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The Reactions of Trimethyloxonium Fluoroborate with Alkylamino- and Phenyl-Substituted Cyclotriphosphonitriles[1]

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The reactions of mono-, bis-, tris-, tetrakis-, and hexakisdimethylamino-substituted chlorocyclotriphosphonitriles as well as tetrakisisopropylaminodichlorocyclotriphosphonitrile and its bisdimethylamino derivative with the alkylating agent trimethyloxonium fluoroborate are described. The compounds have been characterized by microanalysis and conductivity. The position of alkylation has been studied by hydrolytic degradation of the resulting cyclotriphosphonitrile salts and by ^1H nmr whenever possible. The factors affecting the position of alkylation are discussed. The alkylated hexaphenylcyclotriphosphonitrile has been prepared and the ultraviolet spectra of the parent and alkylated compounds are discussed.

Introduction

The ability of certain cyclotriphosphonitriles, $N_3P_3Y_6$ (Y = –Cl, $-CH_3$, alkylamino), to function as Lewis bases to form adducts and salts has been established;[2] however, only a few studies have been performed on these compounds to elucidate their structures.[2d,e] The amino-substituted cyclotriphosphonitriles have two possible basic sites, the exocyclic nitrogen and the ring nitrogen. Shaw, *et al.*,[3] have studied the pK_a's of mono- and diprotonation equilibria in nitrobenzene of a number of amino-substituted cyclotriphosphonitriles and offered arguments based on ΔpK_a for protonation of the ring nitrogen rather than the exocyclic nitrogen. Ring protonation has been confirmed in one instance by the crystal structure[4] of $N_3P_3Cl_2(NH\text{-}i\text{-}C_3H_7)_4 \cdot HCl$. We[5] have reported the synthesis of $\{N_3P_3[N(CH_3)_2]_6CH_3\}^+BF_4^-$ and $\{(N_3P_3(N(CH_3)_2)_6(CH_3)_2\}^{2+}(BF_4^-)_2$ by alkylation of the alkyl aminophosphonitrile by $(CH_3)_3O^+BF_4^-$. A structural characterization by hydrolysis indicates that alkylation occurs on the exocyclic nitrogen.

We report herein the generalization of this alkylation reaction to other alkylaminochloro, mixed alkylamino, and aryl derivatives of phosphonitriles, and the position of their alkylation. Also the ultraviolet spectra of hexaphenylphosphonitrile and its alkylated derivative have been measured.

Experimental Section

Analyses.—Elemental analyses were performed by Galbraith Laboratories, Inc., Weiler and Strauss Microanalytical Laboratory, Oxford, England, and Schwarzkopf Microanalytical Laboratory.

Spectra.—The ^1H nmr spectra were obtained on Varian A-60 and HA-100[6] spectrometers at ambient temperature. Ultraviolet spectra were obtained on a Bausch and Lomb Spectronic 505 using 1.0-cm cells. Eastman Spectro-Grade acetonitrile was employed as the uv solvent.

Conductivities.—Conductivities were determined in a constant-temperature bath at 25° with an Industrial Instruments Co. Model RC 16B2 conductance bridge at 1000 cps. The nitrobenzene employed was dried and distilled from P_2O_5.

Hydrolyses.—Whenever the ^1H nmr spectrum did not allow unambiguous structural assignment, a weighed sample of the cyclotriphosphonitrile salt was hydrolyzed in 12 *M* HCl at 100° (5–7 days) in an evacuated glass bomb tube. The hydrolyzed sample was transferred to a Kjeldahl nitrogen apparatus and base was added; the ammonia and amines were distilled into an HCl solution. The distillate was evaporated to dryness, the residue taken up in anhydrous trifluoroacetic acid, the insoluble NH_4Cl filtered off, and the ^1H nmr spectrum of the filtrate examined, following the method of Anderson and Silverstein,[7] in order to ascertain the presence or absence of CH_3NH_3Cl. After running the spectrum of the amine hydrochloride mixture in TFA, the TFA was removed and the spectrum of the mixture was taken in $CHCl_3$, in order to obtain better integration of the signals. The experimental spectra of the amine hydrochloride mixtures were analogous to those of a prepared mixture of $(CH_3)_2NH_2Cl$ and $(CH_3)_3NHCl$ or of other amine hydrochlorides under investigation. The HCl used in this procedure was distilled to remove paramagnetic materials, which cause line broadening in the nmr.

Materials.—Hexachlorocyclotriphosphonitrile was purchased from Millmaster Chemical Co. and purified by vacuum distillation until it gave a melting point in agreement with the literature value. The dimethylamino-substituted phosphonitriles were prepared by the method of Keat and Shaw.[8] These compounds were identified and their purity determined by comparison with literature melting points and by ^1H nmr. Hexaphenylcyclotriphosphonitrile was prepared by the method of Paciorek and Kratzer.[9] The diphenylchlorophosphine used in this procedure was obtained from K & K, and the LiN_3 used was prepared by the method of Hofman-Bang.[10] *gem*-Tetrakisisopropylaminodichlorocyclotriphosphonitrile and *gem*-bisdimethylaminotetrakisisopropylaminocyclotriphosphonitrile were prepared, purified, and identified by the method of Keat and Shaw.[11] Trimethyloxonium fluoroborate was prepared by a modification of the method of Meerwein, *et al.*[12a,b]

(1) Presented before the Inorganic Division at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

(2) (a) S. K. Ray and R. A. Shaw, *Chem. Ind.* (London), 1173 (1961); (b) D. Feakins, N. A. Last, and R. A. Shaw, *ibid.*, 510 (1962); (c) S. K. Das, *et al.*, *ibid.*, 866 (1963); (d) G. Allen, J. Dyson, and N. L. Paddock, *ibid.*, 1832 (1964); (e) T. Moeller and S. G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 875 (1963); (f) M. F. Lappert and G. Srivastava, *J. Chem. Soc., A*, 210 (1966).

(3) (a) D. Feakins, N. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 4464 (1964); (b) D. Feakins, N. A. Last, N. Neemuchwala, and R. A. Shaw, *ibid.*, 2804 (1965); (c) D. Feakins, N. A. Last, S. N. Nabi, and R. A. Shaw, *ibid.*, *A*, 1831 (1966).

(4) N. V. Mani and A. J. Wagner, *Chem. Commun.*, 658 (1968).

(5) J. N. Rapko and G. R. Feistel, *ibid.*, 474 (1968).

(6) The HA-100 was purchased with funds made available through NSF Grant No. GP 8510 and is gratefully acknowledged.

(7) W. R. Anderson and R. M. Silverstein, *Anal. Chem.*, **37**, 1417 (1965).

(8) R. Keat and R. A. Shaw, *J. Chem. Soc.*, 2215 (1965).

(9) K. L. Paciorek and R. Kratzer, *Inorg. Chem.*, **3**, 594 (1964).

(10) N. Hofman-Bang, *Acta Chem. Scand.*, **11**, 581 (1957).

(11) R. Keat, R. A. Shaw, and B. G. Smith, *J. Chem. Soc., A*, 1677 (1966).

(12) (a) H. Meerwein, *et al.*, *Chem. Ber.*, **89**, 2071 (1956). (b) The modification is due to T. Curphey of this department, and he has submitted it to *Organic Syntheses*.

Syntheses.—In general, manipulations involving the oxonium salt were performed in a dry-air box. Melting points are uncorrected. The phosphonitrile salts may be handled in the atmosphere unless otherwise stated.

2-Trimethylammonium-4-dimethylamino-2,4,6,6-tetrachlorocyclotriphosphonitrile Fluoroborate (I).—An excess of *trans*-2,4-bisdimethylamino-2,4,6,6-tetrachlorocyclotriphosphonitrile (1.0 g, 2.7 mmol) was mixed with 0.3 g (2.2 mmol) of $(CH_3)_3O^+BF_4^-$ in a test tube. The mixture was melted in an oil bath at 120° under a N_2 atmosphere until the reaction subsided (~15 min). The mixture was cooled and the solid extracted with 10 ml of CH_2Cl_2 and gravity filtered through a coarse glass frit to remove any solid. The CH_2Cl_2 was removed by evaporation and 25 ml of $(C_2H_5)_2O$ was added to extract the starting phosphonitrile. The product, 0.5 g (70%), was collected by suction filtration through a fine glass frit in a drybox. Purification of the product was achieved by dissolving in CH_2Cl_2 and adding $(C_2H_5)_2O$ to precipitate the product. The compound begins to melt at 120° with decomposition. *Anal.* Calcd for $C_5H_{15}BCl_4F_4N_5P_3$: C, 12.87; H, 3.24; N, 15.00. Found: C, 13.97; H, 3.65; N, 14.29.

2-Trimethylammonium-4,6-bisdimethylamino-2,4,6-trichlorocyclotriphosphonitrile Fluoroborate (II).—An excess of 2-*trans*-4,6-trisdimethylamino-2,4,6-trichlorocyclotriphosphonitrile (0.90 g, 2.4 mmol) was mixed with 0.3 g (2.0 mmol) of $(CH_3)_3O^+BF_4^-$. The reaction conditions and work up procedures are the same as for compound I. The product, 0.30 g (54%), appeared to melt at 114–117° and melted completely at 139° with decomposition. *Anal.* Calcd for $C_7H_{21}BCl_3F_4N_6P_3$: C, 17.69; H, 4.45; N, 17.68; P, 19.55. Found: C, 17.90; H, 4.31; N, 17.40; P, 19.78.

6-Trimethylammonium-2,4,6-trisdimethylamino-2,4-dichlorocyclotriphosphonitrile Fluoroborate (III).—A 1:1 mole ratio of 2-*cis*-4,6,6-tetrakisdimethylamino-2,4-dichlorocyclotriphosphonitrile (2.3 g, 6.0 mmol) and $(CH_3)_3O^+BF_4^-$ (0.9 g, 6.0 mmol) were mixed in sufficient CH_3NO_2 to dissolve the reactants. After standing overnight, the CH_3NO_2 was removed on a rotary evaporator and the resulting oil treated with $(C_2H_5)_2O$ to affect solidification. Upon solidification, the $(C_2H_5)_2O$ was removed by filtration. Recrystallization of the solid from dioxane gave white flakes, mp 167–168° dec, yield 65%. The compound is soluble in $CHCl_3$, CH_2Cl_2, and polar organic solvents. *Anal.* Calcd for $C_9H_{27}BCl_2F_4N_7P_3$: C, 22.32; H, 5.62; N, 20.25; P, 19.20. Found: C, 22.90; H, 5.62; N, 20.80; P, 19.09.

Trimethylammoniumpentakisdimethylaminocyclotriphosphonitrile Fluoroborate (IV).—This compound was prepared in a manner similar to compound III, using a 1:1 mole ratio of hexakisdimethylaminocyclotriphosphonitrile (1.0 g, 2.5 mmol) and $(CH_3)_3O^+BF^-$ (0.4 g, 2.5 mmol) but with dropwise addition of the oxonium salt from a dropping funnel. The compound was recrystallized from anhydrous THF and gave a 64% yield. It started melting at 181° and decomposed at 200°. It is soluble in $CHCl_3$, CH_2Cl_2, and polar organic solvents. Small amounts of compound V, which is insoluble in THF, were isolated from this reaction. *Anal.* Calcd for $C_{13}H_{39}BF_4N_9P_3$: C, 31.15; H, 7.84; N, 25.14; P, 18.54. Found: C, 31.16; H, 7.71; N, 24.85; P, 17.90.

Bistrimethylammoniumtetrakisdimethylaminocyclotriphosphonitrile Difluoroborate (V).—Hexakisdimethylaminocyclotriphosphonitrile (1.0 g, 2.5 mmol) was dissolved in 25 ml of CH_3NO_2 and 0.74 g (5.0 mmol) of $(CH_3)_3O^+BF^-$ was added. The mixture was stirred to dissolve the oxonium salt, stoppered, and allowed to stand overnight. Removal of the solvent on a rotary evaporator yielded an oily residue which solidified upon treatment with $(C_2H_5)_2O$. Upon solidification, the $(C_2H_5)_2O$ was removed by filtration and the solid recrystallized from anhydrous CH_3OH giving 0.9 g (60%) of a white, powdery solid, mp 207–209° dec The compound is soluble in CH_3CN, $(CH_3)_2CO$, DMF, and DMSO and insoluble in less polar solvents. *Anal.* Calcd for $C_{14}H_{42}B_2F_8N_9P_3$: C, 27.88; H, 7.02; N, 20.90; P, 15.41. Found: C, 27.72; H, 7.25; N, 20.94; P, 14.90.

2,2-Bisdimethylamino-4,4,6,6-tetrakisisopropylamino-5-N-methylcyclotriphosphonitrilium Fluoroborate (VI).—2,2-Bisdimethylamino-4,4,6,6-tetrakisisopropylaminocyclotriphosphonitrile (1.5 g, 3.2 mmol) was dissolved in 10 ml of CH_3NO_2. A solution of $(CH_3)_3O^+BF_4^-$ (0.50 g, 3.2 mmol) in 20 ml of CH_3NO_2 was added dropwise over 45 min. After stirring overnight, the solvent was evaporated and the resulting oil was treated with $(C_2H_5)_2O$ to give a white solid. After filtering more solid could be obtained from the $(C_2H_5)_2O$ filtrate. The ^1H nmr indicated the crude product was rather pure. However further purification could be obtained by dissolving the product in a minimum amount of hot chlorobenzene and adding an equal volume of $(C_2H_5)_2O$ to the cooled solution; yield 51%, mp 178–180.5°. *Anal.* Calcd for $C_{17}H_{47}N_9P_3BF_4$: C, 36.64; H, 8.50; N, 22.62. Found: C, 36.70; H, 8.42; N, 22.49.

2-Trimethylammonium-2-dimethylamino-4,4,6,6-tetrakisisopropylamino-5-N-methylcyclotriphosphonitrilium Difluoroborate (VII).—2,2-Bisdimethylamino-4,4,6,6-tetrakisisopropylaminocyclotriphosphonitrile (0.50 g, 1.1 mmol) and $(CH_3)_3O^+BF_4^-$ (0.33 g, 2.2 mmol) were stirred in 10 ml of CH_3NO_2 overnight. After removal of the solvent and addition of 25 ml of $(C_2H_5)_2O$ a white solid formed. It was filtered and recrystallized three times from anhydrous ethanol. The yield was 62.5% and the compound melted with decomposition at 211–213°. It is soluble in acetone, acetonitrile, and nitrobenzene and insoluble in tetrahydrofuran and ethyl acetate. *Anal.* Calcd for $C_{18}H_{50}N_9P_3B_2F_8$: C, 32.80; H, 7.65; N, 19.12. Found: C, 32.47; H, 7.65; N, 19.45.

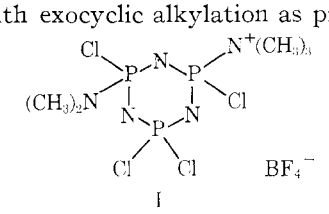
4,4,6,6-Tetrakisisopropylamino-2,2-dichloro-5-N-methylcyclotriphosphonitrilium Fluoroborate (VIII).—4,4,6,6-Tetrakisisopropylamino-2,2-dichlorocyclotriphosphonitrile (3.0 g, 6.9 mmol) was dissolved in 20 ml of CH_3NO_2. $(CH_3)_3O^+BF_4^-$ (1.0 g, 6.9 mmol) was added. After 30 min large crystals formed. The mixture was left standing 4 hr, after which filtration yielded the product. Additional product could be obtained by evaporation of the filtrate. The overall yield was 62%. The compound can be recrystallized from chlorobenzene (mp 205–208°). *Anal.* Calcd for $C_{18}H_{35}BCl_2F_4N_7P_3$: C, 28.91; H, 6.53; N, 18.15. Found: C, 29.10; H, 6.62; N, 18.02.

Hexaphenyl-N-methylcyclotriphosphonitrilium Fluoroborate (IX).—The compound was prepared and purified in the same manner as compound III using hexaphenylcyclotriphosphonitrile (1.0 g, 1.6 mmol) and $(CH_3)_3O^+BF_4^-$, (0.25 g, 1.6 mmol). The analytical sample was recrystallized from chlorobenzene; yield 57%, mp 220–222°. *Anal.* Calcd for $C_{37}H_{33}BF_4N_3P_3$: C, 63.54; H, 4.76; N, 6.02; P, 13.28. Found: C, 63.81; H, 5.02; N, 6.02; P, 13.78.

Results

Dimethylamino Derivatives.—The bis-, tris-, tetrakis-, and hexakisdimethylamino derivatives of $N_3P_3Cl_6$ have been monoalkylated using $(CH_3)_3O^+BF_4^-$. The hexakis derivative has also been dialkylated.

The 60 MHz ^1H nmr spectrum of compound I is shown in Figure 1. The low-field doublet at δ 3.45 is in the ratio of 3:2 to the pattern centered at δ 2.80. The high-field pattern is a typical virtually coupled pattern that often occurs in phosphonitriles. The nmr is thus consistent with exocyclic alkylation as pictured below.



I

It is not possible to tell by nmr whether the compound is *cis* or *trans;* however, presumably it is *trans* since the starting material is *trans*.

The ^1H nmr of compound II is similar to that of I and indicates exocyclic alkylation except that II is a

mixture of isomers which could not be separated. These isomers can result from either the alkylation of *cis* dimethylamino groups or the *trans* dimethylamino group in 2-*trans*-4,6-trisdimethylamino-2,4,6-trichlorocyclotriphosphonitrile.

The ^1H nmr spectra of compounds III, IV, and V are complicated as a consequence of overlapping bands and unresolved peaks. Hydrolysis in these cases and I and II shows that alkylation occurs exocyclically at the dimethylamino nitrogen. The hydrolysis data are summarized in Table I.

TABLE I
HYDROLYSIS DATA FOR VARIOUS ALKYLATED AMINO-SUBSTITUTED CYCLOTRIPHOSPHONITRILES

Compound	Mol ratio[a] $(CH_3)_2NH_2Cl$/ $(CH_3)_3NHCl$ Calcd	Found	Mol ratio i-$C_3H_7NH_3Cl$/ CH_3NH_3Cl Calcd	Found
$[N_3P_3Cl_4(N(CH_3)_2)(N(CH_3)_3)]^+$	1.0/1.0	0.96/1.0	...	...
$[N_3P_3Cl_3(N(CH_3)_2)_2(N(CH_3)_3)]^+$	2.0/1.0	2.1/1.0	...	...
$[N_3P_3Cl_2(N(CH_3)_2)_3(N(CH_3)_3)]^+$	3.0/1.0	3.1/1.0	...	...
$[N_3P_3(N(CH_3)_2)_5(N(CH_3)_3)]^+$	5.0/1.0	5.2/1.0	...	...
$[N_3P_3(N(CH_3)_4(N(CH_3)_3)_2]^{2+}$	2.0/1.0	2.3/1.0	...	...
$[H_3C{-}N_3P_3Cl_2(NH\text{-}i\text{-}C_3H_7)_4]^+$	...	...	8.0/1.0	7.8/1.0
$[H_3C{-}N_3P_3(N(CH_3)_2)(N(CH_3)_3)(NH\text{-}i\text{-}C_3H_7)_4]^{2+}$[b]				

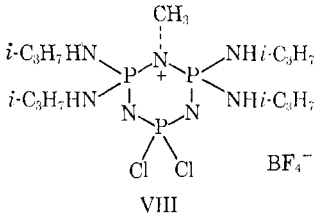
[a] Determination by integration of nmr spectrum. [b] Integration complicated by signal overlap. Indicates presence of CH_3NH_3Cl, $(CH_3)_2NH_2Cl$, $(CH_3)_3NHCl$, and i-$C_3H_7NH_3Cl$.

Alkylation of dimethylaminopentachlorocyclotriphosphonitrile was attempted by the melt method used in the preparation of I. These are very potent alkylating conditions. The ^1H nmr spectrum of the crude reaction mixture dissolved in chloroform is shown in Figure 2. The low-field doublet at δ 3.50 is characteristic of the $(CH_3)_3N^+$ group by comparison with I and II. The other peaks in the spectrum belong to starting material and the by-product $(CH_3)_2O$. Attempts to isolate the alkylated product have been unsuccessful to date. Thus, although the evidence is not complete it appears that the monodimethylamino derivative, a very weak base,[3c] alkylates exocyclically. Furthermore, no peaks for a possible ring alkylated product were present in the crude reaction mixture.

The proton nmr data for the compounds are summarized in Table II.

Attempts to alkylate $N_3P_3Cl_6$ have so far failed, presumably as a consequence of its low nucleophilicity.

Isopropylamino Derivatives.—The ^1H nmr spectrum of compound VIII is shown in Figure 3. The appearance of a triplet at δ 2.91, assigned to the ring nitrogen methyl group, and the appearance of only one type of signal for the methyl groups of the isopropylamino groups (signal ratio 1:8) establishes the position of alkylation. The proposed structure of compound VIII is



VIII

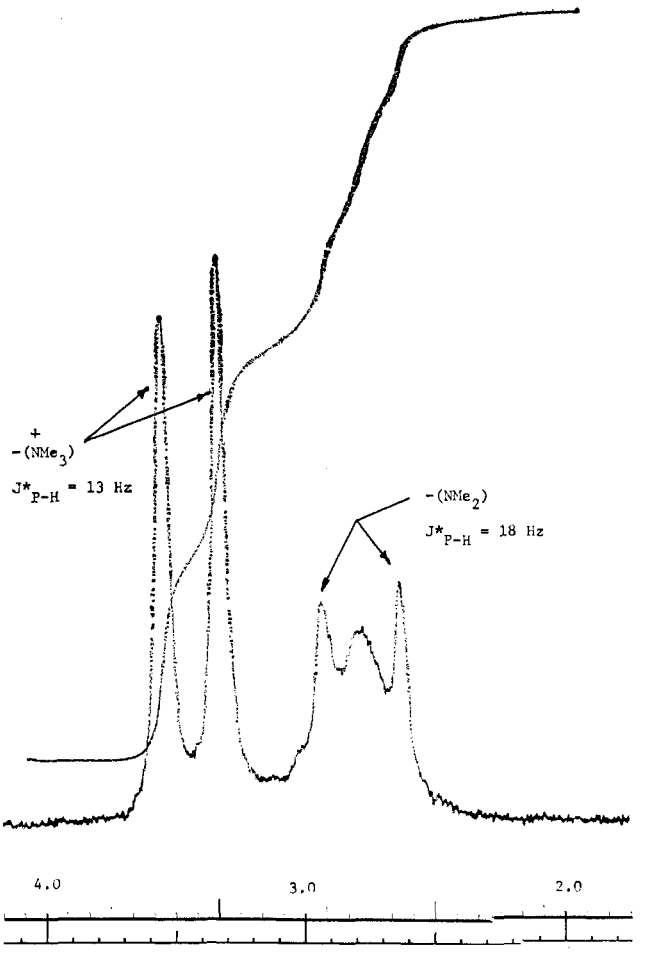


Figure 1.—^1H nmr spectrum of $[N_3P_3Cl_4(N(CH_3)_2)N(CH_3)_3]^+$-$BF_4^-$ from 2.0 to 4.0 ppm.

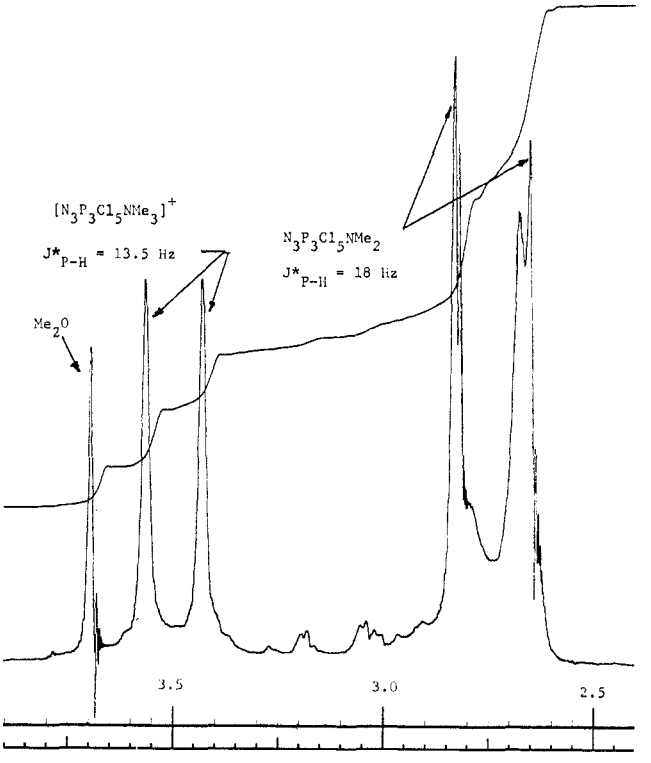


Figure 2.—^1H nmr spectrum of the reaction mixture of an excess of $(CH_3)_3O^+BF_4^-$ with $N_3P_3Cl_5N(CH_3)_2$.

TABLE II

^{1}H NMR DATA FOR ALKYLATED PHOSPHONITRILE FLUOROBORATES

Cation	$H_3C-\overset{+}{N}=$ δ, ppm	$H_3C-\overset{+}{N}=$ J^*_{P-H}	$-N(CH_3)_2$ δ, ppm	$-N(CH_3)_2$ J^*_{P-H}	$-\overset{+}{N}(CH_3)_3$ δ, ppm	$-\overset{+}{N}(CH_3)_3$ J^*_{P-H}	
$[N_3P_3Cl_5(N(CH_3)_3)]^+$					3.50	13.5	*a*
$[N_3P_3Cl_4(N(CH_3)_2)(N(CH_3)_3)]^+$			2.80	18.0	3.45	13.0	*a*
$[N_3P_3Cl_3(N(CH_3)_2)_2(N(CH_3)_3)]^+$			2.76	17.0	3.42	13.0	*a*
$[N_3P_3Cl_2(N(CH_3)_2)_3(N(CH_3)_3)]^+$			2.77[c]	18.0[c]	3.12	10.5	*a*
			3.02[d]	11.0[d]			
$[CH_3N_3P_3Cl_2(NH\text{-}i\text{-}C_3H_7)_4]^+$	2.91	10.0					*a*
$[CH_3N_3P_3(N(CH_3)_2)_2(NH\text{-}i\text{-}C_3H_7)_4]^+$	2.85	10.0					*a*
$[CH_3N_3P_3(N(CH_3)_2)(N(CH_3)_3)(NH\text{-}i\text{-}C_3H_7)_4]^{2+}$	2.83	12.0	2.98	10.5	3.03	10.0	*b*
$[CH_3N_3P_3(C_6H_5)_6]^+$	2.70	11.0					*b*

[a] In $CHCl_3$. [b] In CD_3CN. [c] On phosphorus bearing chloride. [d] On phosphorus bearing $N(CH_3)_3$ group.

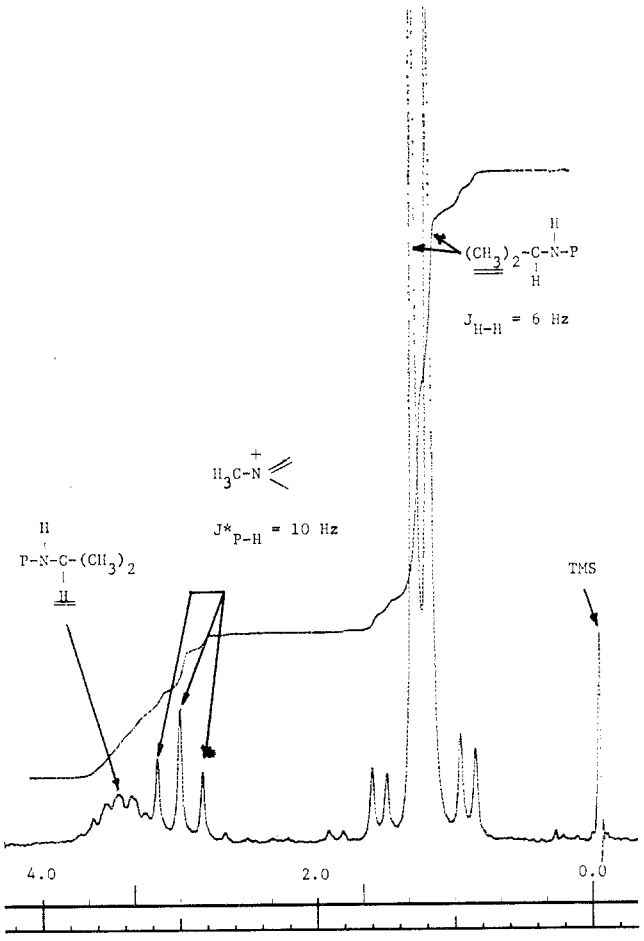
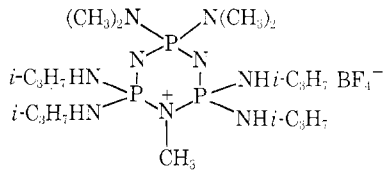


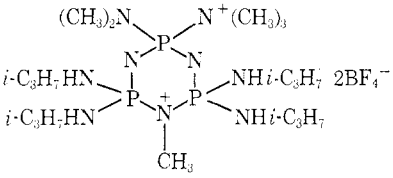
Figure 3.—^{1}H nmr spectrum of $[CH_3N_3P_3Cl_2(NH(i\text{-}C_3H_7))_4]^+$-$BF_4^-$ from 0.0 to 4.0 ppm.

Compounds VI and VII are the mono- and dialkylated species, respectively, of the mixed dimethylamino isopropylamino derivative of trimeric phosphonitrile. The ^{1}H nmr of VI has a triplet at δ 2.85 characteristic of a methyl group on a ring nitrogen atom. On the other hand, VII is alkylated both on the ring and exocyclically as shown by hydrolysis and nmr. Thus in the mixed amino derivative, alkylation occurs preferentially at the ring nitrogen.

Hexaphenyl Derivative.—Only one site is available for alkylation in hexaphenylcyclotriphosphonitrile, namely the ring nitrogen. Compound IX shows a



VI



VII

triplet characteristic of a methyl group on a ring nitrogen atom at δ 2.70. This compound was prepared so that the effect of placing a positive charge next to an atom that is capable of $p\pi$–$d\pi$ bonding to a phenyl ring could be investigated. The ultraviolet spectra of IX and its precursor are summarized in Table III. No large shifts in λ_{max} or changes in ε are noted.

TABLE III

ULTRAVIOLET SPECTRAL DATA FOR $N_3P_3(C_6H_5)_6$ AND $[H_3C-N_3P_3(C_6H_5)_6]^+BF_4^-$ IN CH_3CN

$N_3P_3(C_6H_5)_6$		$H_3C-N_3(C_6H_5)BF_4$	
λ_{max}	log ϵ_{max}	λ_{max}	log ϵ_{max}
222	4.69	224	4.72
264	3.62	267	3.73
272	3.37	274	3.55

Conductivities

The ionic nature of these salts is exemplified by the conductivities in nitrobenzene solution. The data summarized in Table IV are in accord with the literature data for 1:1 and 1:2 electrolytes in this solvent with the exception of compound VII which is somewhat low.[13] Furthermore, the addition of sodium tetraphenylborate in CH_2Cl_2–CH_3CN to a solution of the phosphonitrile salt results in the immediate precipitation of $NaBF_4$.

Discussion

We have observed three types of alkylation of phosphonitriles which depend on the substituents on

(13) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).

TABLE IV
CONDUCTIVITY OF ALKYLATED CYCLIC PHOSPHONITRILE FLUOROBORATES IN 10^{-3} *M* NITROBENZENE SOLUTION

Compound	A, mhos
$[N_3P_3Cl_4(N(CH_3)_2)(N(CH_3)_3)]^+BF_4^-$	38.96
$[N_3P_3Cl_3(N(CH_3)_2)_2(N(CH_3)_3)]^+BF_4^-$	32.32
$[N_3P_3Cl_2(N(CH_3)_2)_3(N(CH_3)_3)]^+BF_4^-$	31.54
$[N_3P_3(N(CH_3)_2)_5(N(CH_3)_3)]^+BF_4^-$	31.73
$[N_3P_3(N(CH_3)_2)_4(N(CH_3)_3)_2]^{2+}(BF_4^-)_2$	54.75
$[CH_3N_3P_3Cl_2(NH\text{-}i\text{-}C_3H_7)_4]^+BF_4^-$	24.69
$[CH_3N_3P_3(N(CH_3)_2)_2(NH\text{-}i\text{-}C_3H_7)_4]^+BF_4^-$	25.27
$[CH_3N_3P_3(N(CH_3)_2)(N(CH_3)_3)(NH\text{-}i\text{-}C_3H_7)_4]^{2+}(BF_4^-)_2$	32.50
$[CH_3N_3P_3(C_6H_5)_6]^+BF_4^-$	24.39

phosphorus. Exocyclic alkylation occurs when the substituents are dimethylamino groups. Ring nitrogen alkylation occurs when the substituents are isopropylamino groups, and mixed alkylation occurs when both dimethylamino and isopropylamino substituents are present, but ring nitrogen alkylation occurs first.

In the case of the exocyclic alkylation of the dimethylamino groups, the product resembles that which would be expected from the reaction of a phosphonitrilic halide with trimethylamine. For example the following reaction might be expected

$$(PNCl_2)_3 + N(CH_3)_3 \longrightarrow P_3N_3Cl_5N(CH_3)_3{}^+Cl^-$$

This reaction[14] however has been carried out by Burg and Caron and has been found to produce dimethylamino derivatives of phosphonitrile and tetramethylammonium chloride by cleavage of trimethylamine.

It is difficult at present to ascertain what controls the position of alkylation. Our observation that the ultraviolet absorption in the phenyl region for hexaphenylphosphonitrile does not change appreciably on alkylation indicates that d orbitals capable of exocyclic π bonding do not interact much with π orbitals of substituents even though the d orbitals must be considerably contracted by the placement of a formal positive charge next to phosphorus. That there is little exocyclic π bonding is in agreement with other observations on phosphonitriles including those with substituents bearing lone pairs of electrons.[15] It is also in agreement with theoretical predictions.[16] Thus it is likely that electronic effects of substituents are transmitted by σ inductive effects or by the perturbing of the $d_{xz}\pi$–$p\pi$ system rather than by exocyclic π bonding.

The basicity studies of Shaw give some evidence that protonation occurs at the ring nitrogen and this is in agreement with one crystal structure of a hydrochloride adduct of an aminophosphonitrile.[4] Our alkylation of the same aminophosphonitrile to give compound VIII also occurs at the ring nitrogen paralleling the protonation studies and in agreement with the fact that nucleophilicities normally parallel basicities for second row elements in the absence of steric effects. While isopropylamino groups are bulky, in this particular compound the four isopropylamino groups can be arranged sterically so that the alkyl part is away from the alkylation site and the amino hydrogen is next to the alkylation site; thus steric effects are expected to be small here.

On the other hand the alkylation of the dimethylaminophosphonitriles indicates that the most nucleophilic site and perhaps the most basic site is at the exocyclic nitrogen. Two factors could account for exocyclic alkylation. The presence of a second alkyl group on the amine substituent as compared to the isopropylamino derivative could increase the electron density more at the exocyclic site than at the ring site making alkylation or protonation more favorable there. The presence of a second alkyl group may cause steric hindrance at the ring nitrogen since now there are two alkyl groups on nitrogen present which cannot be arranged to be away from the reaction site. The steric effects in these compounds are hard to evaluate using models. The extent of hindrance at ring nitrogen depends on the number of dimethylamino groups present and the conformation of the ring, since some conformations, according to the models, would be less hindered than others. Also there is the possibility of hindrance at the exocyclic ligand, which would hinder exocyclic alkylation due to the bulkiness of the trimethylamino group formed. That ring nitrogen alkylation is possible when the phosphorus bears large groups is indicated by the alkylation of hexaphenylphosphonitrile. The phenyl groups would have about the same steric requirements as a dimethylamino group. It is noteworthy that there is evidence for exocyclic alkylation of monodimethylaminophosphonitrile, where the possibility of steric hindrance at the ring nitrogen would be much reduced over other dimethylamino derivatives. Although one is tempted to conclude that protonation in dimethylaminophosphonitriles would occur exocyclically more definitive evidence is needed.

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