LEVEL II

12

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 10	2. GOVT ACCESSION NO.: AD-A108 782
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with Tert- and n-Butyl Lithium Reagents	5. TYPE OF REPORT & PERIOD COVERED: Technical Report
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Kolikkara Ramachandran and Christopher W. Allen	8. CONTRACT OR GRANT NUMBER(s): N001477C-0605
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of Vermont, Burlington, Vermont 05405	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11. CONTROLLING OFFICE NAME AND ADDRESS: Department of the Navy, Office of Naval Research, Arlington, VA 22217	12. REPORT DATE: December 4, 1981
	13. NUMBER OF PAGES: 19
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release and sale; its distribution is unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC ELECTE DEC 22 1981 S D E

18. SUPPLEMENTARY NOTES

Accepted for Publication in Journal of the American Chemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

fluorophosphazenes
phosphazenes
alkylphosphazenes
Regioselectivity
Stereoselectivity
nmr
mass spectrometry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The reactions of tert- and n-butyl lithium reagents with hexafluorocyclotriphosphazene ($N_3P_3F_6$) have been examined. In contrast to the behavior of n-butyl lithium, the reaction of t-butyl lithium with $N_3P_3F_6$ gives good yield of $N_3P_3F_5C_4H_9$. While the n-butyl lithium reaction follows a geminal pathway at the stage of disubstitution, the t-butyl lithium reaction gives exclusively the trans non-geminal isomer for the compounds $N_3P_3F_{6-n}(t\text{-}C_4H_9)_n$ (n = 2,3). This is the first example of a regio and stereospecific reaction in

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

81 12 22 089

AD A108782

DTIC FILE COPY

20. ABSTRACT

phosphazene chemistry. At the stage of trisubstitution solvent (diethyl ether) cleavage by t-butyl lithium is competitive with phosphazene substitution resulting in the concomitant formation of trans-2,4,6-$N_3P_3F_3(OC_2H_5)(t\text{-}C_4H_9)_2$. These results are discussed in terms of competing steric and electronic effects. The butylphosphazenes are characterized by mass spectrometry and infrared and NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) spectroscopy.

OFFICE OF NAVAL RESEARCH
Contract N001477C-0605
Project NR 356-663
Technical Report No. 10

Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with Tert- and n-Butyl Lithium Reagents

by

Kolikkara Ramachandran and Christopher W. Allen

Accepted for Publication in the
Journal of the American Chemical Society

University of Vermont
Department of Chemistry
Burlington, Vermont 05405

Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with Tert- and n-Butyl Lithium Reagents.[1]

Kolikkara Ramachandran and Christopher W. Allen*

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405. Received

Abstract: The reactions of tert- and n-butyl lithium reagents with hexafluorocyclotriphosphazene ($N_3P_3F_6$) have been examined. In contrast to the behavior of n-butyl lithium, the reaction of t-butyl lithium with $N_3P_3F_6$ gives good yields of $N_3P_3F_5C_4H_9$. While the n-butyl lithium reaction follows a geminal pathway at the stage of disubstitution, the t-butyl lithium reaction gives exclusively the trans non-geminal isomer for the compounds $N_3P_3F_{6-n}(t\text{-}C_4H_9)_n$ (n = 2,3). This is the first example of a regio and stereospecific reaction in phosphazene chemistry. At the stage of trisubstitution solvent (diethyl ether) cleavage by t-butyl lithium is competitive with phosphazene substitution resulting in the concomitant formation of trans-2,4,6-$N_3P_3F_3(OC_2H_5)(t\text{-}C_4H_9)_2$. These results are discussed in terms of competing steric and electronic effects. The butylphosphazenes are characterized by mass spectrometry and infrared and NMR (^1H, ^{13}C, ^{19}F, ^{31}P) spectroscopy.

Introduction

One of the most active fields of investigation in cyclophosphazene chemistry is the study of substitution reactions.[2-4] Aminolysis and alcoholysis reactions of hexachloro cyclotriphosphazene, $N_3P_3Cl_6$, have received a great deal of attention and various substitution patterns have been observed.[2,3] On the other hand, reaction of organometallic reagents with $N_3P_3Cl_6$ and $N_3P_3F_6$ are less well understood.[4] One reason for this is the complexity of these reactions. Depending on the nature of the reagents, these reactions give rise to substitution of halogen atoms[4,5] and/or cleavage of the phosphazene ring.[6] Previous studies in this laboratory[7,8] and elsewhere[9-11] have shown that reactions of $N_3P_3F_6$ with organometallic reagents follow both geminal and nongeminal pathways with the geminal pathway being more frequently observed.[4]

In any attempt to identify factors involved in the stereochemical control of phosphazene substitution reactions, studies of the reactions of alkyl lithium reagents would be of value due to the electronic simplicity of the organic function. While a detailed study of the reaction of methyl lithium with $N_4P_4F_8$ has appeared,[11] only brief reports of the reactions of alkyl lithium reagents with $N_3P_3F_6$ are available.[9,13,14] Part of the lack of interest in these derivatives is related to the low yields obtained in their syntheses. While various proposals have been advanced to rationalize this observation, the most reasonable suggestion appears to be that facile deprotonation of the alkyl group α to the phosphorus atom leads to an anionic center at the exocyclic position.[15,16] These heteroatom stabilized α-anions[17] can lead to intramolecular ring degradation[16] or intermolecular cross linking.[18] In this investigation we have chosen to test this model by examining the reactions of an alkyl lithium reagent without α hydrogen atoms (tert-butyl lithium) and to explore the effect of steric requirements

of the alkyl group on the stereochemistry of the substitution reaction.

Experimental Section

Materials and Methods. Hexafluorocyclotriphosphazene ($N_3P_3F_6$) was prepared from $N_3P_3Cl_6$ (Ethyl Corp.) by a previously reported procedure.[19] Tert-butyl lithium (2.0 M solution in pentane) and n-butyl lithium (1.55 M solution in hexane) were obtained from Aldrich. Diethyl ether was distilled fr sodium-benzophenone ketyl. Pentane, hexane, petroleum ether (b.p. 35-55°C) and benzene (Fisher) were distilled over sodium ribbon. NMR spectra (in $CDCl_3$) were recorded on a Brucker WM250 spectrometer operating at 250.1 MHz(^1H), 62.9 MHz (^{13}C), 235.2 MHz (^{19}F) and 101.2 MHz (^{31}P). Tetramethyl silane, TMS, (for ^1H and ^{13}C) and fluorotrichloromethane, $CFCl_3$, (for ^{19}F) were used as internal references. For ^{31}P NMR, 85% H_3PO_4 was used as an external reference. Chemical shifts upfield to the reference are assigned a negative sign. ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded under conditions of broad band decoupling. Infrared (IR) spectra were obtained as their films (NaCl discs) or KBr pellets on a Beckman IR 20 A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 60 eV. Elemental analyses were performed by Integral Microanalytical Laboratories.

All reactions were carried out under anhydrous conditions in a three necked round bottomed flask fitted with a reflux condenser and a pressure-equalizing dropping funnel. The system was stirred magnetically and flushed with nitrogen which exited through a mercury bubbler. Lithium reagents were transferred using syringe techniques.

Reaction of $N_3P_3F_6$ with One Equivalent of $t\text{-}C_4H_9Li$. Tert-butyl lithium (15 ml, 0.03 mol) was added over a one hour period to a solution of $N_3P_3F_6$ (7.5 g, 0.03 mol) in 200 ml diethyl ether which was cooled in a dry ice-acetone bath. The reaction mixture was allowed to come to room temperature and stirred for three hours. The solvent was removed under reduced pressure and 150 ml of hexane was added. The solid was removed by filtration and the solvent was removed from the filtrate. The resulting liquid was distilled at reduced pressure (0.02mm Hg) to yield 5.8 g (67.4% of theory) of a colorless liquid (b.p. 28° at 0.02 mm Hg). Anal. Calcd. for $N_3P_3F_5C_4H_9$(I): C, 16.72; H, 3.14; N, 14.63; mol wt 287. Found: C, 16.80; H, 3.20; N, 14.51; mol wt 287 (mass spectrum[20]).

^{1}H NMR[21]: $\delta_{C\text{-}(C\underline{H}_3)_3}$ = 1.226 (d), $^3J_{P\text{-}H}$ = 19.823. ^{13}C NMR: $\delta_{C\text{-}(\underline{C}H_3)_3}$ = 23.187 (d), $^2J_{P\text{-}C}$ = 16.062; $\delta_{\underline{C}\text{-}(CH_3)_3}$ = 31.968(m), $^1J_{P\text{-}C}$ = 142.817; $^2J_{F\text{-}C}$ = 26.502. ^{31}P NMR: $\delta_{=P\underline{P}F_2}$ = 9.088 (m, 2P), $^1J_{P\text{-}F}$ = 935.914; $\delta_{\underline{P}F(t\text{-}C_4H_9)}$ = 56.461 (m, 1P), $^1J_{P\text{-}F}$ = 1048.306. ^{19}F NMR: $\delta_{=PF_2}$ = -68.243, $^1J_{P\text{-}F}$ = 900.711; $\delta_{=PF_2}$ = -69.820, $^1J_{P\text{-}F}$ = 894.433; $\delta_{=P\underline{F}(t\text{-}C_4H_9)}$ = 79.298, $^1J_{P\text{-}F}$ = 1033.177. IR[22]: 1265 (S, νP=N), 970 (m, PF asym), 935 (m, PF asym), 805 (m, PF sym.), 735 (s, PF sym.).

At higher distillation temperatures, 0.26 g (2.7% of theory) of a second product was obtained. The colorless liquid, b.p. 50° at 0.02 mm Hg, was identified as bis(t-butyl)tetrafluorocyclotriphosphazene(II). Anal. Calcd. for $N_3P_3F_4C_8H_{18}$: C, 29.53; H = 5.54; N = 12.92; mol wt. 325. Found C, 29.56; H = 5.84; N = 12.80; mol wt. 325 (mass spectrum[20]).

^{1}H NMR[21]: $\delta_{C\text{-}(C\underline{H}_3)_3}$ = 1.223 (d), $^3J_{P\text{-}H}$ = 19.531. ^{13}C NMR: $\delta_{C\text{-}(\underline{C}H_3)_3}$ = 23.288 (d), $^2J_{P\text{-}C}$ = 26.000, $\delta_{\underline{C}\text{-}(CH_3)_3}$ = 32.097 (m), $^1J_{P\text{-}C}$ = 147.914, $^2J_{F\text{-}C}$ = 25.569, $^3J_{P\text{-}C}$ = 4.949. ^{19}F NMR: $\delta_{=P\underline{F}_2}$ = -68.964 (m, 2F), $^1J_{P\text{-}F}$ = 902.832,

$\delta_{=PF(t\text{-}C_4H_9)}$ = -78.017 (m, 2F), $^1J_{P-F}$ = 1022.909. ^{31}P NMR: $\delta_{=PF_2}$ = 9.548 (m, 1P), $^1J_{P-F}$ = 903.320, $^2J_{P-P}$ = 51.270, $^3J_{P-F}$ = 6.103, $\delta_{=PF(t\text{-}C_4H_9)}$ = 56.202 (m, 2P), $^1J_{P-F}$ = 1021.632. IR[21]: 1265 (s, ν P=N), 970 (m, PF asym.), 935 (s, PF asym.), 850 (s, PF sym.) 825 (s, PF sym.), 725 (s, PF sym.)

Reaction of $N_3P_3F_6$ with t-C_4H_9Li in Pentane. The method employed for this reaction was identical to that previously described except that pentane was used in place of diethyl ether. After nine hours, 2.5 g (0.01 mol) of $N_3P_3F_6$ yielded (in addition to unreacted t-C_4H_9Li) 0.4 g of a mixture of the mono(I) and di-t-butylfluorocyclotriphosphazenes(II)

Reaction of $N_3P_3F_6$ with Two Equivalents of t-C_4H_9Li. The reaction of t-C_4H_9Li (20 ml, 0.04 mol) with $N_3P_3F_6$ (5.0 g, 0.02 mol) in diethyl ether at -78° was conducted as previously described. Reduced pressure fractional distillation of the colorless liquid product yielded: $N_3P_3(t\text{-}C_4H_9)F_5$(I), b.p. 28° (0.02 mm Hg), 1.2 g (20.9%) and $N_3P_3(t\text{-}C_4H_9)_2F_4$(II), b.p. 50° (0.02 mm Hg) 2.7 g (41.5%). Separation of the above products can also be achieved by column chromatography over silica gel using petroleum ether as eluant.

Reaction of $N_3P_3F_6$ with Three Equivalents of t-C_4H_9Li. The reaction of t-C_4H_9Li (45 ml, 0.09 mol) with $N_3P_3F_6$ (7.5 g, 0.03 mol) in 150 ml of diethyl ether at 0° was conducted as previously described. The oily product mixture was separated on a silica gel column using a benzene-hexane (1:1) mixture as the eluent. The first product was identified as $N_3P_3F_4(t\text{-}C_4H_9)_2$ (II) (3.2 g, 32.8%). The second component was identified as tris(t-butyl)-trifluorocyclotriphosphazene(III) (0.12 g, 1.1%) mp 80°. Anal. Calcd. for $N_3P_3F_3C_{12}H_{27}$: C, 39.67; H = 7.44; mol wt 363. Found: C, 39.95; H = 7.72; mol wt 363 (mass spectrum[20]).

^{1}H NMR[21]: $\delta_{C\text{-}(CH_3)_3}$ = 1.216 (d, 18H), $^3J_{P-H}$ = 18.516; $\delta_{C\text{-}(CH_3)_3}$ = 1.201 (d, 9H), $^3J_{P-H}$ = 18.516. ^{31}P NMR: $\delta_{=PF(t\text{-}C_4H_9)}$ = 33.176 (m, 1P), $^1J_{P-F}$ =

1012. 789; $\delta_{\equiv P\underline{F}(t\text{-}C_4H_9)}$ = 31.122 (m, 2P), $^1J_{P\text{-}F}$ = 1007.179. ^{19}F NMR: $\delta_{\equiv P\underline{F}(t\text{-}C_4H_9)}$ =-72.140 (m, 1F), $^1J_{P\text{-}F}$ = 1011.658; $\delta_{\equiv P\underline{F}(t\text{-}C_4H_9)}$ = -77.148 (m, 2F), $^1J_{P\text{-}F}$ = 1007.080. The third compound eluted was found to be mono(ethoxy)bis(t-Butyl)trifluorocyclotriphosphazene, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$ (IV) 1.7 g, 16.1%), m.p. 40-42°C. Anal. Calcd for $N_3P_3F_3OC_{10}H_{23}$: C, 34.18; H, 6.55; mol wt 351. Found: C, 34.10; H, 6.91, mol wt 351 (mass spectrum[20]).

^1H NMR[21]: $\delta_{C\text{-}(\underline{C}H_3)_3}$ = 1.214 (d), $^3J_{P\text{-}H}$ = 19.090; $\delta_{O\text{-}C\underline{H}_2\text{-}CH_3}$ = 4.154 (m), $^3J_{P\text{-}H}$ = 15.863, $^3J_{H\text{-}H}$ = 6.991; $\delta_{O\text{-}CH_2\text{-}C\underline{H}_3}$ = 1.369 (t), $^3J_{H\text{-}H}$ = 6.991. ^{13}C NMR: $\delta_{C\text{-}(\underline{C}H_3)_3}$ = 23.545 (d), $^2J_{P\text{-}C}$ = 9.637; $\delta_{\underline{C}\text{-}(CH_3)_3}$ = 31.923 (m), $^1J_{P\text{-}C}$ = 136.125, $^2J_{F\text{-}C}$ = 26.101, $^3J_{P\text{-}C}$ = 2.409; $\delta_{O\text{-}\underline{C}H_2\text{-}CH_3}$ = 63.675 (d), $^2J_{P\text{-}C}$ = 6.425; $\delta_{O\text{-}CH_2\text{-}\underline{C}H_3}$ = 15.922 (d), $^3J_{P\text{-}C}$ = 8.031. ^{31}P NMR: $\delta_{\equiv P\underline{F}(OC_2H_5)}$ = 12.581 (m, 1P), $^1J_{P\text{-}F}$ = 892.857; $\delta_{\equiv P\underline{F}(t\text{-}C_4H_9)}$ = 54.299 (m, 2P), $^1J_{P\text{-}F}$ = 1007.441. ^{19}F NMR: $\delta_{\equiv P\underline{F}(OC_2H_5)}$ = -63.862 (m, 1F), $^1J_{P\text{-}F}$ = 892.334; $\delta_{\equiv P\underline{F}(t\text{-}C_4H_9)}$ = -76.033 (m, 1F), $^1J_{P\text{-}F}$ = 1015.625, $\delta_{\equiv P\underline{F}(t\text{-}C_4H_9)}$ = -77.187 (m, 1F), $^1J_{P\text{-}F}$ = 1009.304. IR[22]: 1250 (s, ν P=N), 1050 (s, P-O), 990 (m, P-F asym.) 920 (m, P-F asym.) 895 (m, PF sym.), 835 (s, PF sym.), 805 (s, PF sym.).

Attempts at introduction of additional t-butyl groups by employing $t\text{-}C_4H_9Li$ to $N_3P_3F_6$ ratios greater than 3:1 were unsuccessful.

Reaction of $N_3P_3F_6$ with One Equivalent of $n\text{-}C_4H_9Li$. The reaction of $n\text{-}C_4H_9Li$ (20 ml, 0.03 mol) with $N_3P_3F_6$ (7.5 g, 0.03 mol) in 200 ml of diethyl ether at -78° was conducted as previously described. Reduced pressure (0.02 mm Hg) distillation of the product at room temperature gave a colorless liquid which was characterized as mono(n-butyl) pentafluorocyclotriphosphazene, $N_3P_3(n\text{-}C_4H_9)F_5$(V), 0.67 g (7.8% of theory, lit.[13] 11-14%) b.p. 25° (0.02 mm Hg). Anal. Calcd. for $N_3P_3F_5C_4H_9$: C, 16.72; H, 3.14; mol wt 287. Found: C, 16.01; H, 3.04; mol wt 287 (mass spectrum[20])

^{1}H NMR[21]: $\delta_{\underline{CH}_2-(CH_2)_2-CH_3}$ = 1.992 (m, 2H), $\delta_{CH_2-\underline{CH}_2-CH_2-CH_3}$ = 1.631 (m, 2H), $\delta_{(CH_2)_2-\underline{CH}_2-CH_3}$ = 1.469 (m, 2H), $\delta_{(CH_2)_3-\underline{CH}_3}$ = 0.960 (t, 3H), $^{3}J_{H-H}$ = 7.254. ^{13}C NMR: δ_{C_α} = 28.207 (m), $^{1}J_{P-C}$ = 141.709, $^{2}J_{F-C}$ = 15.474, $^{3}J_{P-C}$ = 7.737; δ_{C_β} = 23.4054 (d), $^{2}J_{P-C}$ = 4.298, δ_{C_γ} = 23.227 (d), $^{3}J_{P-C}$ = 18.053; δ_{C_Δ} = 13.408 (s). ^{19}F NMR: $\delta_{\equiv P\underline{F}_2}$ =-69.714 (m, 2F); $^{1}J_{P-F}$ = 934.738; $\delta_{\equiv P\underline{F}_2}$ = -67.874 (m, 2F); $^{1}J_{P-F}$ = 929.675; $\delta_{\equiv P\underline{F}(n-C_4H_9)}$ = -59.977 (d, t, 1F), $^{1}J_{P-F}$ = 1009.521, $^{3}J_{P-F}$ = 11.597. ^{31}P NMR: $\delta_{\equiv\underline{P}F_2}$ = 9.548, $^{1}J_{P-F}$ = 925.293. $\delta_{\equiv\underline{P}F(n-C_4H_9)}$ = 50.211, $^{1}J_{P-F}$ = 1008.301, $^{2}J_{P-P}$ = 63.476, $^{3}J_{P-F}$ = 19.531. IR[22]: 1275 (s, ν P=N), 970-750 (s, unresolved, includes P-F).

At higher distillation temperatures (~100°), a second product (0.20 g 2.1%) which solidified on cooling, was obtained. The solid, mp 55°, was identified as bis(n-butyl)tetrafluorocyclotriphosphazene (VI). Anal. Calcd. for $N_3P_3F_4C_8H_{18}$: C, 29.53; H, 5.54; mol wt 325. Found: C, 28.48; H, 5.68; mol wt 325 (mass spectrum[20]).

^{1}H NMR[21]: $\delta_{\underline{CH}_2-(CH_2)_2-CH_3}$ = 1.744 (m, 2H), $\delta_{CH_2-\underline{CH}_2-CH_2-CH_3}$ = 1.567 (m, 2H), $\delta_{(CH_2-)_2-\underline{CH}_2-CH_3}$ = 1.434 (m, 2H), $\delta_{(CH_2)_3-\underline{CH}_3}$ = 0.945 (t, 3H), $^{3}J_{H-H}$ = 7.172. ^{13}C NMR: δ_{C_α} = 30.903 (d, t), $^{1}J_{P-C}$ = 92.843, $^{3}J_{P-C}$ = 5.158; δ_{C_β} = 22.689 (d), $^{2}J_{P-C}$ = 5.158; δ_{C_γ} = 23.508 (d), $^{3}J_{P-C}$ = 17.193, δ_{C_Δ} = 13.531 (s). ^{19}F NMR: $\delta_{\equiv P\underline{F}_2}$ = -68.612; $^{1}J_{P-F}$ = 928.173. ^{31}P NMR: $\delta_{\equiv\underline{P}F_2}$ = 9.753 (m, 2P), $^{1}J_{P-F}$ = 917.608; $\delta_{\equiv\underline{P}(n-C_4H_9)_2}$ = 48.294 (t, 1P), $^{2}J_{P-P}$ = 35.400. IR[22]: 1250 (s, ν P=N), 935 (s, PF), 825 (m, PF) 785 (m, PF).

The residue remaining after the above distillation solidified on cooling. The material, which was gummy and of low solubility, resisted further characterization.

Results and Discussion

The reaction of t-butyl lithium with $N_3P_3F_6$ in diethyl ether gives the partially substituted fluorocyclotriphosphazene derivatives,

$N_3P_3(t\text{-}C_4H_9)_nF_{6-n}$, n = 1, 2 and 3, and an ethoxy derivative, $N_3P_3(OC_2H_5)$-$(t\text{-}C_4H_9)_2F_3$. Reaction of one equivalent of t-butyl lithium with one equivalent of $N_3P_3F_6$ in diethyl ether at -78° gives the monosubstituted compound, $N_3P_3(t\text{-}C_4H_9)F_5$(I) (67.4%) and a small amount (2.7%) of the disubstituted compound, $N_3P_3(t\text{-}C_4H_9)_2F_4$(II). The yield of the disubstituted compound (II) can be increased substantially by the reaction of two equivalents of t-butyl lithium with one equivalent of $N_3P_3F_6$ at -78°. A 1:3 ($N_3P_3F_6$: t-butyl lithium) reaction gives the disubstituted compound (II), the trisubstituted compound $N_3P_3(t\text{-}C_4H_9)_3F_3$(III) and an unexpected product, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$(IV). These compounds can be separated by column chromatography over silica gel. The source of ethoxide ion for the formation of compound IV is from the cleavage of diethyl ether by t-butyl lithium[23]. Reaction of t-butyl lithium with $N_3P_3F_6$ in pentane gives only (t-butyl)fluorocyclotriphosphazenes $N_3P_3(t\text{-}C_4H_9)_nF_{6-n}$ n=1,2 in significantly reduced yields. This observation is consistent with the increased carbanionic character of organolithium reagents in the presence of Lewis bases.

The synthetic results demonstrate a significant increase in the difficulty of effecting higher degrees of substitution. This observation is most directly related to the steric hinderance associated with each of the t-butyl substituents. Similar observations have been made in the reactions of other organometallic reagents[24] and bulky amines[25] with halocyclophosphazenes.

The reaction of n-Butyl lithium with $N_3P_3F_6$ in diethyl ether gives the previously reported[13] mono- and disubstituted cyclotriphosphazenes, $N_3P_3(n\text{-}C_4H_9)F_5$(V) and $N_3P_3(n\text{-}C_4H_9)_2F_4$(VI). In contrast to the excellent yields obtained in the t-butyl lithium reaction, the yields of n-butyl

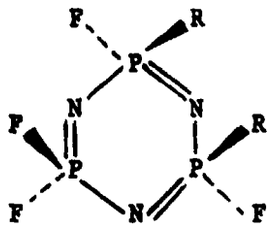
fluorocyclotriphosphazenes are poor. This observation confirms our hypothesis that organophosphazenes without α-hydrogen atoms may be prepared in good yields since the degradative routes *via* the heteroatom stabilized α-anions[16,18] are not available. It is reasonable to expect that one should be able to prepare partially substituted polyorganophosphazenes using t-butyl lithium without the cross linking observed with other alkyl lithium reagents.[18]

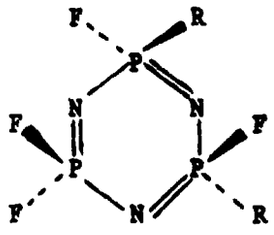
The various t-butyl- and n-butyl fluorocyclophosphazenes have been characterized by elemental analysis and spectroscopic data (mass, NMR and IR). As expected, two distinct phosphorus environments are observed in the ^{31}P NMR spectra of the mono-t-butyl compound (I) and mono-n-butyl compound (V). The phosphorus nuclei to which the alkyl group is attached is surprisingly deshielded compared to $\equiv PF_2$ groups. Similar deshielding is observed in the ^{31}P NMR spectra of all the t-butyl- and n-butyl derivatives prepared in this work. The electron donating alkyl groups are expected to cause shielding of the phosphorus resonances. A similar reversal of trend has been noted in the NMR spectra of other phosphorus compounds[26-28]. The ^{31}P NMR spectra of compounds I and V are complicated by second order effects. The values of chemical shift and coupling constants have been deduced based on first order approximations. In the $\equiv PFR$ centers the ^{31}P NMR resonances are first order and values for $^{2}J_{P-P}$ and $^{3}J_{P-F}$ can be deduced. The ^{19}F NMR spectra of monosubstituted compounds I and V indicate three distinct fluorine environments as might be expected.

Disubstituted cyclotriphosphazenes of the type $N_3P_3F_4R_2$ can exist in three isomeric forms: geminal or 2,2-$N_3P_3F_4R_2$ and non-geminal cis-2,4-$N_3P_3F_4R_2$ and trans-2,4-$N_3P_3F_4R_2$. The identity of these material may be

established by ^{31}P and ^{19}F NMR spectroscopy.[11] Using this approach the bis n-butyl derivative (VI) has been assigned a geminal structure. The ^{31}P NMR spectrum of compound VI shows two distinct phosphorus resonances. A small triplet (J = 35.400 Hz) at δ 48.294 is assigned to the $\equiv P(n\text{-}C_4H_9)_2$ group. The large triplet (J = 917.608 Hz) at δ = 9.753 is assigned to $\equiv PF_2$ groups. These assignments are further substantiated by the observations of a single fluorine environment in the ^{19}F NMR spectrum. While there is no significant structural information contained in the ^{1}H NMR spectrum, the ^{13}C data is of value. The significant decrease of $^{1}J_{PC}$ and loss of $^{2}J_{FC}$ on going from V to VI is supportive of the geminal assignment. The formation of the geminal isomer appears to be the preferred pathway in most organolithium reactions.[43]

The ^{1}H NMR spectrum of the bis t-butyl derivative (II) shows a doublet with $^{3}J_{PH}$ very similar to that observed for the mono t-butyl derivative (I). This data along with the observation of similar values for $^{1}J_{PC}$ and $^{2}J_{FC}$ in the ^{13}C spectra in compounds I and II suggest a non-geminal configuration for II. The magnitude of $^{3}J_{P-C}$ is greater than that of $^{2}J_{P-C}$. Similar observations have been noted in various organophosphorus compounds by McFarlane.[29] The ^{31}P NMR spectrum for II shows both $\equiv PF_2$ and $\equiv PFR$ groups thus confirming the non-geminal assignment. The large triplet (δ 9.548 ppm, J = 903.320 Hz) is assigned to $\equiv PF_2$ group. The large doublet at δ 51.270 ppm with a J value of 1021.632 Hz is assigned to the $\equiv PF(t\text{-}C_4H_9)$ centers. The large deshielding of the $\equiv PFR$ center is again noted. The conclusive assignment of structure comes from the ^{19}F NMR data. The fluorine atoms of a $\equiv PF_2$ center are inequivalent with respect to R in a cis isomer but are equivalent in a trans isomer. The observed ^{19}F NMR spectrum of II shows





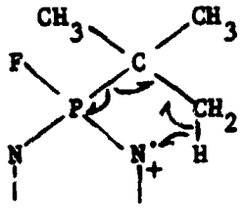
two sets of first-order doublets, thus demonstrating the trans disposition of organic groups and the power of high field ^{19}F NMR for structural work in the study fluorophosphazenes. There are no observable signals due to the cis isomer.[11] The exclusive formation of the trans isomer represents the first example of a regio and stereospecific reaction in phosphazene chemistry.

Like the bis derivative (II), the tris compound, $N_3P_3(t\text{-}C_4H_9)_3F_3$ (III), can have three possible structures: geminal, nongeminal cis and trans. The ^{31}P NMR spectrum of compound (III) shows two distinct phosphorus environments. If compound III were to have a cis structure, then its phosphorus spectrum should be a simple A_3X_3 type. Thus a cis structure can be ruled out readily. Since the phosphorus spectrum does not show the presence of a $\equiv PR_2$ group, a geminal structure can also be ruled out. Thus, compound (III) is assigned a trans structure. This conclusion is strongly supported by the ^{19}F spectrum for III which shows two distinct fluorine environments. A cis structure should give rise to a single fluorine environment. The observation of two simple doublets in the ratio 2:1 in the ^1H NMR spectrum of compound III is in complete agreement with the trans structure proposed.

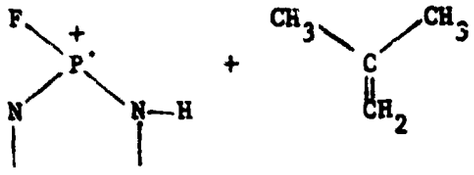
The argument outlined above can be extended to arrive at the structure of the ethoxy derivative, $N_3P_3(OC_2H_5)(t\text{-}C_4H_9)_2F_3$ (IV). All the NMR spectroscopic data clearly prove a trans structure for compound IV. Therefore, the regio and stereo selective nature of this process is maintained at the level of trisubstitution. The fact that the same isomer is formed with either the ethoxy or t-butyl reagent as the incoming groups, suggest that the stereochemistry is controlled by the substituents on the ring in II.

Infrared spectroscopy is of limited use in structural assignments to organocyclophosphazenes[2,3] and is used for only finger printing purposes. All the t-butyl- and n-butylfluorocyclotriphosphazenes show characteristic P-N stretching vibrations.

A close look at the mass spectrometry data (Table I[20]) for compounds (I) - (VI) reveal several interesting points. In all the t-butyl and n-butyl fluorocyclotriphosphazenes, the ions corresponding to the loss of fluorine atoms are weak compared to those corresponding to the loss of the alkyl group(s). This observation indicates that P-C band cleavage is more facile than P-F bond cleavage. Similar behavior has been observed earlier in arylfluorocyclotriphosphazenes[30]. In the mono-t-butyl compound, I, the molecular ion is the most intense ion and the most prominent fragment is $N_3P_3F_5H^+$. In compounds (II) and (III) the most intense species are $N_3P_3F_4C_4H_{10}^+$ (m/e = 269) and $N_3P_3F_3C_8H_9^+$ (m/e = 307) respectively. These species may be thought to be formed by a McLafferty rearrangement of the molecular ion. This process appears to represent a significant fragmentation route for a variety of organophosphazenes.[8,30] The mass spectra of the mono V) and bis (VI) n-butyl derivatives also exhibit significant alkyl group cleavage.



m/e = 325



m/e = 269

We have previously proposed[7] a model for the directive effect in the formation of organophosphazenes in which the electron releasing ability of the organic function in $N_3P_3F_5R$ results in preferential transfer of nitrogen lone pair electron density to a $\equiv PF_2$ center. The $\equiv PFR$ center is now more susceptible to nucleophilic attack and geminal substitution is favored. This rationale accounts for the structure of the bis n-butyl derivative (V) but not those of the t-butyl derivatives, II-IV. The steric requirements of the t-butyl group present a significant barrier to geminal substitution and consequently a non-geminal process becomes the low energy pathway. The magnitude of this steric control is demonstrated by the exclusive formation of the trans isomer in the non-geminal series and by the reluctance of the reaction to proceed past the trisubstituted stage.

Acknowledgements. This work was supported in part by the Office of Naval Research. Institutional grant funds from the University of Vermont were provided for the purchase of a ^{19}F nmr probe.

Supplementary Material Available. A listing of major mass spectral fragments and their relative intensities (Table I). Ordering infomration is given on any current masthead page.

References and Notes

(1) Part 14: Allen, C.W.; Brunst, G.E.; Perlman, M.E., Inorg. Chim. Acta, 1980, 41, 265.

(2) Allcock, H.R., "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972. Allcock, H.R., Chem. Rev., 1972, 72, 315.

(3) Krishnamurthy, S.S.; Sau, A.C.; Woods, M. , Adv. Inorg. Chem. Radiochem., 1978, 21, 41.

(4) Allen, C.W., Ind. Eng. Chem. Prod. Res. Dev., 1981, 77, 20.

(5) Allcock, H.R.; Harris, P.J., J. Am. Chem. Soc., 1978, 100, 6512; 1979, 101, 6221.

(6) Biddlestone, M.; Shaw, R.A., J. Chem. Soc. A, 1969, 178; 1971, 2715; Phosphorus, 1973, 3, 95.

(7) Allen, C. W., J. Chem. Soc. Chem. Commun., 1970, 152.

(8) Dupont, J.G.; Allen, C.W., Inorg. Chem., 1978, 17, 3093.

(9) Paddock, N.L.; Ranganathan, T.N.; Todd, S.M., Can. J. Chem., 1971, 49, 164.

(10) Chivers, T., Inorg. Nucl. Chem. Lett., 1971, 7, 827.

(11) Allen, C.W.; Moeller, T., Inorg. Chem., 1968, 7, 2177.

(12) Ranganathan, T.N.; Todd, S.M.; Paddock, N.L., Inorg. Chem., 1973, 12, 316.

(13) Moeller, T.; Failli, A.; Tsang, F.Y., Inorg. Nucl. Chem. Lett., 1965, 1, 49.

(14) Blumentritt, J.; Moeller, T., Inorg. Nucl. Chem. Lett., 1978, 14, 263.

(15) Calhoun, H.P.; Oakley, R.T.; Paddock, N.L.; Todd, S.M., J. Chem. Soc. Chem. Commun., 1975, 343.

(16) Calhoun, H.P.; Oakley, R.T.; Paddock, N.L., J. Chem. Soc. Chem. Commun., 1975, 454; Oakley, R.T.; Paddock, N.L.; Rettig, S.J.; Trotter, J., Can. J. Chem., 1977, 55, 2534.

(17) Krief, A., Tetrahedron, 1980, 36, 2531.

(18) Evans, T.L.; Patterson, D.B.; Suszko, P.R.; Allcock, H.R., Macromolecules, 1981, 14, 218.

(19) Moeller, T.; John, K.; Tsang, F., Chem. Ind. (London) 1961, 347.

(20) Mass spectrometry data is given in the supplementary material.

(21) Chemical shifts in ppm and coupling constants in Hz.

(22) In cm^{-1}.

(23) Wakefield, B.J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974, p. 198.

(24) Allen, C.W.; Toch, P.L., Inorg. Chem., 1981, 20, 9.

(25) Krishnamurthy, S.S.; Ramachandran, K.; Vasudeva Murthy, A.R.; Shaw, R.A.; Woods, M., J. Chem. Soc. Dalton Trans., 1980, 840.

(26) Van Wazer, J.R.; Callis, C.F.; Schoolery, J.N.; Jones, R.C., J. Am. Chem. Soc., 1956, 78, 5715.

(27) Grim, S.O.; McFarlane, W.; Davidoff, L.F.; Martes, T.J., J. Phys. Chem., 1966, 70, 581.

(28) Reiss, J.; Van Wazer, J.R.; Letcher, J.H., J. Phys. Chem., 1967, 71, 1925.

(29) McFarlane, W., Proc. Roy. Soc. A. 1968, 306, 185.

(30) Allen, C.W.; Toch, P.L., J. Chem. Soc. Dalton Trans., 1974, 1685.

Material to be placed in microfilm edition

Kolikkara Ramachandran and Christopher W. Allen

Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with Tert- and n-Butyl Lithium Reagents.

Table I. Selected Mass Spectra for Butyl Substituted Fluorocyclotriphosphazenes

$N_3P_3F_5(t\text{-}C_4H_9)$ (I)

287(100%, $N_3P_3F_5C_4H_9^+$), 272(32.8%, $N_3P_3F_5C_3H_6^+$), 269(8.6%, $N_3P_3F_4C_4H_{10}^+$), 268(12.1%, $N_3P_3F_4C_4H_9^+$), 257(6.9%, $N_3P_3F_5C_2H_3^+$), 231(96.6%, $N_3P_3F_5H^+$), 230(37.9%, $N_3P_3F_5^+$), 212(25.9%, $N_3P_3F_4H^+$)

$N_3P_3F_4(t\text{-}C_4H_9)_2$ (II)

325(88.7%, $N_3P_3F_4C_8H_{18}^+$), 310(43.5%, $N_3P_3F_4C_7H_{15}^+$), 306(8.9%, $N_3P_3F_3C_8H_{18}^+$), 270(71.0%, $N_3P_3F_4C_4H_{11}^+$), 269(100%, $N_3P_3F_4C_4H_{10}^+$), 268(42.0%, $N_3P_3F_4C_4H_9^+$), 257(56.5%, $N_3P_3F_2C_6H_{12}^+$), 254(52.4%, $N_3P_3F_4C_3H_2^+$), 249(12.9%, $N_3P_3F_3C_4H_9^+$), 230(34.7%, $N_3P_3F_2C_4H_9^+$), 229(62.9%, $N_3P_3F_2C_4H_8^+$), 228(16.1%, $N_3P_3F_2C_4H_7^+$), 227(13.7%, $N_3P_3F_2C_4H_6^+$), 221-224 metastable, 214(58.1%, $N_3P_3F_3C_2H_5^+$), 213(85.5%, $N_3P_3F_3C_3H_4^+$) 212(33.9%, $N_3P_3F_2C_4H_{10}^+$), 197(56.5%, $N_3P_3FC_3H_7^+$), 168(19.4%, $N_3P_3FCH_2^+$), 167 (39.5%, $N_3P_3CH^+$), 149(42.7%, $N_3P_3CH_2^+$)

$N_3P_3F_3(t\text{-}C_4H_9)_3$ (III)

363(87.7%, $N_3P_3F_3C_{12}H_{27}^+$), 348(26.3%, $N_3P_3F_3C_{11}H_{24}^+$), 347(68.4%, $N_3P_3F_3C_{11}H_{23}^+$), 308(77.2%, $N_3P_3F_3C_{18}H_{20}^+$), 367(100%, $N_3P_3F_3C_8H_{19}^+$), 306(61.4%, $N_3P_3F_3C_8H_{18}^+$) 305(45.6%, $N_3P_3F_3C_8H_{17}^+$), 293(63.2%, $N_3P_3F_3C_7H_{17}^+$), 269(61.4%, $N_3P_3FC_8H_{19}^+$), 258-281 - metastable, 252(63.2%, $N_3P_3C_8H_{21}^+$), 251(94.7%, $N_3P_3C_8H_{20}^+$), 250 (61.4%, $N_3P_3C_8H_{19}^+$), 246(50.9%, $N_3P_3F_3C_4H_6^+$), 231(64.9%, $N_3P_3F_2C_4H_{10}^+$), 219(63.2%, $N_3P_3C_6H_{12}^+$), 218(36.8%, $N_3P_3C_6H_{11}^+$), 211(26.3%, $N_3P_3FC_4H_9^+$), 204-208(70%, metastable), 196(28.1%, $N_3P_3FC_3H_6^+$), 195(70.2%, $N_3P_3C_4H_{12}^+$), 194(61.4%, $N_3P_3C_4H_{11}^+$), 193(52.6%, $N_3P_3C_4H_{10}^+$), 181(68.4%, $N_3P_3FC_2H_3^+$)

$N_3P_3F_3(OC_2H_5)(t\text{-}C_4H_9)_2$ (IV)

351(88.3%, $N_3P_3F_3C_{10}H_{23}O^+$), 336(9.9%, $N_3P_3F_3C_9H_{20}O^+$), 331(29.9%, $N_3P_3F_2C_{10}H_{22}O^+$), 325(16.2%, $N_3P_3F_3C_8H_{19}O^+$), 295(42.3%, $N_3P_3F_3C_6H_{15}O^+$), 294(100%, $N_3P_3F_3C_6H_{14}O^+$), 281(28.4%, ?), 269(42.3%, $N_3P_3F_3C_4H_{13}O^+$), 268(58.6%, $N_3P_3F_3C_3H_8O^+$), 267(48.6%, $N_3P_3F_3C_3H_7O^+$), 266(23.4%, $N_3P_3F_3C_3H_6O^+$), 251(29.7%, $N_3P_3F_2C_4H_{14}O^+$), 239(80.2%, $N_3P_3F_2C_3H_{14}O^+$), 213(25.2%, $N_3P_3F_2C_3H_{14}^+$), 212(27.9%, $N_3P_3F_2C_3H_{13}^+$), 211(73.0%, $N_3P_3FC_4H_9^+$), 210(28.1%, $N_3P_3FC_4H_8^+$), 195(43.2%, $N_3P_3FC_3H_5^+$), 169(35.2%, $N_3P_3FCH_3^+$), 131(16.2%, ?)

$N_3P_3F_5(n\text{-}C_4H_9)$ (V)

287(18.9%, $N_3P_3F_5C_4H_9^+$), 272(71.2%, $N_3P_3F_5C_3H_6^+$), 268(22.5%, $N_3P_3F_4C_4H_9^+$), 259(32.4%, $N_3P_3F_5C_2H_5^+$), 258(78.4%, $N_3P_3F_5C_2H_4^+$), 248(11.7%, $N_3P_3F_3C_4H_8^+$), 246(25.2%, ?), 245(100%, $N_3P_3F_5CH_3^+$), 244(12.6%, $N_3P_3F_5CH_2^+$), 243(26.1%, $N_3P_3F_5CH^+$), 238(9.9%, ?), 232(57.7%, $N_3P_3F_5H_2^+$), 231(92.8, $N_3P_3F_5H^+$), 230(81.1%, $N_3P_3F_5^+$), 226(9.0%, $N_3P_3F_4CH_3^+$), 216(36.9%, ?), 212(52.3%, $N_3P_3F_4H^+$), 197(36.9%, ?), 171(30.6%, ?), 167(26.1%, ?), 131(61.2%, ?).

$N_3P_3F_4(n\text{-}C_4H_9)_2$ (VI)

325(42.3%, $N_3P_3F_4C_8H_{18}^+$), 306(7.2%, $N_3P_3F_3C_8H_{18}^+$), 296(78.4%, $N_3P_3F_4C_6H_{13}^+$), 283(58.8%, $N_3P_3F_4C_4H_{10}^+$), 268(70.1%, $N_3P_3F_4C_4H_9^+$), 254(43.3%, $N_3P_3F_4C_3H_7^+$), 250(7.2%, $N_3P_3F_3C_4H_{10}^+$), 241(100%, $N_3P_3F_4C_2H_6^+$), 238(10.3%, $N_3P_3F_4C_2H_3^+$), 227(76.3%, $N_3P_3F_4CH_4^+$), 226(25.8%, $N_3P_3F_4CH_3^+$), 213(12.4%, $N_3P_3F_4H_2^+$), 212(90.7%, $N_3P_3F_4H^+$), 211(19.6%, $N_3P_3F_4^+$), 197(16.5%, $N_3P_3F_2^+$), 167(31.9%, ?), 154(14.4%, $N_3P_3F^+$), 149(17.5%, ?), 141(20.6%, ?).

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1
U. S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

	No. Copies
Dr. T. C. Williams Union Carbide Corporation Chemical and Plastics Tarrytown Technical Center Tarrytown, New York	1
Dr. R. Soulen Contract Research Department Pennwalt Corporation 900 First Avenue King of Prussia, Pennsylvania 19406	1
Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1
Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1
Dr. H. Allcock Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	1
Dr. R. Lenz University of Massachusetts Department of Chemistry Amherst, Massachusetts 01002	1
Dr. M. David Curtis University of Michigan Department of Chemistry Ann Arbor, Michigan 48105	1
Dr. M. Good Division of Engineering Research Louisiana State University Baton Rouge, Louisiana 70803	1
Douglas Aircraft Company 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library C1 290/36-84 AUTO-Sutton	1
NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 49-1	1
Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1
Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	1
Dr. Martin H. Kaufman, Head Materials Research Branch (Code 4542) Naval Weapons Center China Lake, California 93555	1
Dr. J. Magill University of Pittsburg Metallurgical and Materials Engineering Pittsburg, Pennsylvania 22230	1
Dr. D. Bergbreiter Texas A&M University Department of Chemistry College Station, Texas 77843	1
Professor R. Drago Department of Chemistry University of Illinois Urbana, Illinois 61801	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

	No. Copies
Dr. F. Brinkman Chemical Stability & Corrosion Division Department of Commerce National Bureau of Standards Washington, D.C. 20234	1
Professor H. A. Titus Department of Electrical Engineering Naval Postgraduate School Monterey, California 93940	1
COL R. W. Bowles, Code 100M Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217	1
Professor T. Katz Department of Chemistry Columbia University New York, New York 10027	1
Professor James Chien Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1
Professor Malcolm B. Polk Department of Chemistry Atlanta University Atlanta, Georgia 30314	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1
Mr. Keith B. Baucom Director of Contract Research ICM-PCR Incorporated P.O. Box 1466 Gainesville, Florida 32602	1