV (X = CH_3, R = C_6H_5)	bp 150 °C (0.1 mm)	64	1625 w	1180 vs 1215 vs	409/409[e]	26.28/26.09	2.43/2.48	10.22/10.06
VII (X = CH_3, R = CH_3)	mp 131 °C	83[f] (100[g])	1730 s	1180 vs 1200 sh 1230 s	347/347[e]	13.75/13.60	2.29/2.41	12.03/12.31
VII (X = CH_3, R = C_6H_5)	mp 145 °C	4	1675 m	1185 vs 1200 sh 1215 s	409/409[e]	26.28/26.48	2.43/2.61	10.22/10.22
X	mp 84 °C	70	1650 mw	1170 vs 1205 vs	361/361[e]	*h*		
XI	mp 95 °C	100[g]	1640 m	1185 vs 1215 s	361/361[e]	16.53/16.51	2.75/2.81	11.57/11.51

[a] Infrared spectra were recorded with a Perkin-Elmer 710B infrared spectrometer. The samples were prepared as KBr pellets. m = medium, w = weak, s = strong, v = very, sh = shoulder. [b] Mass spectra were obtained on a Varian Associates GC/MS instrument. Samples were introduced into the spectrometer via the probe inlet system. [c] Elemental analyses were performed at the Virginia Polytechnic Institute and State University Analytical Services Department. [d] A Cl_5 isotope pattern was observed. [e] A Cl_4 isotope pattern was observed. [f] Prepared from the cupriophosphazene (see Experimental Section). [g] Prepared via the rearrangement of compound X. [h] Analytical data were not obtained for this compound due to its facile rearrangement to compound XI.

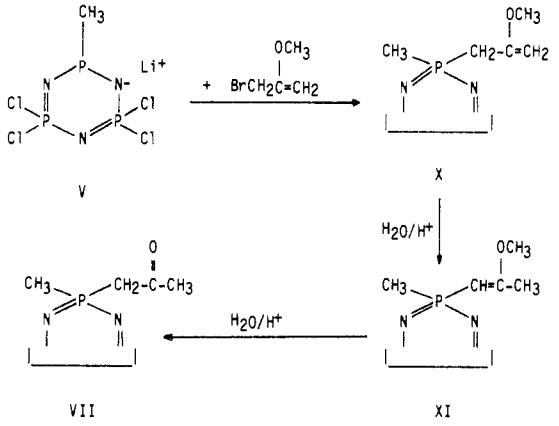
hexachlorocyclotriphosphazene and methylmagnesium chloride in tetrahydrofuran.[3] Further investigation of the reaction mixture by the use of chemical ionization mass spectrometry indicated the presence of small amounts of 1-methyl-1-bromotetrachlorocyclotriphosphazene (IX).[12] Thus, it was concluded that this reaction probably proceeds via a metal–halogen exchange pathway as shown in Scheme II.

Compounds VIII[3] and IX[12] have been previously reported; however, this particular reaction appears to be a novel route to the formation of bis(cyclotriphosphazenes) (III).

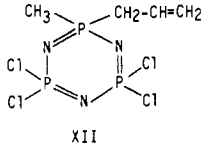
A high-yield synthesis of the acetonyl-substituted phosphazene compound VII (R = CH_3) was achieved by allowing the cupriophosphazene (VI) to react with 2-methoxyallyl bromide, followed by a subsequent hydrolysis step.[16] This procedure led to the isolation of compound VII in >80% yield. In order to study this chemistry in somewhat greater detail, the reaction of the lithiophosphazene (V) with 2-methoxyallyl bromide was also investigated. This reaction led to some interesting results as shown in Scheme III. The initial product of the reaction was found to be the 2-methoxyprop-2-enyl-substituted compound X. However, this material was found to undergo a rapid rearrangement to yield compound XI, where the phosphazene substituent was now a 2-methoxy-

(16) Jacobson, A. M.; Raths, R. A.; McDonald, J. H., III *J. Org. Chem.* **1977**, *42*, 2545.

Scheme III

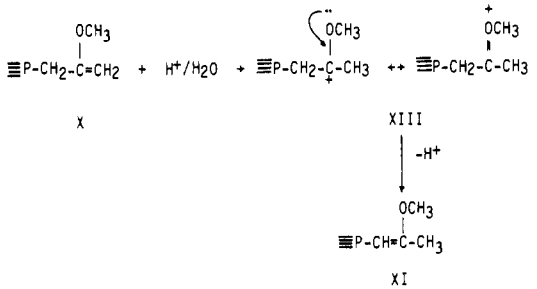


prop-1-enyl group. Initially it was thought that this rearrangement was catalyzed by trace amounts of the organometallic reagent used to generate the lithiophosphazene (V), in a manner similar to the rearrangement observed in the case of prop-2-ynyl- to prop-1-ynyl-substituted phosphazenes.[14] This was not found to be the case. Attempts to rearrange compound X as well as 1-methyl-1-prop-2-enyltetrachlorocyclotriphosphazene (XII)[15] with butyllithium were unsuccessful.



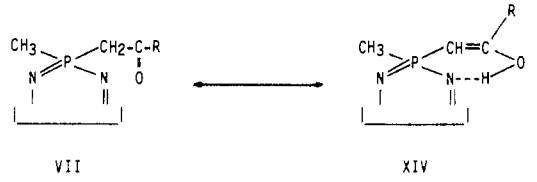
XII

It was found that compound X rearranged to compound XI in the presence of trace amounts of water. This was confirmed by contaminating a ^1H NMR sample of compound X with a trace of D_2O. From the integration of the ^1H NMR spectrum after the rearrangement was complete, it was clear that a deuterium atom had been incorporated into the terminal (3) methyl group of compound XI. From these results, it appears that this rearrangement reaction involves initial protonation of the double bond in compound X to yield the resonance-stabilized carbonium ion XIII. Subsequent loss of a proton



from the carbon atom α to the phosphazene ring yields the product XI, where the double bond is now in "conjugation" with the phosphazene ring. Attempts to rearrange the prop-2-enyl compound (XII) with acid were unsuccessful, presumably due to the absence of the methoxy group.

The subsequent hydrolysis of compound XI to the acetonyl-substituted product VII was readily accomplished by the use of ~0.01 M HCl. A hydrolysis reaction performed on compound XI with the use of DCl/D_2O yielded compound VII, where the α-carbon was substituted with deuterium. Methanol was found to be a byproduct of these hydrolysis reactions (^1H NMR). Compounds VII, X, and XI, as well as the deuterio complexes of XI and VII, were all characterized by IR, NMR (^1H and ^{31}P), and mass spectral data and elemental analysis. These results are included in Tables I and II.



VII XIV

The "driving force" for the rearrangement of compound X to XI (as well as the prop-2-ynyl to prop-1-ynyl rearrangement[14]) might well be thought to be the desire of the carbon–carbon multiple bond to become "conjugated" with the phosphazene ring. If this type of conjugation were possible, then the keto-substituted phosphazenes (VII) might be expected to show a high degree of enol character, and the enol form should be especially stable due to the possible formation of a six-membered ring such as XIV as well as the C=CP=N conjugation.

This, nevertheless, is not the case. Both the acetonyl- and acetophenonyl-substituted phosphazene products showed no discernible enol tautomer in their ^1H NMR spectra. Further investigations into the possibilities of resonance interactions between an exocyclic carbon π system and the phosphazene ring are under way in our laboratory at present.[13]

Experimental Section

Hexachlorocyclotriphosphazene (I) was purchased from Aldrich or Alfa-Ventron and was purified by vacuum sublimation, followed by two recrystallizations from *n*-hexane. Organolithium, Grignard reagents, and all the alkyl halides were also purchased from Aldrich or Alfa-Ventron. Tetrahydrofuran (THF) was distilled into the reaction flask from a sodium–benzophenone ketyl drying agent under an atmosphere of dry nitrogen. Hexane was similarly distilled from a sodium–benzophenone–tetraglyme ketyl drying agent. Dichloromethane was dried by distillation from P_4O_{10}. The reagents 2-methoxyallyl bromide,[16] methylpentachlorocyclotriphosphazene,[12] and 1-methyl-1-hydrotetrachlorocyclotriphosphazene[8] were all synthesized by published procedures. All the reactions described in this work were performed under an atmosphere of dry nitrogen.

Reactions of Enolate Anions. The enolate anions of acetaldehyde,[9] acetone, and acetophenone[17] were prepared by published procedures. These anions were all reacted with the phosphazene compounds in the same manner. The following is a typical procedure: Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) was dissolved in THF and cooled to −80 °C. The enolate anion (0.015 mol) was then added slowly and the mixture stirred for 15 h, during which time the temperature was allowed to rise to ~25 °C. Removal of the solvent under reduced pressure and vacuum distillation of the residue gave the products. Yields are listed in Table II.

Reactions of Metallophosphazenes. The lithio-[14] and cuprio-phosphazene[8,15] anions were generated by published procedures.

a. Reactions with α-Haloketones. The metallophosphazene (0.014 mol) was generated as previously described. The α-haloketone (0.015 mol) was then added to the metallophosphazene solution, which was held at −80 °C. The reaction mixture was allowed to stir for 15 h, during which time the temperature was allowed to rise to ~25 °C. The solvent was removed under reduced pressure, and the products were extracted with toluene (250 mL). This toluene extract was washed with water (2 × 250 mL portions) and dried over magnesium sulfate. The solvent was again removed under reduced pressure. A ^{31}P NMR spectrum of the products at this stage indicated a complex mixture. Only in the reaction of the lithiophosphazene with α-bromoacetophenone was any ketone product isolated. This was recovered by extraction of the products with *n*-hexane followed by successive recrystallizations from this solvent at −80 °C. The yield was ~5%.

b. Reaction with 2-Bromo-1,1-diethoxyethane. The lithiophosphazene (0.014 mol) was generated as described above and held at −80 °C. A solution of 2-bromo-1,1-diethoxyethane (0.015 mol) in THF was slowly added to the metallophosphazene, and the mixture was stirred for 6 h, during which time the temperature was allowed to rise to ~25 °C. The solvent was then removed under reduced pressure and the residue extracted with dichloromethane. Recrys-

(17) Dupont, J. G.; Allen, C. W. *Inorg. Chem.* **1977**, *16*, 2964.

tallization from *n*-hexane/dichloromethane yielded the bis(cyclotriphosphazene) (VIII) in ~60% yield. The spectra of this compound were identical to those previously reported.[3] The cupriophosphazene was found not to react with 2-bromo-1,1-diethoxyethane.

c. Reactions with 2-Methoxyallyl Bromide. i. The cupriophosphazene (0.014 mol) was generated as described above. The alkyl halide (0.60 mol) was added, and the mixture was stirred for 48 h at room temperature. The solvent was then removed under reduced pressure, and the products were dissolved in toluene (250 mL). This organic layer was washed with aqueous HCl (~10% solution, 250 mL) and dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave the crude product (VII), which was recrystallized from *n*-hexane/dichloromethane.

ii. The lithiophosphazene (0.014 mol) was generated at −80 °C as described above. The 2-methoxyallyl bromide (0.015 mol) was added slowly, and the mixture was allowed to stir for 16 h, during which time the temperature was allowed to rise to ~25 °C. The solvent was then removed under high vacuum, and *n*-hexane was distilled onto the residues. The resultant solution was filtered through infusorial earth by using Schlenk techniques, and the solvent was again removed under high vacuum to leave a crude product. Recrystallization from freshly distilled *n*-hexane yielded compound X.

Rearrangement/Hydrolysis Reactions. All of the reactions described in this section of the work were initially monitored by ^1H NMR. The solvent, $CDCl_3$, was freshly distilled from P_4O_{10}, and the rearrangement or hydrolysis was accomplished with the use of either H_2O, D_2O, H_2O/HCl, or D_2O/DCl.

a. Rearrangement of Compound X to Compound IX. The 2-methoxyprop-2-enyl-substituted compound (X) was dissolved in dichloromethane. Two or three drops of water were introduced into the solution, and the mixture was stirred for 1 h. The solution was then dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave compound XI, which was recrystallized from *n*-hexane.

b. Hydrolysis of Compound XI to Compound VII. The 2-methoxyprop-1-enyl-substituted compound (XI) was dissolved in dichloromethane and treated with ~5 drops of HCl (0.01 M solution). This mixture was allowed to stir for 16 h and was then dried over magnesium sulfate. The solvent was then removed under reduced pressure to leave the acetonyl-substituted phosphazene (VII), which was recrystallized from *n*-hexane.

c. Rearrangement/Hydrolysis of Compound X to Compound VII. This reaction was accomplished by treatment of a dichloromethane solution of compound X with aqueous HCl in an identical manner to that described above for compound XI.

d. Attempted Rearrangement of Compound XII. i. The prop-2-enyl-substituted phosphazene (XII) (3.0 g, 0.009 mol) (synthesized as previously reported[15]) was dissolved in THF (100 mL) and cooled to −80 °C. Then, *n*-butyllithium (0.5 mL of a 2.0 M solution in *n*-hexane) was introduced, and the mixture was allowed to stir for 16 h, during which time the temperature was allowed to rise to ~25 °C. After removal of the solvent under reduced pressure, a subsequent analysis of the ^1H NMR spectrum of the product indicated that no rearrangement of compound XII had occurred.

ii. The prop-2-enyl compound (XII) was treated with dilute HCl in a manner identical with that described above for compound XI. Inspection of the ^1H NMR of the product indicated that no rearrangement of compound XII had occurred.

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Registry No. I, 940-71-6; II, 71332-21-3; III (R = H), 82056-02-8; III (R = CH_3), 85319-90-0; III (R = C_6H_5), 82056-06-2; IV (R = H), 85319-91-1; IV (R = CH_3), 85319-92-2; IV (R = C_6H_5), 85319-93-3; V, 77217-61-9; VI, 75083-25-9; VII (R = CH_3), 85319-94-4; VII (R = C_6H_5), 85319-95-5; VIII, 80241-37-8; IX, 77589-25-4; X, 85319-96-6; XI, 85319-97-7; XII, 72474-22-7; lithium ethenolate, 2180-63-4; lithium 2-propenolate, 67863-40-5; lithium 1-phenylethenolate, 35249-09-3; α-bromoacetophenone, 70-11-1; 2-bromo-1,1-diethoxyethane, 2032-35-1; 2-methoxyallyl bromide, 26562-24-3.

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Phosphoranes. 12. Synthesis and Dynamic NMR Study of Methyltris(trifluoromethyl)phosphorane, $CH_3(CF_3)_3PH$

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The fluxional phosphorane $CH_3(CF_3)_3PH$ has been obtained from the reaction of $CH_3(CF_3)_3PCl$ with $RSiH_3$ (R = CH_3, H). Above room temperature $CH_3(CF_3)_3PH$ is thermally unstable, forming $CH_3(CF_3)_2P$ and CF_3H. Low-temperature limiting ^{19}F and ^{31}P NMR spectra suggest that the ground-state geometry has two axial CF_3 groups on a trigonal-bipyramidal framework. Line-shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra yielded a barrier (ΔG^*_{298} = 14.2 ± 0.8 kcal) to the intramolecular exchange process that equilibrates the two CF_3 environments. This barrier is compared to those already known for related molecules $CH_3(CF_3)_3PY$ (Y = F, Cl, OCH_3, SCH_3, $N(CH_3)_2$, CH_3). Infrared and mass spectral data of the new hydride are reported.

Introduction

In series of similar phosphoranes, comparison[1-3] of the barrier height to intramolecular rearrangement has provided some insight into the relative contribution of an individual substituent. The simplest substituent Y = H in the two series Y_2PF_3[2] and YPF_4[3] alters the value of the barrier substantially having an effect comparable to a methyl group, but when barriers are ordered[2,3] the relative positions of H and CH_3 appear to vary inexplicably, especially the low barrier for CH_3PF_4. Earlier[1] we showed that the barrier to intramolecular exchange of CF_3 groups in the phosphoranes $CH_3(CF_3)_3PY$ increases for Y in the order F < Cl < OCH_3 < SCH_3 < $N(CH_3)_2$ < CH_3. Reported here is the synthesis of another member of this series, $CH_3(CF_3)_3PH$, and a determination of its barrier to rearrangement that permits inclusion of Y = H in the above order. Application of a parameterized estimation of barriers to the hydrides is discussed.

Experimental Section

Standard vacuum-line techniques were used for all manipulations. Stopcocks were lubricated with Apiezon N grease. Silane, CH_3SiH_3, and $(C_4H_9)_3SnH$ were purchased from Matheson, Columbia, and Alfa Products, respectively. The phosphoranes $CH_3(CF_3)_3PX$ (X = Cl, F)[4] were prepared by reported procedures.

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