AD-A062 292 PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY F/G 7/3
THE PARTIAL AMINOLYSIS OF (NPF2)3 OR 4.(U)
DEC 78 T L EVANS, H R ALLCOCK N00014-75-C-0685
UNCLASSIFIED TR-6 NL

1 OF 1
ADA
062292

END
DATE
FILMED
3 -79
DDC

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LEVEL II

(12)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: (14) TR-6
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): (6) THE PARTIAL AMINOLYSIS OF $(NPF_2)_3$ or 4,
5. TYPE OF REPORT & PERIOD COVERED: (9) Interim Technical Report,
6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): (10) Thomas L. Evans and Harry R. Allcock
8. CONTRACT OR GRANT NUMBER(s): (15) N00014-75-C-0685

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
The Pennsylvania State University
University Park, Pa. 16802

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 356-577

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of the Navy
Office of Naval Research
Arlington, Virginia 22217

(11) 1 December 1978
12. REPORT DATE
13. NUMBER OF PAGES
11

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
(12) 13p.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution unlimited; approved for publication

DDC RECEIVED DEC 19 1978 D

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

18. SUPPLEMENTARY NOTES

Submitted for publication in the Journal - Inorganic Chemistry

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

Phosphazenes, aminolysis, partial substitution, non-geminal, reactivities, cyclic compounds, fluorine.

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

Fluorocyclophosphazenes are different from chlorocyclophosphazenes in their reactions with primary or secondary amines. Amines replace only one fluorine per phosphorus because of the poor leaving-group ability of fluorine and the low nucleophilicity of the amines.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE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)

Office of Naval Research

Contract No. N00014-75-C-0685

Project No. NR 356-577

Technical Report No. 6

THE PARTIAL AMINOLYSIS OF $(NPF_2)_{3 \text{ or } 4}$

by

T. L. Evans and H. R. Allcock

Prepared for publication in
Inorganic Chemistry

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

December 1, 1978

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pa. 16802

The Partial Aminolysis of $(NPF_2)_{3 \text{ or } 4}$ [1]

T. L. Evans and H. R. Allcock*

Received

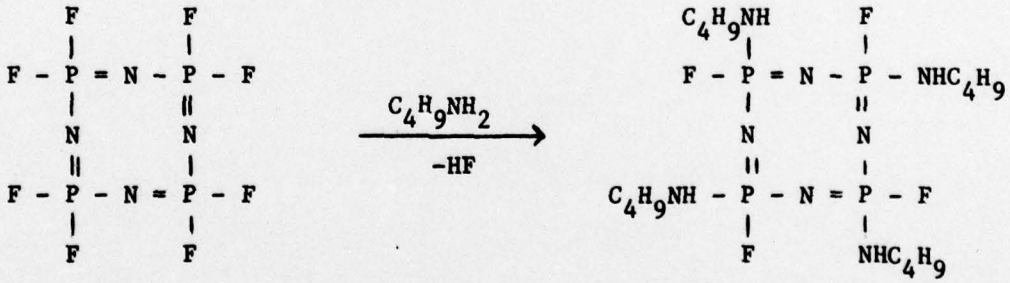
The reactions of cyclic or high polymeric chlorophosphazenes, such as $(NPCl_2)_{3,\ 4,\ \text{or}\ n}$, with primary or secondary amines or with alkoxides or aryloxides have been studied in detail.[2] Under suitable reaction conditions all the chlorine atoms can normally be replaced by amino, alkoxy, or aryloxy residues to yield cyclic or high polymeric phosphazenes of formula, $[NP(NHR)_2]_{3,\ 4,\ \text{or}\ n}$, $[NP(NR_2)_2]_{3,\ 4,\ \text{or}\ n}$, or $[NP(OR)_2]_{3,\ 4,\ \text{or}\ n}$. The only exceptions are reactions that involve highly hindered nucleophiles, such as diethylamine, diphenylamine, or amino-azo dyes, especially in reactions with the high polymer, $(NPCl_2)_n$.[3,4]

Fluorocyclophosphazenes, such as $(NPF_2)_{3 \text{ or } 4}$, closely resemble chlorophosphazenes in their behavior toward alkoxides or aryloxides. For example, $(NPF_2)_4$ reacts readily with CF_3CH_2ONa or C_6H_5ONa to yield $[NP(OCH_2CF_3)_2]_4$ or $[NP(OC_6H_5)_2]_4$ (see Experimental section). However, a survey of the literature revealed a curious absence of reports of fully aminolyzed phosphazene trimers or tetramers derived from $(NPF_2)_{3 \text{ or } 4}$. Compounds such as $N_3P_3F_5NHMe$, $N_3P_3F_3(NMe_2)_3$, $N_4P_4F_7NH_2$, or $N_4P_4F_4(NMe_2)_4$ had been reported,[5-7] but no species containing more than three or four amino residues were described. This was of particular interest to us because of our intention to utilize high molecular

weight poly(difluorophosphazene) as a substrate for the synthesis of mixed substituent poly(aminophosphazenes).

We wish to report here the significant difference that apparently exists between the aminolysis reactions of $(NPF_2)_3$ (I) or $(NPF_2)_4$ (II) and those of the corresponding chlorophosphazenes when these compounds are allowed to interact with an excess of primary or secondary amine. Specifically, I and II react with methylamine, n-butylamine, or dimethylamine with replacement of only one fluorine atom per phosphorus under conditions that lead to total replacement of chlorine in $(NPCl_2)_{3 \text{ or } 4}$. In fact, so far we have been unable to find reaction conditions that lead to the complete aminolysis of fluorocyclophosphazenes.

The reaction conditions and the results of the present work are summarized in Table I and in the Experimental section. A typical example is given by the conversion of II to III in the presence of butylamine.



II III

The reaction products were identified by a combination of vpc-mass spectrometric and ^{31}P nmr data as three different isomers of the non-geminal species III and two non-geminal isomers of $N_4P_4F_5(NHC_4H_9)_3$. Only trace amounts, if any, of

$N_4P_4F_3(NHC_4H_9)_5$ were detected. Similar results were obtained when II reacted with methylamine to yield $N_4P_4F_5(NHMe)_3$ and $[NPF(NHMe)]_4$, or with dimethylamine to yield $N_4P_4F_5(NMe_2)_3$ and $[NPF(NMe_2)]_4$. By contrast, $(NPCl_2)_4$ reacted with n-butylamine, methylamine, or dimethylamine under similar reaction conditions to yield $[NP(NHC_4H_9)_2]_4$, $[NP(NHMe)_2]_4$, or $[NP(NMe_2)_2]_4$. A similar reaction pattern was followed when the cyclic trimer, $(NPF_2)_3$, interacted with methylamine, n-butylamine, or dimethylamine to yield $N_3P_3F_4(NHMe)_2$, $N_3P_3F_4(NHC_4H_9)_2$, or $N_3P_3F_4(NMe_2)_2$ plus only traces of the tri-amino derivatives under reaction conditions that lead to complete aminolysis of $(NPCl_2)_3$.

These differences cannot be ascribed to a simple steric resistance to the second substitution at each phosphorus, even after taking into account the relative shortness of a phosphorus-fluorine bond. Lithium dimethylamide, $LiNMe_2$, reacted with II to give $N_4P_4F_2(NMe_2)_6$, $N_4P_4F(NMe_2)_7$, and a trace of $[NP(NMe_2)_2]_4$. A similar reaction of $LiNMe_2$ with I yielded mainly $[NPF(NMe_2)]_3$ and $N_3P_3F_2(NMe_2)_4$. A reaction between $LiNMe_2$ and $(NPCl_2)_3$ gave $[NP(NMe_2)_2]_3$. Lithium dimethylamide is clearly more reactive toward I and II than is dimethylamine in spite of the similarity in the expected steric hindrance effects. It should also be noted that the aminolysis results cannot be ascribed to the precipitation of partially aminolyzed fluorophosphazenes from the reaction medium. In all these cases the phosphazenes remained in solution until the end of the reaction.

One other mechanistic explanation for the partial aminolysis behavior seems to be unacceptable. In theory, it is possible that the aminolysis reactions of I and II are equilibrium-controlled and that amino groups can be displaced by the hydrogen fluoride formed in the earlier stages of the reaction. Two items of evidence are incompatible with this viewpoint. First, the insolubility of the amine hydrofluorides in the reaction medium would make such a displacement

reaction unlikely. Second, reactions between II and n-butylamine carried out in the presence of lithium bromide gave products that were virtually identical to those formed in the absence of this latter reagent. In such a system, any free fluoride would be expected to be removed from solution in the form of insoluble lithium fluoride.

The results appear to be more compatible with an explanation based on the relative reactivities of $(NPF_2)_3$ and $_4$ and $(NPCl_2)_3$ and $_4$ and on the relative nucleophilicities of the reagents employed. Electron-supply from one amino residue attached to phosphorus probably deactivates the second phosphorus -fluorine bond at that site. The combined influences of the low nucleophilicity of a free amine and the poor leaving group ability of the fluoride ion would exaggerate this effect. In these terms, the higher reactivities of sodium trifluoroethoxide, sodium phenoxide, and lithium dimethylamide can be attributed to their higher nucleophilicities. The deactivating effect appears to be slightly more pronounced with $(NPF_2)_3$ than with $(NPF_2)_4$.

Experimental Section

Materials and Equipment. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (donated by the Firestone Tire and Rubber Company) was purified by sublimation, followed by two recrystallizations from n-heptane. Octachlorocyclotetraphosphazene, $(NPCl_2)_4$, was obtained from the sublimation residues of the trimer purification. It was purified by resublimation and recrystallization from heptane. Conversion of $(NPCl_2)_3$ and $(NPCl_2)_4$ to $(NPF_2)_3$ and $(NPF_2)_4$ was accomplished by treatment with sodium fluoride in acetonitrile or nitrobenzene,[8] followed by fractional distillation. The reaction solvents and amines were dried before use by distillation from calcium hydride. Reagent grade tetrahydrofuran (THF) and diethyl ether were also distilled from lithium aluminum hydride.

The mass spectrometric analyses were obtained with the use of an AEI, M.S. 902 mass spectrometer instrument. ^{31}P Nmr spectra were obtained by means of a JEOL nmr spectrometer instrument operated at 40 MHz in the FT mode with 32 scans being employed for a typical spectrum. Chemical shifts are reported relative to 85% phosphoric acid in water.[9]

Reaction of $(NPF_2)_4$ with Sodium Trifluoroethoxide. A sample of $(NPF_2)_4$ (2.0 g, 0.006 mol) in THF (10 ml) was added to a solution of sodium trifluoroethoxide (prepared from 5.52 g (0.24 mol) of sodium and 31.2 g (0.312 mol) of trifluoroethanol in 150 ml THF) and the reaction mixture was boiled at reflux for 48 hr.. The reaction mixture was concentrated to 25 ml on a rotary evaporator and was added to a dilute aqueous hydrochloric acid solution. The solid was then collected by filtration and was recrystallized from a THF-pentane mixture (70:30 ratio). The mass spectral data were consistent with the presence of $[NP(OCH_2CF_3)_2]_4$, M/e= 972. A ^{31}P nmr spectrum yielded a singlet at -0.96 ppm. The total yield was 60% (mp = 63°C).

Reaction of $(NPF_2)_4$ with Sodium Phenoxide. A sample of $(NPF_2)_4$ (2.0 g, 0.006 ml) in 10 ml of THF was added to a solution of sodium phenoxide (prepared from 11.04 g (0.48 mol) sodium and 58.7 g (0.62 mol) of phenol in 150 ml of THF), and the reaction mixture was boiled at reflux for 48 hr.. The reaction mixture was evaporated to dryness and 50 ml of diethyl ether were added. The diethyl ether phase was filtered and was then washed consecutively with dilute HCl, Na_2CO_3, and neutral water. The product was then collected by cooling the diethyl ether solution to 0°C. Mass spectral analysis yielded the parent ion at M/e = 924. ^{31}P nmr data were consistent with the presence of $[NP(OC_6H_5)_2]_4$, with a singlet at -12.88 (THF as solvent). The total yield of this product was 52% (mp = 86°C).

Reactions of $(NPF_2)_4$ and $(NPCl_2)_4$ with n-Butylamine. In each of three addition funnels was placed a solution of $(NPF_2)_4$ (1.0 g, 0.003 mol) in dry THF (20 ml). Each solution was then added dropwise to reaction vessels that contained n-butylamine (10.4 g, 0.144 mol) in THF (100 ml). The first mixture was boiled at reflux for 12 hr, the second was allowed to react at 25°C for 12 hr, and the third was maintained at 25°C for 336 hr. Each reaction mixture was then evaporated to dryness and the solid residue was dissolved in diethyl ether, and this solution was extracted several times with water to remove salts. Removal of the ether yielded products or mixtures of products that were analyzed by gas-liquid chromatography, mass spectrometry, and ^{31}P nmr analysis. The products were as follows: Reaction 1, $N_4P_4F_4(NHC_4H_9)_4$; Reaction 2, $N_4P_4F_4(NHC_4H_9)_4$ and $N_4P_4F_5(NHC_4H_9)_3$ in a 1:5 ratio; Reaction 3, $N_4P_4F_4(NHC_4H_9)_4$. The ^{31}P nmr spectra were compatible with a non-geminal substitution pattern. The experimental details for this and other amination reactions are summarized in Table I. Only the isolation procedures are described in detail in the following sections.

Similar reactions were carried out between $(NPCl_2)_4$ and n-butylamine in THF or diethyl ether for 12 hr or 14 hr at 25°C. The product from both reactions was the fully-substituted tetramer, $[NP(NHC_4H_9)_2]_4$ (80% yield from THF, 90% from diethyl ether). It was purified by recrystallization from heptane and was characterized by ^{31}P nmr and mass spectral analysis (mp = 87°C).

Reaction of $(NPF_2)_4$ with n-Butylamine in the Presence of NEt_3 and LiBr. The reaction conditions are shown in Table I. After the reactions, the mixtures were evaporated to dryness, re-dissolved in diethyl ether and extracted several times with water. The diethyl ether phases were evaporated to dryness and the

yellow oils were analyzed by mass spectrometry. Both oils showed the presence of the parent ions for $N_4P_4F_4(NH^nBu)_4$ (M/e = 544) and $N_4P_4F_5(NH^nBu)_3$ (M/e = 491).

The Reactions of $(NPF_2)_4$ with Methylamine and Dimethylamine. The reaction conditions were as shown in Table I. Both reaction mixtures were evaporated to dryness, redissolved in diethyl ether, and extracted several times with water. The diethyl ether solutions were then evaporated to dryness and were subjected to mass spectrometric study. Parent ions were detected for $N_4P_4F_5(NHMe)_3$ (M/e = 365) and $N_4P_4F_4(NHMe)_4$ (M/e = 376) for the reaction with methylamine. and $N_4P_4F_5(NMe_2)_3$ (M/e = 407) and $N_4P_4F_4(NMe_2)_4$ (M/e = 432) for the reaction with dimethylamine. The ^{31}P nmr spectra of both samples (in THF with D_2O capillary lock) further supported the absence of any geminal amino substitution. (Complex doublet and triplet structures only were seen). ^{19}F nmr spectra confirmed the presence of PF_2 units [center of doublet = 35.5 ppm (relative to an external C_6H_5F reference); coupling constant = 894 hz]. The centers of the doublets for the PF(NRA') units were, on the average, 9 ppm further downfield.

Reaction of $(NPCl_2)_4$ with Methylamine and Dimethylamine. The reaction conditions are listed in Table I. The reaction mixtures were added to water and, in the case of the reaction with dimethylamine, the precipitated product was collected. The methylamino-substituted product was obtained by extraction of the aqueous phase with warm $CHCl_3$. Mass spectrometric evidence obtained for the parent ions $N_4P_4(NHMe)_8$ (M/e = 420) and $N_4P_4(NMe_2)_8$ (M/e = 532). No products that contained unreacted chlorine were detected. Isolation of these products gave crystals, mp 206°C ($N_4P_4(NHMe)_8$), and 230°C ($N_4P_4(NMe_2)_8$).

Reactions of $(NPF_2)_3$ and $(NPCl_2)_3$ with Lithium Dimethylamide. A solution of $(NPF_2)_3$ (1.0 g, 0.004 mol) in THF (20 ml) was added dropwise to a solution of $LiNMe_2$ [prepared from methyllithium (0.16 mol) and dimethylamine (7.9 g, 0.18 mol)] in THF (100 ml). The reaction mixture was stirred at 25°C for 12 hr before the products were treated with isopropanol. Removal of the solvent, solution in diethyl ether, extraction of the salts by water, and removal of the ether by evaporation left a white solid. Mass spectral analysis indicated that the main product was non-gem $N_3P_3F_3(NMe_2)_3$, but $N_3P_3F_2(NMe_2)_4$ was also present. A similar reaction with $(NPCl_2)_3$ yielded $[NP(NMe_2)_2]_3$.

Reaction of $(NPF_2)_4$ with Lithium Dimethylamide. A solution of $(NPF_2)_4$ (2.0 g, 0.006 mol) in THF (20 ml) was added dropwise to a solution of $LiNMe_2$ [prepared at 0°C from methyllithium (0.054 mol) and dimethylamine (10 g, 0.22 mol) in THF (100 ml)]. The reaction mixture was stirred at 25°C for 12 hr before the product was treated with isopropanol. The reaction mixture was evaporated to dryness, washed with water, filtered, and the filtrate was dried, redissolved in THF, filtered, and the solution was evaporated to dryness. The pale yellow solid product yielded mass spectral parent ions for $N_4P_4(NMe_2)_6F_2$ (M/e = 482); $N_4P_4(NMe_2)_7F$ (M/e = 507) and trace amounts of $N_4P_4(NMe_2)_8$ (M/e = 532).

Reactions of $(NPF_2)_3$ with Methylamine, n-Butylamine, and Dimethylamine. The reaction conditions are shown in Table I. All three reaction mixtures were evaporated to dryness, redissolved in diethyl ether, and extracted several times with water. The diethyl ether solutions were then evaporated to dryness and the

resultant oils were subjected to vapor phase chromatography-mass spectrometric study. Parent ions were detected for $N_3P_3F_4(NHMe)_2$ with $N_3P_3F_4(NH^nBu)_2$ and $N_3P_3F_4(NMe_2)_2$. Only trace amounts of the tris amino derivatives could be detected. The absence of geminal amino structures was confirmed by ^{31}P nmr spectra which indicated only complex doublet and triplet signals from P-F or PF_2 coupling.

Nmr Spectra of Reaction Mixtures. Although only partly aminolyzed cyclophosphazenes were isolated from the reactions of $(NPF_2)_{3 \text{ or } 4}$ with amines, the possibility existed that this was an artifact due to the preferential extraction of the more highly substituted species or their hydrofluoride salts during the washing of the mixture with water. For this reason, ^{31}P nmr spectra were obtained of the crude reaction mixtures from the interaction of $(NPF_2)_{3 \text{ or } 4}$ with methylamine or butylamine before any isolation or purification of products was attempted. These ^{31}P nmr spectra showed mixtures of partly aminolyzed species that were identical to those obtained after isolation and purification of the products. It was estimated that the analytical methods employed (^{31}P nmr and mass spectrometry) could easily have detected higher-substituted species if they had represented only 10% of the total products.

Acknowledgments. We thank the Office of Naval Research for the support of this work through grant N00014-75-C-0685. We also thank A. Freyer for recording the nmr spectra and R. Minard for the mass spectrometric data.

References and Notes

(1) For previous paper in this series see H. R. Allcock, P. P. Greigger, J. E. Gardner, and J. L. Schmutz, J. Am. Chem. Soc. (in press).

(2) For a review of this topic see H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, New York, 1972.

(3) H. R. Allcock, W. J. Cook, and D. P. Mack, Inorg. Chem., 11, 2584 (1972).

(4) H. R. Allcock, S. D. Wright, and K. M. Kosydar, Macromolecules, 11, 357 (1978).

(5) T. Moeller and S. G. Kokalis, J. Inorg. Nucl. Chem., 25, 1397 (1963).

(6) O. Clemson, E. Niecke, and H. Thamm. Z. Naturforsch., 25B, 754 (1970).

(7) T. Chivers, O. T. Oakley, and N. L. Paddock, J. Chem. Soc. (A), 2326 (1970).

(8) R. Schmutzler, Inorg. Syntheses, 9, 75 (1967).

(9) The ^{31}P nmr shifts reported here are based on the sign convention recently recommended by I.U.P.A.C.. Upfield shifts from H_3PO_3 are reported as negative values and downfield shifts as positive values. This convention is the opposite of the one used in earlier publications from our laboratory and from most other laboratories in North America.

Table I Reaction Conditions for Halophosphazene Aminolysis Reactions[a]

Phosphazene	Grams Phosphazene (mol)	Solvent for Phosphazene (mL)	Amine	Grams Amine (mol)	Solvent for Amine (mL)	Temp. (°C)	Time (hr)
$(NPF_2)_4$	1.0 (0.003)	THF (20)	$C_4H_9NH_2$	10.4 (0.144)	THF (100)	reflux	12
$(NPF_2)_4$	1.0 (0.003)	THF (20)	$C_4H_9NH_2$	10.4 (0.144)	THF (100)	25	12
$(NPF_2)_4$	1.0 (0.003)	THF (20)	$C_4H_9NH_2$	10.4 (0.144)	THF (100)	"	336
$(NPF_2)_4$	2.0 (0.006)	THF (20)	$C_4H_9NH_2$	35.1 (0.48)	Et_2O (200)	"	14
$(NPCl_2)_4$	2.0 (0.0043)	THF (10)	$C_4H_9NH_2$	25.6 (0.35)	THF (100)	"	12
$(NPF_2)_4$	1.0 (0.003)	THF (10)	$C_4H_9NH_2$	10.4 (0.144)	THF (100)	"	24
			LiBr	2.2 (0.025)			
$(NPF_2)_4$	1.0 (0.003)	THF (10)	$C_4H_9NH_2$	10.4 (0.144)	THF (100)	"	24
			$(C_2H_5)_3N$	2.53 (0.025)			
$(NPF_2)_4$	1.0 (0.003)	THF (10)	CH_3NH_2	7.47 (0.24)	THF (100)	"	24[b]
$(NPF_2)_4$	1.0 (0.003)	THF (10)	$(CH_3)_2NH$	12.0 (0.27)	THF (100)	"	24[b]
$(NPCl_2)_4$	2.0 (0.0043)	THF (10)	CH_3NH_2	10.0 (0.32)	THF (100)	"	12[b]
$(NPCl_2)_4$	2.0 (0.0043)	THF (10)	$(CH_3)_2NH$	15.0 (0.33)	THF (100)	"	12[b]
$(NPF_2)_3$	1.0 (0.004)	THF (20)	CH_3NH_2	5.27 (0.17)	THF (100)	"	24[b]
"	1.0 (0.004)	THF (20)	$(CH_3)_2NH$	7.70 (0.17)	THF (100)	"	24[b]
"	1.0 (0.004)	THF (20)	$C_4H_9NH_2$	12.40 (0.17)	THF (100)	"	24

[a] All reactions were carried out by the dropwise addition of the solution of the halophosphazene to a stirred solution of the amine.

[b] The volatile amines were condensed into each reaction mixture by means of a Dry Ice condenser, and the solutions of the amines in THF were cooled to 0°C until the halophosphazene addition was complete. At that point, the mixtures were allowed to warm to 25°C.