Synthesis and Characterization of some Aminophosphonium Chlorides

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Abstract

R_3P reacts with $NR'R''Cl$ to give good yields of a new homologous series of aminophosphonium chlorides, $[R_3PNR'R'']Cl$, in which R = Me, Et, n-Pr and Ph; R′ and/or R″ = H, Me. IR, NMR and mass spectral data suggest that the phosphorus is tetracoordinate. When MeN(H)Cl is synthesized by the gas phase reaction of $MeNH_2$ and Cl_2, an optically active solution of MeN(H)Cl is obtained and the resulting aminophosphonium chlorides exhibit chirality. Electrical conductivity and temperature and concentration dependent NMR studies indicate ion pairing between the $[R_3PNR'R'']^+$ and Cl^- ions in solution. Quaternization of the phosphorus produces a large ^{31}P downfield chemical shift, a downfield ^1H chemical shift for the protons in the alkyl chains and an upfield ^{13}C chemical shift for the carbons in the alkyl chains. α- and β-deshielding and γ-shielding effects are observed in the ^{13}C NMR spectra with substitution on the phosphorus and nitrogen atoms. The mass spectral data, fragment ion identities and fragmentation modes are given for the compounds. Ions corresponding to a variety of P_2N and PN containing species in addition to those associated with fragmentation of the R_3P moieties are observed.

Introduction

Previous studies have established that chloramine [1–3], monomethylchloramine [3] and dimethylchloramine [2] react with trialkylphosphines and triphenylphosphines to give aminophosphonium chlorides. Syntheses involving chloramine have received considerably more attention than those using monomethylchloramine and dimethylchloramine as the electrophile. In this paper, we report the preparation; properties; and IR, multinuclear NMR and mass spectral data of a new homologous series of aminophosphonium chlorides, $[R_3PNR'R'']Cl$, in which R, R′ and R″ are varied in a systematic manner, *i.e.*, R = Me, Et, n-Pr and Ph; R′ and/or R″ = H, Me (Table I). All compounds were prepared by the chloramination of the respective tertiary phosphines. The first optically active aminophosphonium salts prepared by this procedure are reported. Whereas the literature contains several reports dealing with the ^{13}C and/or ^{31}P nuclear magnetic resonance studies of phosphonium salts [1, 4–10], only one [1] considers phosphonium salts containing the P–N bond. We were interested in noting any structural and electronic effects on ^{31}P, ^{13}C and ^1H chemical shifts that are produced by varying R, R′ and R″; determining the character of the P–N bond; and establishing the coordination number of the phosphorus atom in these compounds.

Experimental

All storing and transferring of phosphines and experimental purification work were conducted in a dry nitrogen atmosphere. All reactions were carried out in an atmosphere of prepurified nitrogen or *in vacuo*. All solvents were dried and distilled over calcium hydride and stored in the dry-lab over molecular sieve.

All synthesized compounds were characterized by elemental analysis*; mp.; IR; ^1H, ^{13}C and ^{31}P NMR; electron impact mass spectrometry (EI-MS); and electrical conductivity. Optical rotation data were obtained on those compounds that exhibited chirality. Melting points were determined by using the Thomas–Hoover capillary melting point apparatus with an uncorrected thermometer (Table I). Infrared spectra were recorded on a Perkin Elmer IR 283 spectrometer, interfaced to a PRIME 750 computer. The spectra were obtained on the solids in the form of Kel-F mulls by using KBr plates for the 4000–1300 cm^{-1} range and as Nujol mulls by using CsI plates for the 1330–500 cm^{-1} range†.

All NMR studies were conducted using a Nicolet 300 MHz multinuclear Fourier-Transform NMR

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*Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. (Table I).

†Previously unreported infrared absorption peaks of all compounds are filed as a supplementary table with the Editor-in-Chief.

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TABLE I *(continued)*

Compound	Chemical formula	Mp. data (°C)	% Yield	Elemental analyses, %[a]				
				C	H	N	P	Cl
I	$[Me_3PNH_2]Cl$	219–220 [3]						
II	$[Me_3PN(H)Me]Cl$	111 shrink; 130 gel; liq. by 140	21	32.32 (33.92)	8.72 (9.26)	9.28 (9.90)	20.84 (21.88)	26.47 (25.05)
III	$[Me_3PN(H)Me]Cl$[b]	172–174	73	33.06 (33.92)	9.44 (9.26)	10.60 (9.90)	20.25 (21.88)	26.42 (25.05)
IV	$[Me_3PNMe_2]Cl$	>265	50	38.34 (38.59)	9.72 (9.72)	8.77 (9.00)	20.31 (19.90)	22.73 (22.79)
V	$[Et_3PNH_2]Cl$	111 phase change; mp. 116–117	87	42.64 (42.46)	10.18 (10.11)	8.31 (8.26)	17.97 (18.27)	20.38 (20.88)
VI	$[Et_3PN(H)Me]Cl$	145 phase change; semisolid by 165; liq. by 180	85	45.52 (45.74)	10.35 (10.46)	7.39 (7.63)	17.13 (16.87)	19.42 (19.31)
VII	$[Et_3PN(H)Me]Cl$[b]	153	43	45.52 (45.78)	10.27 (10.43)	7.90 (7.63)	– (16.86)	– (22.92)
VIII	$[Et_3PNMe_2]Cl$	semisolid by 185; mp. 204–206.5	94	48.63 (48.58)	10.95 (10.71)	7.16 (7.09)	15.50 (15.67)	17.70 (17.94)
IX	$[n\text{-}Pr_3PNH_2]Cl$	51–52	89	51.18 (51.02)	10.74 (11.00)	6.72 (6.61)	14.42 (14.64)	16.40 (16.77)
X	$[n\text{-}Pr_3PN(H)Me]Cl$	85–86 phase change; liq. by 105	57	52.42 (53.20)	11.09 (11.16)	5.95 (6.20)	13.37 (13.72)	15.15 (15.70)
XI	$[n\text{-}Pr_3PN(H)Me]Cl$[b]	109	54	53.06 (53.20)	11.22 (11.16)	6.11 (6.20)	13.45 (13.72)	15.75 (15.70)
XII	$[n\text{-}Pr_3PNMe_2]Cl$	148–150	96	55.27 (55.08)	11.39 (11.36)	5.97 (5.85)	12.70 (12.92)	14.64 (14.79)
XIII	$[Ph_3PNH_2]Cl$	232–233	34	69.00 (68.90)	5.57 (5.46)	4.89 (4.46)	9.88 (9.87)	11.20 (11.30)
XIV	$[Ph_3PN(H)Me]Cl$	204–206	78	69.57 (69.62)	5.80 (5.84)	3.91 (4.27)	9.31 (9.45)	10.9 (10.82)
XV	$[Ph_3PN(H)Me]Cl$[b]	213–213.5	70					
XVI	$[Ph_3PNMe_2]Cl$	124–127	59	70.24 (70.25)	6.39 (6.20)	4.19 (4.10)	8.82 (9.07)	9.96 (10.38)

[a]Calcs. values given in parentheses. [b]Exhibit optical activity.

spectrometer. The ^1H NMR spectra for the synthesized compounds were recorded as a function of concentration (0.0125–0.2 M) and temperature (−50 °C to 25 °C) with chloroform-d ($CDCl_3$) as the solvent and TMS as the internal reference. The decoupled 75 MHz ^{13}C NMR spectra were obtained over the above temperature range at 0.2 M concentration in $CDCl_3$ (bilevel decoupling with NOE; TMS internal reference). Additionally, the coupled ^{13}C NMR spectra were obtained at 25 °C in order to verify chemical shift assignments. The decoupled ^{31}P NMR data were obtained at 25° on the same samples as used for the ^{13}C NMR experiments. A 85% aqueous H_3PO_4 solution was used as the external reference. No magnetic susceptibility correction was made [11]. All chemical shifts are reported using the convention that a positive δ-value corresponds to higher frequency chemical shifts. The NMR spectral data are listed in Tables II and III.

Electrical conductivity data were collected using a YSI Model 32 conductance meter with YSI 3400 series conductivity cells (cell constant, 1.030 cm^{-1}). All measurements were made in nitromethane at 25 °C over the concentration range of 10^{-3} M to 5×10^{-2} M.

Low and high resolution EI-MS data were recorded with an AEI MS-30 mass spectrometer operated at 70 eV and equipped with a DS-30 data system. Samples were introduced using a direct insert probe. Perfluorokerosene was used for the high-resolution reference standard. The source temperature was maintained near 70 °C. The probe temperature was 25 °C for compounds **II**, **V**, **IX**, **XII**, **XIII** and **XIV**; 250° for **IV**; 240° for **VIII**; and 150° for **XVI***.

All optical activity data were collected on a Perkin Elmer Model 141 Polarimeter using sodium (589 nm) and mercury (578 nm, 546 nm, 436 nm, 365 nm) sources at 24 °C with $CHCl_3$ as the solvent.

*All mass spectral data are filed as supplementary data.

TABLE II. ^{1}H NMR Chemical Shift and Coupling Constant Data on Aminophosphonium Chlorides.

Compound	Chemical shifts, ppm						Coupling constants, Hz		
	Ph	C-1	C-2	C-3	NMe	NH	$^3J_{HCCH}$	$^3J_{HNCH}$	$^4J_{HCCCH}$
Me_3P		1.02(d)							
I		1.87(d)				5.17(br)			
II		2.03(d)			2.69(d)	6.44(br)		5.7	
III		2.04(d)			2.69(dd)	6.35(br)			
IV		2.33(d)			2.82(d)				
Et_3P		1.29(qd)	1.05(dtt)				7.3		
V		2.24(dq)	1.28(dt)			5.73(br)	7.7		
VI		2.32(dq)	1.28(dt)		2.70(dd)	6.72(br)	7.7	4.0	
VII		2.31(dq)	1.28(dt)		2.70(dd)	6.75(br)	7.7	5.6	
VIII		2.69(dq)	1.28(dt)		2.91(d)		7.7		
n-Pr_3P		1.44(m)	1.35(m)	0.99(t)			7.0		
IX		2.14(m)	1.60(m)	1.10(td)		5.78(s)	5.9		1.4
X		2.19(m)	1.60(m)	1.10(td)	2.63(dd)	6.90(br)	6.0	1.0	1.5
XI		2.26(m)	1.72(m)	1.18(td)	2.74(dd)	6.96(dq)	7.2	5.2	
XII		2.59(m)	1.60(m)	1.15(td)	2.88(d)		7.5		1.8
Ph_3P	7.31(m)								
XIII	7.70(m)					7.55(br)			
XIV	7.68(m)				2.73(d)	8.81(br)			
XV	7.74(m)				2.77(dd)	8.64(dq)		5.4	
XVI	7.83(m)				3.09(d)				

Abbreviations: (br) broad unresolved multiplet; (d) doublet; (dd) doublet of doublets; (dq) doublet of quartets; (dt) doublet of triplets; (dtt) doublet of a triplet of triplets; (m) multiplet; (qd) quartet of doublets; (s) singlet; (td) triplet of doublets. All data collected in $CDCl_3$ at 25 °C at 0.2 M with TMS as an internal standard. Carbon atoms are numbered in the alkyl chains as follows: 3 2 1 C–C–C–P.

Data were also collected on the ether solutions of MeNHCl using these sources.

Syntheses

Chloramine, NH_2Cl, was synthesized on a generator by the direct reaction of ammonia and chlorine with nitrogen as a diluting gas [12]. Monomethylchloramine and dimethylchloramine were synthesized by a procedure analogous to the Raschig synthesis of chloramine [13]. Monomethylchloramine was also synthesized by a procedure analogous to that used for NH_2Cl [12]. The rates of flow of monomethylamine, nitrogen and chlorine through the generator were maintained at 1.2:0.3:0.1 mol/h, respectively.

The aminophosphonium chlorides were synthesized using two previously reported procedures, *i.e. Method A*: direct bubbling of the effluent gases from the generator [3] through a diethylether solution of the phosphine and *Method B*: distillation of a solution of the respective chloramine onto a diethylether solution of the phosphine at −76 °C *in vacuo*. When the latter procedure utilized chloramine or monomethylchloramine, the excess ammonia or monomethylamine was removed by passing the ethereal solution through a column of anhydrous copper sulfate [14].

Results and Discussion

The products of the reactions of the substituted chloramines with the trialkylphosphines and triphenylphosphines were found, in each case, to be the aminophosphonium chlorides. The NH_2Cl reactions proceed instantaneously below 0 °C, MeNHCl reactions proceed slower and Me_2NCl reactions proceed the slowest. The latter occur slowly even at room temperature. These results are consistent with those previously observed in the chloraminations of tertiary arsines [15].

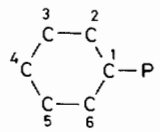
The syntheses of the $[R_3PN(H)Me]Cl$ compounds warrant further discussion. Since the nitrogen atom is an asymmetric center, optically active aminophosphonium species should result. Experimental data suggest that the syntheses carried out using *Method A* selectively favor one isomeric form, whereas those carried out using MeNHCl produced from the modified Raschig procedure give a racemic mixture of products. When the procedures for synthesizing MeNHCl were studied in more detail, we found that the generator synthesis yielded an optically active MeNHCl solution, but the Raschig process produced a solution that exhibited no optical rotation. Since the N-atom in MeNHCl is an asym-

TABLE III. ^{13}C and ^{31}P NMR Chemical Shift Data on Aminophosphonium Chlorides.

Compound	^{13}C chemical shifts, ppm					^{31}P chemical shifts, ppm
	C-1	C-2		C-3	NMe	
Me_3P	16.21(d)					−60.50
I	insoluble in CDCl					
II	11.66(qd)				26.57(qd)	53.17
III	11.66(qd)				26.57(qd)	53.17
IV	10.78(dqh)				36.99(qdq)	62.53
Et_3P	18.26	9.45				−17.97
V	16.02(td)	5.41(qq)				60.67
VI	14.05(td)	5.13(qq)			26.70(qd)	63.74
VII	14.05(td)	5.11(qq)			26.69(qdd)	63.71
VIII	14.18(td)	5.35(dtq)			37.64(qdq)	72.07
Pr_3P	29.74(tm)	19.35(tm)		16.08(qm)		−32.02
IX	25.27(td)	14.89(th)		15.21(qd)		54.31
X	23.25(td)	14.73(th)		15.00(qdp)	26.64(qd)	57.54
XI	23.44(td)	14.90(th)		15.16(qd)	26.81(qd)	54.46
XII	23.14(td)	14.99(th)		14.85(qdp)	37.60(qdq)	66.06
	C(1)	C(2, 6)	C(4)	C(3, 5)	NMe	
Ph_3P	137.15	133.69	128.65	128.44		−4.84
XIII	123.41	132.68	134.40	129.60		36.18
XIV	121.14	133.21	134.47	129.67	28.04	39.35
XV	121.13	133.22	134.50	129.69	28.04	39.19
XVI	119.17	133.46	135.35	130.29	39.22	47.55

Abbreviations: (d) doublet; (dqh) doublet of a quartet of heptets; (qd) quartet of doublets; (qdd) quartet of a doublet of doublets; (qdq) quartet of a doublet of quartets; (qh) quartet of heptets; (qq) quartet of quartets; (qt) quartet of triplets; (qtt) quartet of a triplet of triplets; (td) triplet of doublets; (th) triplet of heptets; (tm) triplet of multiplets; (tq) triplet of quartets. All data collected at 25 °C in $CDCl_3$ at 0.2 M with TMS as an internal standard. ^{31}P NMR chemical shifts reported in ppm with respect to H_3PO_4 (external). Positive values are downfield of H_3PO_4.

[a]Carbon atoms are numbered on the alkyl chains as follows: C–C–C–P 3 2 1. [b]Carbon atoms in the ring are numbered as follows:



metric center, the solution is probably a racemic mixture of MeNHCl.

We are currently studying the gas phase MeNHCl synthesis in more detail, including ORD studies on all isolated products. This synthesis involves one, if not more, side reactions. After about 5 minutes of generator operation, the initial $MeNH_3^+Cl^-$ that forms in the cooler regions of the generator reacts further with the MeNHCl and excess $MeNH_2$ mixture to give a viscous liquid. When the generator delivery tube is heated, no liquid forms and only $MeNH_3^+Cl^-$ deposits. Attempts to isolate and characterize this liquid have been unsuccessful. Upon standing under a stream of $MeNH_2$, the liquid decomposes with gas evolution and deposition of $MeNH_3^+Cl^-$, as confirmed by IR and NMR spectra. **WARNING**: When the liquid is isolated to remove the excess $MeNH_2$, the material explodes to give products having a highly characteristic chlorinated odor.

The exact nature of the side reactions is uncertain, though previous studies [16–18] on the chloramination of amines and hydrazines suggests that 1,2-dimethylhydrazine, 1,2-dimethylhydrazinium chloride and [MeN(H)N(H)MeN(H)Me]Cl should be expected side products. Since each of these products would have more than one asymmetric center and exhibit optical isomerism, their formation could result in a MeNHCl solution that is enriched in one isomeric form. Whereas $[Me_2N(NH_2)_2]Cl$ is stable [16, 17], we might expect [MeN(H)N(H)-MeN(H)Me]Cl to be unstable [20]. We are currently investigating this reaction.

The electrical conductivity data were analyzed in terms of strong electrolyte behavior. The Kohlrausch plots are non-linear, except for **XII** and **XVI**,

which exhibit normal 1:1 electrolyte behavior. The remaining aminophosphonium salts exhibit weak electrolyte behavior** at 0.05 M concentration due to ion-pairing in solution. Upon dilution, the conductivity values increase in a non-linear manner to those expected for a 1:1 electrolyte [19].

^1H NMR Spectra

^1H NMR chemical shift and $^3J_{HCCH}$ coupling constant data for compounds **I–XVI** are given in Table II. Quaternization of the phosphorus atom produces the expected downfield shift in δ_H for all protons on the alkyl groups attached to phosphorus ($\delta_{H(C\text{-}1)} = 0.8$ to 1.3 ppm; $\delta_{H(C\text{-}2)} = 0.2$ ppm; $\delta_{H(C\text{-}3)} = 0.2$ ppm). See footnote 'a' in Table III for numbering notation. Quaternization results in a decrease in electron density on the phosphorus, which has an electron withdrawing effect on all the alkyl group protons. The change in δ_H of the C-1 protons upon quaternization decreases in the order: Me > Et > n-Pr. Such an ordering is consistent with the ordering of the C–P–C bond angle changes that occur upon quaternization [8, 21], *i.e.* largest bond angle changes relate to largest δ_H changes. In the phosphonium salt, the hybrid orbitals involved on the phosphorus atom are undoubtedly sp^3 orbitals as compared with p^3 orbitals in the phosphine. The ^1H NMR spectra indicate that quaternization also causes a change from non-equivalence to equivalence of the C-1 protons.

For a given -N(H)R′ series, δ_{NH} moves downfield as R changes from Me to Et to n-Pr to Ph. The furthest downfield δ_{NH} occurs when R is Ph. This is expected, since the phenyl group serves as an electron withdrawing group toward P and causes a deshielding of the NH proton. Within a given alkyl series, both H-bonding and/or ion-pair interaction arguments support the observed trend. Stronger H-bonding and poorer ion-pair interactions should occur in the order Me < Et < n-Pr. Electrical conductivity data and temperature and concentration NMR studies suggest strong ion-pair interactions between $[R_3PNR'R'']^+$ and Cl^-.

The ^1H NMR chemical shifts are concentration and temperature independent for the $-NH_2$ group in the $-NH_2$ containing compounds, but concentration and temperature dependent for the >NH group in the -N(H)Me containing compounds. For the latter species, δ_{NH} for the -N(H)Me group is always downfield of that of the NH_2 resonance for the respective $-NH_2$ compounds.

In the -N(H)Me compounds, a decrease in concentration results in a shift of δ_{NH} to lower field and a decrease in temperature produces a shift to higher field. This trend is opposite of that expected for H-bonding interactions, but consistent with that predicted for ion-pair formation. Ion-pair formation would be expected to create a shielding effect on the N-H proton. This shielding effect should decrease as the ion-pair interactions are weakened—upon decreasing the concentration and increasing the temperature—and δ_{NH} should shift to lower field.

Since the magnitude of $^3J_{HNCH}$ and the appearance of the spectral pattern changes with temperature and concentration in the -N(H)Me compounds, we can conclude that there is an exchange of >NH protons between compounds. This suggests that structural clustering occurs in solution. Although the ^1H, ^{13}C and ^{31}P chemical shift data are the same for the racemic mixture and the optically active species containing the same alkyl substituent, the $^3J_{HNCH}$ couplings are different. These couplings for the optically active compounds do not change with different alkyl groups, but do for the racemic mixture. This would suggest that structural clustering is more effective in the optically active species.

^{31}P NMR Spectra

^{31}P NMR chemical shift data are given in Table III for compounds **I–XVI** and the parent tertiary phosphines. For any given -NR′R″ group, quaternization of the phosphorus produces a large downfield shift in $\delta_{^{31}P}$. The order of magnitude of chemical shift difference is dependent upon R, *i.e.* Ph < Et < n-Pr < Me for any given -NR′R″. This ordering parallels the ordering of the ^{31}P chemical shifts of the parent phosphines and the bond angle changes that result upon quaternization of the phosphorus [8]. The magnitude of downfield shift is also dependent on the nature of R′ and R″, *i.e.* $-NH_2 < -N(H)Me < -NMe_2$, for any given R_3P-. Replacement of a H with a Me group may be viewed as producing a β-effect [–C–C–C–P–N(α)–C(β)] on the ^{31}P chemical shift [5]. The addition of the second Me group also creates a β-effect, which is more pronounced than the first. This greater downfield shift may be due to a steric effect caused by the branching at the N-atom [5]. The magnitude of this change in δ_P is independent of the nature of R attached to phosphorus. Thus the -NR′R″ group contributes its own shielding effects, but does not strongly interact with the other substituents on phosphorus. This suggest no π-character in the C–P–N bonding system.

As R is changed from methyl to propyl to ethyl for any given -NR′R″, the ^{31}P resonance is shifted downfield. This trend is explained by the β- and γ-effects, *i.e.* deshielding and shielding [5], respectively, that successive lengthening of the carbon chain has on the phosphorus atom: –C(γ)–C(β)–C(α)–P–. The magnitude of the change in chemical shifts produced upon changing the R groups is

**Figure, supplementary data.

independent of the nature of the -NR′R″ group, even when R is phenyl. This suggests that the trialkyl- or triphenylphosphonium group contributes its own characteristic shielding effects, but does not interact with the -NR′R″ group.

The ^{31}P chemical shifts in the phenyl derivatives occur upfield of those observed for phosphorus in the alkyl derivatives. This trend correlates with the greater electronegativity of the phenyl group as compared with the alkyl groups [1, 5, 8].

^{13}C NMR Spectra

^{13}C NMR chemical shift data are given in Table III for compounds **I–XVI** and the parent tertiary phosphines. Quaternization of the phosphorus causes an upfield shift (1 to 7 ppm) for all the carbons in the alkyl chains, *e.g.* 2 to 7 ppm for C-1 carbons, about 4 ppm for C-2 carbons and about 1 ppm for C-3 carbons. This is consistent with earlier reports for phosphonium compounds [10, 22]. Quaternization also causes the chemical shift of the phenyl C(1) directly bonded to P to move upfield by about 14 ppm, while the chemical shift of the C(4) carbon moves downfield. In the quaternized cationic species, the -PNR′R″ group can be viewed as a substituent on the phenyl which polarizes the π electron density in the ring. This polarization increases electron density at the C(1) carbon (upfield shift in δ_C) and reduces the π electron density at the C(4) (*para*) carbon (downfield shift in δ_C) [23]. Opposite trends, but analogous phenomena have been previously observed for anionic species [24]. The chemical shifts of the C(1) phenyl carbon atoms are similar to those of benzene (128 ppm), suggesting that no $p\pi-p\pi$ interaction occurs between the phenyl ring and phosphorus [24].

Substitution of methyl for hydrogen in an unbranched hydrocarbon chain produces a deshielding of C-1 by 9–10 ppm (α-effect), a deshielding of C-2 by greater than 9 ppm (β-effect) and a shielding of C-3 by about 3 ppm (γ-effect) [25]. These effects are observed for the C-1 carbons in each -R′R″ series (Table III). Trends in the data indicate that intrachain α- and β-effects and interchain γ-effects are present [7].

A deshielding β-effect (about 10 ppm) on the first >NMe ^{13}C chemical shift results when the >NH proton is replaced with the second Me group. This is observed in each R_3P series and appears to be independent of the nature of R.

IR Spectra

The infrared bands associated with N–H, C–H, and P–C stretching and P–CH_3 and PNC_2 structural units are observed in the appropriate regions of the spectra. In the Me_2NCl derivatives, strong bands are observed around 1075 and 985 cm^{-1}, which are undoubtedly due to the NC_2 structural unit attached to phosphorus, *i.e.* $\nu_{as}(PNC_2)$ and $\nu_s(PNC_2)$, respectively. Compared with the infrared spectra of the parent tertiary phosphines, the spectra of the respective products show new peaks in the 1100–950 cm^{-1} and 950–880 cm^{-1} regions. These peaks, usually quite strong and broad, are assigned to the asymmetric and symmetric P–N stretching modes, respectively, in these aminophosphonium chlorides [1, 27]. When the hydrogen is replaced with a methyl group on the nitrogen, there is a shift to lower wavenumber for ν_s(P–N). The P–N stretching mode is observed at successively lower wavenumbers as the group attached to phosphorus changes from Me to n-Pr to Et to Ph in the $>NH_2$ compounds and from Me to Ph to n-Pr to Et in the >N(H)Me species. Simple inductive considerations provide no ready explanation for these trends in P–N stretching frequencies. The symmetric PNC_2 stretching frequency varies only about 10 cm^{-1} with the change in R in these compounds. The absence of a new infrared absorption band in the 500–600 cm^{-1} region [associated with ν(P–Cl)] supports the assumption that all these P–N compounds have a tetracoordinate phosphorus and are aminophosphonium chlorides, $[R_3PNR'R'']Cl$.

Mass Spectra

Ions corresponding to P–N containing fragments were observed for all compounds. Fragment ions containing P–Cl bonds were only observed in trace amounts. The $[C]^+$, $[C-1]^+$ and $[C-Me]^+$ (C being the parent cation) ions are observed for all the alkyl substituted P–N compounds. Their presence, in addition to the lack of fragments containing P–Cl bonds (except in very trace amounts) supports our other experimental data in suggesting these P–N compounds are aminophosphonium chlorides. In **(I)** the base peak corresponds to $Me_3P^{\cdot+}$, whereas it is assignable to H_2PNH^+ in **(V)** and **(IX)**.

Ions corresponding to a variety of P_2N species were observed in the spectra of all the alkyl derivatives. Such P_2N species could easily arise from recombination mechanisms within the mass spectrometer. As the length of the alkyl chain increases, the sum of the relative intensities of the P_2N condensed species decreases, of the PN fragments increases and of the RP fragments decreases. Thus increasing the length of the alkyl chain appears to increase the stability of PN bonded fragments. On the other hand, the sum of the relative intensities of the PN fragments decreases and of the RP fragments increases with replacement of the proton on the nitrogen with methyl groups. This suggests that methyl substitution on nitrogen lowers the stability of the PN bonded fragments.

All the spectra indicate ions associated with the fragmentation of the R_3P moiety [28]. The spectra

of the NMe_2 derivatives contain fragments associated with fragmentation of the NMe_2 moiety [28]. As expected, the relative intensities of fragments associated with the alkyl group increases as the length of the alkyl chain increases. The relative intensities of the HCl fragments decrease in going from the NH_2 to the NMe_2 derivatives and in increasing the length of the alkyl chain.

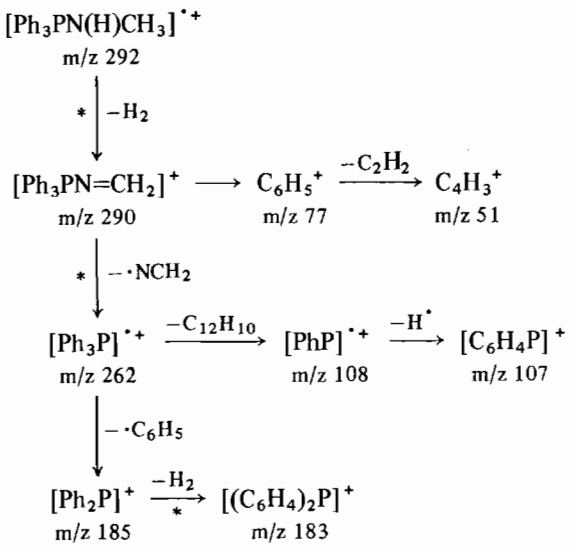
Fragmentation of $[C]^+$ in **(I)** proceeds via loss of $^{\cdot}NH_2$ to give $Me_3P^{\cdot+}$ (confirmed by a metastable at 63.4). A metastable at 76.5 in the spectra of **(VIII)** suggests that the $[C-1]^+$ ion fragments with cleavage of the PN bond to give $Et_3P^{\cdot+}$ (42% abundance). Another important fragmentation process involves loss of C_2H_4 from Et_2PNH^+ to give $EtPNH_2^+$, the base peak (confirmed by a metastable at 55.5). $C_2H_5(C_2H_4)PNH^+$ appears to fragment with loss of C_2H_3 to give the base peak (metastable at 56.3). Other metastables at 42.7 and 68.8 correspond to previously established fragmentation pathways of Et_3P [28].

The metastable at 79.2 in the spectrum of **(IX)** suggests that $C_3H_7PNH_2^+$ fragments with the loss of NH_3 to give $C_3H_6P^+$. Metastables at 56.2, 62.3 and 101.2 correspond to loss of C_2H_4, C_3H_6 and H_2 from PN fragments having m/z values of 105, 133 and 105, respectively.

The fragment ions observed for the triphenylphosphonium salts are essentially all of the PN and Ph_xP type. In **(XV)**, the fragmentation of the $[C-1]^+$ cation proceeds via loss of $H^{\cdot}$ (metastable at 289.1) to give the base peak at m/z 290, which undergoes cleavage of the P–N bond to give $Ph_3P^{\cdot+}$ (metastable at 236.7). The relative intensities of these ions suggest this is an important fragmentation pathway to $Ph_3P^{\cdot+}$ for **(XV)**. Numerous ions are observed that can be associated with the known fragmentation pathways of Ph_3P [29]. The proposed fragmentation path (Scheme 1) is supported by observed (*) and previously reported [29] metastable ions.

Fragmentation of $[Ph_3PN{=}CH_2]^+$ via loss of $^{\cdot}N{=}CH_2$ is also an important fragmentation pathway for **(XVI)** (confirmed by a metastable at 237). No $[C]^+$ or $[C-1]^+$ ions were observed for **(XVI)**.

In both **(XIV)** and **(XV)**, the base peaks are PN species, whereas for **(XVI)** it corresponds to $[(C_6H_4)_2P]^{\cdot+}$. This observation suggests that replacement of the second proton on the nitrogen with a methyl group results in a significant weakening of the P–N bond. This conclusion is further supported by the observation that the sum of the relative intensities of all the PN fragments is less in **(XVI)** than in **(XIV)** and **(XV)**. A major difference between the EI spectra of the triphenylphosphonium and trialkylphosphonium salts is the tendency of the triphenylphosphonium salts to undergo skeletal rearrangements to form the more stable 9-phosphafluorenyl ions: $[(C_6H_4)_2P]^+$ and $[(C_6H_5)_2P]^+$.



Scheme 1.

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