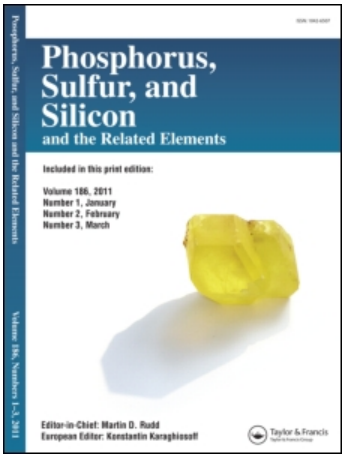

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THE SYNTHESIS AND CHARACTERIZATION OF MIXED (ALKYLAMINO) AND (ARYLAMINO)PHENYLPHOSPHONIUM COMPOUNDS[1]

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The syntheses of alkyl and aryl-substituted tetrakis(amino)phenylphosphonium compounds of type $(RNH)_{4-n}(C_6H_5)_nPX$, where R = n-C_3H_7 (**1**), i-C_3H_7 (**2**), n-C_4H_9 (**3**), s-C_4H_9 (**4**), n-C_6H_{13} (**5**), c-C_6H_{11} (**6**), $C_6H_5CH_2$ (**7**) and C_6H_5 (**8**), and where X = Br, and $(C_6H_5)_4B$, are described. These compounds have been characterized by elemental analysis, melting point and ^1H and ^{31}P NMR spectroscopy. Solubility characteristics in water and organic solvents are given for several derivatives within each series. It has been found that as the number of phenyl substituents on the phosphorus increases, so does the solubility in most solvents investigated. The mild conditions used to synthesize a tetraphenylborate derivative from the corresponding phosphonium bromide indicates the relative ease with which these phosphonium compounds undergo metathesis reactions. Hydrolysis reactions undergone by several partially substituted intermediates, as well as unreacted starting materials have been found to cause lower reaction yields, as evidenced by NMR results. Phosphorus and proton NMR spectra are consistent with a structure for these compounds similar to the regular phosphonium salts, and represented as $[(RNH)_{4-n}(C_6H_5)_nP]^+X^-$, where the substituents are tetrahedrally arranged around the phosphorus central atom.

Key words: Synthesis; aminophenylphosphonium compounds; NMR spectroscopy; solubility; hydrolysis.

INTRODUCTION

The reactions of phosphorus pentachloride with primary amines have been extensively studied and their products well characterized.[3] An understanding of the reactions of phenyl-substituted phosphorus halides with primary amines has yet to be developed, however.

Several tris(amino)phenylphosphonium compounds have been prepared by the reaction of alkyl amines with $(C_6H_5)_4P_4$ and CCl_4.[4] The first report on the synthesis of $Ph_2P(NH_2)_2Cl$, a bis(amino)diphenylphosphonium compound, described its preparation from the reaction between an ammonia-chloramine mixture and diphenylchlorophosphine.[5] Alkyl- or aryl-substituted amine derivatives of the latter have not yet been reported. Sisler[6] and Barna[7] have reported on the synthesis of (amino)trialkylphosphonium compounds based on the following reaction:

$$R_3P: + NH_2Cl \rightarrow (R_3PNH_2)^+X^- \quad (1)$$

An alternate method[8] has been used to prepare similar compounds:

$$(RNH)PPh_2 + RX \rightarrow [(RNH)(R)PPh_2]^+X^- \quad (2)$$

where X = halide.

Several (amino)triphenylphosphonium compounds have been prepared by Horner and Oediger[9] through a similar method:

$$Ph_3PBr_2 + RNH_2 \xrightarrow[C_5H_5N:]{} [Ph_3P(RNH)]^+Br^- + C_5H_5N{:}HBr \quad (3)$$

where R = n-butyl, cyclohexyl, phenyl, m-tolyl, benzyl. The solvents used were benzene, chlorobenzene and pyridine.

IR investigations on (amino)triphenylphosphonium compounds, relating the NH stretching frequency to hydrogen bonding of type N—H · · · X^- and to the amino substituent effect, have been reported by Singh and Zimmer.[10]

In an attempt to extend an earlier study[3] on compounds of type $(RNH)_{4-n}(Ph)_nPX$, where n = 0 and X = Cl, Br, I and ClO_4, several compounds of the n = 1, 2, 3 series have been prepared by the reactions described below:

$$Ph_nPCl_{3-n} + Br_2 \rightarrow Ph_nPCl_{3-n}Br_2 \quad (4)$$

$$Ph_nPCl_{3-n}Br_2 + 2(4\text{-}n)\ RNH_2 \rightarrow [(RNH)_{4-n}Ph_nP]^+Br^- + (3\text{-}n)\ RNH_3Cl + RNH_3Br \quad (5)$$

where n = 1, 2, 3.

This method is similar to that reported by Horner and Oediger.[9]

RESULTS AND DISCUSSION

Synthesis of Mixed $(RNH)_{4-n}(C_6H_5)_nPX$, where n = 1-3 and X = Br^- and $(C_6H_5)_4B$-

Similar problems to those encountered in, and described for the synthesis of $(RNH)_4PX$ compounds in an earlier report[3] have been identified for the syntheses of the title compounds. Lower yields, combined with a much greater number of undesired side-products reflect the increased complexity involved in the present synthesis scheme as compared to the reactions of primary amines with PCl_5,[3] which were single step and free of side-products. Equations (4), (5) and (6) are considered to represent the first step in the synthesis of each series of mixed aminophenylphosphonium compounds presented here. It can be realized, considering the experimentally

$$(C_6H_5)_3P: + Br_2 \rightarrow (C_6H_5)_3PBr_2 \quad (6)$$

observed formation of an initially insoluble solid, $[(C_6H_5)_3PBr]^+Br^-$, that unless this intermediate precipitate is well dispersed and redissolved in solution during the course of the reaction, several problems may occur. First is the formation of an agglomerate, as discussed previously,[3] which yields upon hydrolysis the following side products:

$$Cl_2(C_6H_5)PBr_2 + 3\ H_2O \rightarrow (C_6H_5)(OH)_2P(O) + 2\ HBr + 2\ HCl \quad (7)$$

$$Cl(C_6H_5)_2PBr_2 + 2\ H_2O \rightarrow (C_6H_5)_2(OH)P(O) + 2\ HBr + 2\ HCl \quad (8)$$

$$(C_6H_5)_3PBr_2 + H_2O \rightarrow (C_6H_5)_3P(O) + 2\ HBr \quad (9)$$

The formation of partially substituted hydrolysis side products is also possible.

$$[(C_6H_5)(RNH)ClBrP]^+Br + H_2O \rightarrow (C_6H_5)(RNH)(OH)P(O) + HCl + HBr \quad (10)$$

Similarly, $(C_6H_5)(RNH)_2P(O)$ and $(C_6H_5)_2(RNH)P(O)$ may be obtained. However, these last three side products may only be isolated if R = benzyl or aromatic, as shown in a previous study,[3] and as discussed in the spectroscopy section of this paper.

Due to the experimental apparatus used in the present study, which allowed the oxidation of a phosphine (with Br_2) followed by substitution of the halides with amino groups, the process required the addition of the amine-containing solution to the phosphorus intermediate solution. This unfavorable addition sequence may have caused a sizeable decrease in the yields of the completely substituted (amino)phenylphosphonium product due to the precipitation of partially substituted (amino)phenyl(halo)phosphonium intermediates. This particular problem seems to have contributed significantly to the formation of undesired hydrolysis products, as shown by ^{31}P NMR spectroscopy.

Physical Properties

Of the tris(amino)phenylphosphonium compounds reported in the present study only two have been synthesized previously[4] and by a different synthetic route from the one employed here. The physical properties of these compounds are similar to those of the tetrakis(amino)phosphonium compounds reported earlier,[3] with some noticeable exceptions. For example, while the aromatic derivatives were found to be least soluble in all solvents investigated among the $(RNH)_3(C_6H_5)PX$ series, all compounds in the latter showed increased solubility in all these solvents when compared with their $(RNH)_4PX$ counterparts.

The majority of $(RNH)_3(C_6H_5)PX$ compounds were partially soluble in benzene, the reaction solvent; they partially precipitated upon cooling of the reaction mixture, along with the corresponding ammonium halide salt. Thus, they were found in (a) the benzene-insoluble precipitate isolated by filtration after cooling, and in (b) the residue obtained upon evaporation of the filtered benzene solution. The latter separated as solids or, in some instances, as oils that solidified when treated with the appropriate recrystallization solvent. The reaction yields varied widely. The crude products were difficult to purify since they showed a slight tendency to form oils in commonly used recrystallization solvents and contained undesired side products as impurities, as shown in the spectroscopy section of this paper. Low yields were obtained for the reactions that displayed these characteristics.

To our knowledge, none of the N-substituted bis(amino)diphenylphosphonium compounds synthesized in the present investigation has been reported previously. Benzene was used as the reaction solvent and the products showed similar behavior to those in the above tris(amino)phenylphosphonium series. Various hydrolysis side products were identified by ^{31}P NMR for several reactions, and can explain the unusually low yields obtained for those particular synthesis experiments. The increased oil-formation tendency for this series of compounds, as compared to the preceding $(RNH)_3PhPX$ series, caused greater difficulty in obtaining recrystallized, pure bis(amino)phenylphosphonium products.

Several of the aminotriphenylphosphonium compounds studied in this investigation have been prepared previously.[12,13] They showed increased solubility in the reaction solvent, benzene, over all the preceding series compounds. They showed some tendency to form oils, and appeared in the presence of side products, as shown later by NMR. In general, the compounds in this last series showed a markedly increased solubility in both, water and organic solvents. The product yields for these reactions were found to vary randomly, but were comparable to those reported earlier, as shown in Table I.

When considering the three series of (amino)phenylphosphonium compounds represented by $(RNH)_{4-n}Ph_nPX$, where n = 1, 2, 3 and X = bromide, several trends in their properties may be identified. First, their solubility in most common organic solvents, as well as in water, seems to increase as the number of phenyl substituents directly bonded to the phosphorus central atom increases. Since within a series of compounds where R = phenyl, for example, the only change from n = 1 to n = 3 is the size of the substituted phosphonium cation, decreasing in the order n = 1, 2, 3, a relationship must exist between cation size and effective

TABLE I

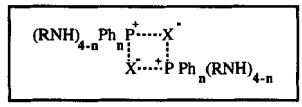
$(RNH)(C_6H_5)_3P^+X^-$ Reaction solvents and yields

		This Work		Published Work	
R	X	% Yield	Solvent	% Yield	Solvent
$n\text{-}C_3H_7$	Br	90	Benzene	80.5[a]	Benzene
$i\text{-}C_3H_7$	Br	52	Benzene	70.0[a]	Benzene
$n\text{-}C_4H_9$	Br	Oil	Benzene	65[b]	Benzene
$s\text{-}C_4H_9$	Br	Oil	Benzene		
$s\text{-}C_4H_9$	Ph_4B		Ethanol		
$n\text{-}C_6H_{13}$	Br	Oil	Benzene		
$c\text{-}C_6H_{11}$	Br	48	Benzene	85[b]	Chlorobenzene
$C_6H_5CH_2$	Br	65	Benzene		
C_6H_5	Br	82	Benzene	60[b]	Benzene

a. Obtained from reference 10.

b. Obtained from reference 9.

solvation. This relationship should be quite important for polar solvents, expected to solvate the anion effectively (such as in the case of water, methanol and ethanol), and where no tight ion pair formation is expected to occur. However, in the case of nonpolar, low dielectric constant, hydrocarbon solvents the formation of tight ion pairs of the type



is expected to occur readily. In this latter instance, solubility may be influenced by the number of amino groups bonded to the phosphorus. These amino substituents provide more room for ion-pairing to take place to a considerable extent and could help explain the decreased solubility observed in the order n = 3, 2, 1.

Spectroscopy

^{31}P NMR Spectra. Phosphorus NMR spectra were recorded for all isolated recrystallized compounds, as well as for several reaction mixtures and impure products. The chemical shifts assigned to the pure phosphonium products obtained upon recrystallization, $\delta(^{31}P)$ in ppm, are summarized in Table II. All the values are consistent with those expected for tetracoordinate phosphonium salts, as discussed in a previous report.[3] Three distinct groups of similar $\delta(^{31}P)$ values can be identified corresponding, within each series, to those compounds deriving from unbranched (A), α-carbon branched (B), and anilino (C) N-substituents:

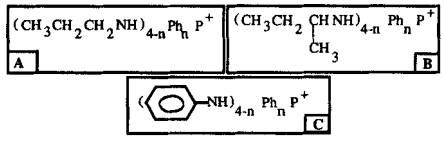


TABLE II

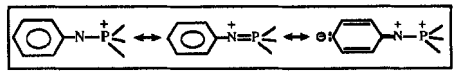
Summary of ^{31}P NMR results $(RNH)_{4-n}(C_6H_5)_nP^+X^-$ $\delta(^{31}P)$ in ppm[a]

R	n = 0	n = 1	n = 2	n = 3
n-C_3H_7	29	36	38	39
i-C_3H_7	20	29	34	36
C_6H_5	6.8	20	-	33

a. All numbers rounded off to two significant figures.

b. All values obtained with respect to 85% H_3PO_4, used as external reference in a concentric tube.

According to Van Wazer and Lechter,[14] ^{31}P NMR chemical shifts seem to be controlled by electronic (inductive and mesomeric) and steric effects due to the different substituents around the phosphorus central atom. Consequently, it is expected that for structures with aliphatic substituents, such as (A) and (B) above, steric effects will predominate, while for aromatic substituents, such as (C), electronic effects will exert greater influence on the chemical shift $\delta(^{31}P)$ values characteristic of the tetracoordinate phosphorus center in these compounds. Thus, the difference in $\delta(^{31}P)$ values between (A) and (B) type structures must be due largely to steric hindrance increasing with branching in the α-carbon of the chain. Electronic effects, however, must be responsible to a greater extent for the difference in $\delta(^{31}P)$ values between (C) type and (A) and (B) type structures. This difference is consistent with the electron delocalization expected to take place in anilino-substituted aminophosphonium compounds:



An important advantage of ^{31}P NMR, in general, is that it allows the identification of the different types of phosphorus atoms present during various stages of reactions, as well as in the products. Phosphorus NMR was used to monitor the various side products and byproducts obtained during the course of the above reactions, thereby giving information related to the reaction pathway, critical conditions to avoid undesired side products, and a possible explanation for low phosphonium product yields. The ^{31}P NMR spectral data summarized in Table VI illustrate the above points. The spectrum of the impure solid product obtained from the reaction of cyclohexylamine with phenyldibromodichlorophosphorane gives the peaks recorded in Table III(A). The major peak appearing at 28.9 ppm is due to the expected tris(cyclohexylamino)phenylphosphonium bromide. The minor peaks are due to side products resulting from hydrolysis that has taken place at different stages of the reaction. The peak at 22.2 ppm is due to the presence of phenylphosphonic acid produced by the reaction represented in Equation (7). Most likely, the latter was a result of unreacted $[PhCl_2BrP]^+Br^-$, present at the time the reaction was stopped and the resultant solution exposed to moisture during the filtration procedure. A third peak at 12.2 ppm is due to bis(cyclohexylamino)phenylphosphine oxide, the product formed by the hydrolysis of an incompletely substituted intermediate:

$$[(C_6H_{11}NH)_2(C_6H_5)XP]^+X^- + H_2O \rightarrow (C_6H_{11}NH)_2(C_6H_5)P(O) + 2\,HX_{(g)} \quad (11)$$

where X = Br, Cl. The spectrum corresponding to the pure $[(C_6H_{11}NH)_3(C_6H_5)P]^+Br^-$ compound, showing a single peak at 28.9 ppm, is obtained upon recrystallization of the reaction precipitate from acetonitrile. Phosphorus NMR has indicated that, in the case of the above synthesis experiment, incomplete reaction of two intermediate products has caused a decrease in the yield of the desired phosphonium product by allowing the formation of hydrolysis side products. Multiple reasons could explain incomplete substitution of these intermediates. Among them, a rapid addition rate, inefficient stirring, and too short a reflux period.

TABLE III
Summary of $\delta(^{31}P)$ NMR results for several product mixtures

	REACTION	$\delta(^{31}P)$ in ppm	Assignment
A	c-$C_6H_{11}NH_2$	28.9	(c-$C_6H_{11}NH)_3PhP^+Br^-$
	+	22.2	$PhP(O)(OH)_2$
	[$PhCl_2P$: + Br_2]	12.2	(c-$C_6H_{11}NH)_2PhP(O)$
B	sec-$C_4H_9NH_2$	36.7	(sec-$C_4H_9NH)_2Ph_2P^+Br^-$
	+	28.9	$Ph_2P(O)(OH)$
	[Ph_2ClP: + Br_2]		
C	$C_6H_5CH_2NH_2$	39.2	$(C_6H_5CH_2NH)Ph_3P^+Br^-$
	+	29.4	$Ph_3P(O)$
	[Ph_3P: + Br_2]	-5.4	Ph_3P:
D	i-$C_3H_7NH_2$	36.2	(i-$C_3H_7NH)Ph_3P^+Br^-$ (pptt)
	+	29.4	$Ph_3P(O)$ (pptt + sol)
	[Ph_3P: + Br_2]	-5.4	Ph_3P: (sol)
E	c-$C_6H_{11}NH_2$	36.1	(c-$C_6H_{11}NH)Ph_3P^+Br^-$
	+	29.5	$Ph_3P(O)$
	[Ph_3P: + Br_2]		

For the reaction of sec-butylamine with Ph_2ClPBr_2 only two phosphorus products were obtained, as shown in Table III(B): (sec-$C_4H_9NH)_2Ph_2P^+Br^-$, $\delta(^{31}P)$ 36.7 ppm, and diphenylphosphinic acid, $Ph_2P(O)(OH)$, $\delta(^{31}P)$ 28.9 ppm. Both products were isolated, purified, and further identified by elemental analysis.

The product solution obtained from the reaction of benzylamine with triphenyldibromophosphorane was filtered and evaporated. Table III(C) summarizes the peaks appearing in the spectrum obtained for the acetone-soluble fraction of the brown solid residue remaining from the product solution. Peaks were obtained at 39.2 ppm, 29.4 ppm and −5.4 ppm, corresponding to the expected $(C_6H_5CH_2NH)Ph_3P^+Br^-$, $Ph_3P(O)$, and unreacted Ph_3P:, respectively. Recrystallization of the remaining solid with a $CHCl_3$:$(CH_3CH_2)_2O$ mixture resulted in pure aminophosphonium product (39.2 ppm). This particular sequence of reactions involving the oxidation of Ph_3P: to Ph_3PBr_2, followed with substitution of bromide by (RNH_2), provide an ideal system for study by ^{31}P NMR. The only possible hydrolysis side product is $Ph_3P(O)$, a well-characterized species. In fact, in this reaction sequence, two reasons for lower product yields were clearly observed:

first, the hydrolysis of the Ph_3PBr_2 intermediate, and second, the presence of unreacted starting material (Ph_3P:).

Table III(D) gives the peaks obtained from the ^{31}P NMR spectra corresponding to (a) a white precipitate, insoluble in benzene, and (b) a solid obtained after evaporation of benzene, the solvent used for the reaction between isopropylamine and Ph_3PBr_2. In this particular reaction, unreacted Ph_3P:, $\delta(^{31}P)$-5.4 ppm, and $Ph_3P(O)$, $\delta(^{31}P)$ 29.4 ppm, the expected hydrolysis side product, were found as the only phosphorus-containing compounds remaining in solution after the reaction reflux period was completed (b). The solid precipitate obtained during the course of this reaction also contained $Ph_3P(O)$, besides the expected major product, $(i\text{-}C_3H_7NH)Ph_3P^+Br^-$, appearing at 36.2 ppm. It is important to note that for this particular reaction the side product arising from the hydrolysis of the Ph_3PBr_2 intermediate has appeared in both reaction product phases obtained. It is not clear from this instance alone whether the $Ph_3P(O)$ product appears in both phases due to its partial solubility in benzene, or because of the presence of unreacted intermediate in both phases prior to treatment in the presence of moisture followed by hydrolysis upon complete evaporation of the solvent.

For the reaction of cyclohexylamine with Ph_3PBr_2, no phosphorus product was observed in the solid precipitate. From the benzene-soluble fraction, however, was obtained a solid upon evaporation of most of the solvent, which was found to contain the desired phosphonium product, $(c\text{-}C_6H_{11}NH)Ph_3P^+Br^-$, $\delta(^{31}P)$ 36.1 ppm. The hydrolysis product $Ph_3P(O)$, $\delta(^{31}P)$ 29.5 ppm, was also observed in this fraction of the reaction product. The corresponding spectral data is given in Table III(E). The spectrum corresponding to the recrystallized solid yields a single peak at 36.1 ppm.

All these observations obtained by ^{31}P NMR for the above reactions suggest that the presence of the identified hydrolysis products will not only result in lower reaction yields, but may also promote in some cases the formation of oils by preventing crystallization of the pure products. This may be caused by the similar solubilities expected for the hydrolysis side-products identified and the phosphonium compounds sought, in view of their repeated appearance in the same reaction product phase.

^1H NMR Spectra. Representative ^1H NMR spectra are shown in Figure 1. A summary of assigned chemical shifts is given in Tables IV, V, and VI for the n-propylamino, isopropylamino and benzylamino series of phosphonium compounds, respectively. These tables include the results from a previous report[3] on the tetrakis(amino)phosphonium compound series, for comparison purposes. All the spectra were obtained in $CDCl_3$. In order to determine the N—H shift, D_2O was added to each $CDCl_3$ solution to promote a H—D exchange.[15] This exchange resulted in a decrease or disappearance of the N—H peak in each case, as illustrated clearly in Figure 1(bottom).

A clear trend can be observed for the N—H chemical shift within each of the three series presented in Tables IV, V and VI. The $\delta(^1H)$ value for the amino proton increases with an increase in the number of phenyl groups bonded to the central phosphorus atom. The $\delta(^1H)$ values expected for the respective alkyl amines would be in the range 0.5 to 3.5 ppm. The $\delta(^1H)$ values expected for aromatic amines are in the range 2.9 to 4.8 ppm.[15] Even in the absence of phenyl groups

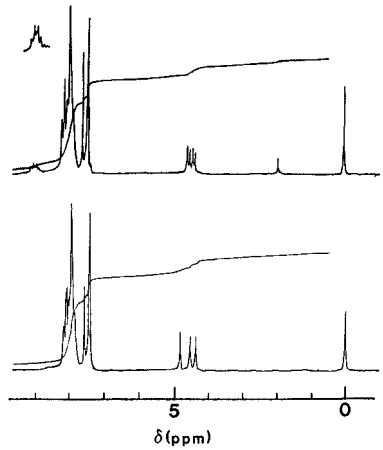


FIGURE 1 ^1H NMR spectrum obtained for $(C_6H_5CH_2NH)(C_6H_5)_3P^+Br^-$ in $CDCl_3$ (top) and in $CDCl_3$ + D_2O (bottom).

TABLE IV

Summary of ^1H NMR results $(n\text{-}C_3H_7NH)_{4-n}(C_6H_5)_nP^+X^-$ $\delta(^1H)$ in ppm[a]

Peak	n = 0	n = 1	n = 2	n = 3
N-H	5.0 (M)	5.2 (B,M)	6.3 (M)	7.7 (B)
CH_2(N)	2.9 (M)	2.9 (M)	2.9 (M)	2.9 (M)
CH_2(C)	1.4 (M)	1.4 (M)	1.65 (M)	1.8 (M)
CH_3(C)	0.9 (T)	0.9 (T)	0.8 (T)	0.9 (T)
C_6H_5(P)	-	7.3-8.0 (B)	7.4-7.9 (B)	7.7 (B)

a. All values obtained with respect to TMS, used as the internal reference standard.

B: Broad; M: Multiplet; T: Triplet.

bonded to phosphorus, the δ(N—H) values shown in Tables IV, V and VI fall in the range typical of aromatic amines. These may be explained by considering that the P(V) cation withdraws electron density from the nitrogen to which it is bonded, resulting in a deshielded signal for the N—H proton with respect to the corresponding free amine.

Moreover, as the number of phenyl groups bonded to the P(V) cation increases, deshielding of the N—H proton should also increase, resulting in the values observed and given in Tables IV–VI.

Hydrogen bonding of the type N—H $\cdots$ X^-, proposed earlier,[3] should also be of importance in determining δ(N—H). If present to a significant extent in this compound, it would be expected to cause a more deshielded proton signal. How-

TABLE V

Summary of ^1H NMR results $(i\text{-}C_3H_7NH)_{4-n}(C_6H_5)_nP^+X^-$ $\delta(^1H)$ in ppm[a]

Peak	n = 0	n = 1	n = 2	n = 3
N-H	4.8 (M)	5.4 (M)	6.4 (M)	7.7 (B,M)
CH(N)	3.3 (M)	3.3 (M)	3.3 (M)	3.1 (M)
$CH_3(C)$	1.2 (D)	1.2 (D)	1.3 (D)	1.3 (D)
$C_6H_5(P)$		7.4-8.0 (B)	7.4-7.9 (B)	7.7 (B)

a. All values obtained with respect to TMS, used as the internal reference standard.

B: Broad; D: Doublet; M: Multiplet; T: Triplet.

TABLE VI

Summary of ^1H NMR results $(C_6H_2CH_2NH)_{4-n}(C_6H_5)_nP^+X^-$ $\delta(^1H)$ in ppm[a]

Peak	n = 0	n = 1	n = 2	n = 3
N-H	5.0 (M)	6.0 (M)	7.0 (B)	9.0 (M)
	5.2 (B)[b]			
CH_2	4.0 (DD)	4.1 (DD)	4.1 (B)	4.4 (DD)
	3.8 (DD)[b]			
$C_6H_5(C)$	7.5 (S)	7.5 (S)	7.5-7.8 (B)	7.4 (D)
$C_6H_5(P)$	-	7.3 (M)	7.5-8.1 (B)	8.0 (M)

a. All values obtained with respect to TMS, used as the internal reference standard.

b. Phosphonium Iodide in CCl_4, obtained from reference 3.

B: Broad; D: Doublet; M: Multiplet; DD: Doublet of doublets; S: Singlet.

ever, within the series of compounds studied here the largest effect on the $\delta(^1H)$ values for N—H protons is suggested to be a consequence of the sizable electronic and structural changes induced by the subsequent replacement of each amino substituent by a phenyl group.

The rest of the chemical shift values presented in Tables IV–VI are consistent with the tetrahedral cation structure proposed earlier[3] for these types of compounds,

and are shown to support and complement the structural evidence obtained by ^{31}P NMR. More specifically, and an ideal example for structural evidence, the spectra shown in Figure 1, obtained for a benzylamine derivative may be briefly discussed. In this figure the multiplet corresponding to N—H appears at ca. 9.0 ppm (a), but its signal disappears in the presence of D_2O (b). A most interesting feature is the set of peaks appearing at ca. 4.4 ppm due to splitting of the $=CH_2$ protons by the P—N—H group, giving rise to a doublet of doublets. Each doublet originates from coupling to N—H and N—P, respectively. Further proof is obtained by examining spectrum (b). The H—D exchange has caused the disappearance of the N—H peak, and also its coupling to the CH_2 protons. Only splitting due to CH_2—N—P coupling is observed in this case for the doublet appearing at ca. 4 ppm.

Similar spectra are obtained for the related (benzylamino)phenyl-substituted phosphonium compounds belonging to the n = 0, 1, and 2 series described earlier, as summarized in Table VI, where a pronounced variation in δ(N—H) can be noticed.

Conclusion

The synthesis and properties of three series of substituted aminophosphonium compounds, $(RNH)_{4-n}Ph_nP^+X^-$, where n = 1, 2, 3, have been investigated.

Hydrolysis of partially substituted intermediates and unreacted starting materials have been found as the main reasons causing the low yields observed for several of the described synthesis reactions.

Spectroscopic results (^{31}P and ^1H NMR) suggest these compounds are very similar in structure to the well known phosphonium salts, $R_4P^+X^-$, and consist of a substituted tetrahedral phosphorus cation interacting electrostatically with an anion (halide or Ph_4B^-).

EXPERIMENTAL

Starting Materials. Benzene, barium oxide, n-propylamine, isopropylamine and n-butylamine were obtained from Fisher Scientific. Deuterochloroform was obtained from Norell, Inc. Acetone, acetonitrile, aniline, benzaldehyde, bromine, chloroform and sodium hydroxide were obtained from J. T. Baker Chemical Co. d,l-sec-Butylamine and triphenylphosphine were obtained from Matheson, Coleman and Bell. d,l-Alphamethylbenzylamine, isoamylamine, cyclohexylamine, n-heptylamine and n-hexylamine were obtained from the Eastman Kodak Co. Benzylamine, anhydrous calcium chloride and phosphorus pentoxide were obtained from Mallinckrodt, Inc. All starting materials used were of reagent grade quality, unless otherwise specified.

General Procedures. Solvents were dried over anhydrous calcium chloride for several days prior to their use. Amines were stored over sodium hydroxide for several days, and were subsequently distilled from fresh sodium hydroxide and collected over barium oxide. All other reagents were used as received. Reactions were carried out under a stream of nitrogen gas passed through a $CaCl_2$ drying tube, an H_2SO_4 gas-washing bottle and a P_2O_5 drying tube.

Measurements. Phosphorus (^{31}P) NMR spectra were recorded on a Varian XL-100 FT spectrometer coupled to a Nicolet Multi-Observe Nuclei Accessory (MONA) unit (23.5 KG, 40.5 MHz). Several measurements were performed on an IBM 200 spectrometer. H_3PO_4 (85%) was used as an external reference (in a concentric tube) for all ^{31}P NMR measurements. The chemical shifts are listed as positive downfield and negative upfield with respect to the phosphoric acid reference peak (0.0 ppm). Proton (^1H) NMR spectra were recorded on a Varian EM 360 spectrometer, operating at 60 MHz, and also on a Varian XL-100 FT spectrometer, operating at 100 MHz. Tetramethylsilane was used as an internal reference while deuterochloroform was used as solvent and internal lock. Mixtures of $CDCl_3$ and other

solvents such as EtOH, CH_3OCH_3, C_6H_6, and CH_2Cl_2, were used for those compounds which were insoluble in pure $CDCl_3$.

IR spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer using both CCl_4 and Nujol mulls to obtain solution and solid state spectra, respectively.

Melting points were obtained using an Electrothermal melting point apparatus, and are not corrected. Elemental analyses were performed by Dr. F. Kasler, Department of Chemistry, University of Maryland.

Reactions of primary amines with $[PhX_3P]^+Br^-$. Synthesis of tris(alkylamino/arylamino)phenylphosphonium compounds $(RNH)_3(C_6H_5)PX$ (R = n-C_3H_7 (**1**), i-C_3H_7 (**2**), n-C_4H_9 (**3**), s-C_4H_9 (**4**), n-C_6H_{13} (**5**), c-C_6H_{11} (**6**), $C_6H_5CH_2$ (**7**), C_6H_5 (**8**)). These substituted aminophosphonium compounds were prepared similarly. The typical procedure described below is for **6**. The reaction apparatus included two side-arm addition funnels, a thermometer, and a condenser fitted with an anhydrous $CaCl_2$ drying tube outlet. A solution of 13.2 ml (0.1 mol) $(C_6H_5)PCl_2$ in benzene (250 ml) was stirred inside a 500 ml round bottom flask under a stream of dry nitrogen gas. A second solution containing 5 ml (0.1 mol) Br_2 in benzene (35 ml) was added dropwise from a small side-arm addition funnel. Immediate formation of a yellow-orange solid and a yellow solution was observed, presumably indicating the formation of $(C_6H_5)Cl_2PBr_2$. Once the Br_2 addition was completed, a third solution containing 73 ml (0.6 mol) cyclohexylamine in benzene (60 ml) was added very slowly from a second addition funnel fitted with a dry nitrogen gas inlet. Upon completion of the last addition step the resulting solution was allowed to reflux for two hours. During initial heating of this final solution a color change (dark to light yellow) was observed while the yellow-orange solid that formed with the Br_2 addition redissolved entirely. After the reflux period, and upon cooling to room temperature a white solid was separated from the rest of the light yellow solution by vacuum filtration. This white solid product contained no phosphorus (no ^{31}P NMR signal was observed) and was assumed to be the corresponding ammonium halide salt by-product. The remaining solution was evaporated to yield a brown oil. Upon treatment and recrystallization with acetone, a white solid (24.7 g) was obtained. The approximate reflux periods were 2 h for **5**, 3 h for **8**, 4 h for **1** and **4**, 8 h for **3**, and 10 h for **2** and **7**. All addition steps were performed at room temperature. Benzene was used as the solvent in all experiments. Compounds **6** and **8** were recrystallized from acetone, compound **4** from acetone-ethyl acetate, compound **2** from acetonitrile, and compound **7** from methanol-water. **1**: oil; ^{31}P NMR 35.2 ppm. No anal. obtained. Soluble in chloroform, acetone, ethanol and methanol. Partially soluble in benzene, acetonitrile and water. Insoluble in carbon tetrachloride and ether. **2**: yield 89%; m.p. 138–140°C; ^{31}P NMR 29.2 ppm. Anal. calcd for $C_{15}H_{29}BrN_3P$: C, 49.73; H, 8.07; N, 11.60. Found: C, 50.65; H, 8.48; N, 11.87. Soluble in chloroform, ethanol, methanol, and N,N-dimethylformamide. Partially soluble in benzene, methylene chloride, acetone, acetonitrile and water. Insoluble in carbon tetrachloride and ether. **3**: oil; ^{31}P NMR 35.0 ppm. No anal. obtained. Soluble in chloroform, ethanol and methanol. Partially soluble in benzene, acetone and acetonitrile. Insoluble in water. **4**: yield 74%; m.p. 102–104°C; ^{31}P NMR 29.5 ppm. Anal. calcd for $C_{18}H_{35}BrN_3P$: C, 53.46; H, 8.72; N, 10.39. Found: C, 53.75; H, 8.95; N, 10.34. Soluble in carbon tetrachloride, chloroform, methylene chloride, acetone, ethanol, methanol, N,N-dimethylformamide and acetonitrile. Partially soluble in benzene and water. Insoluble in ether. **5**: oil; ^{31}P NMR 35.1 ppm. No anal. obtained. Soluble in acetone, ethanol, methanol and acetonitrile. Partially soluble in benzene. Insoluble in water. **6**: yield 51%; m.p. 205°C; ^{31}P NMR 29.0 ppm. Anal. calcd for $C_{24}H_{41}PBrN_3P$: C, 59.74; H, 8.56; N, 8.71. Found: C, 60.04; H, 8.70; N, 8.94. Soluble in carbon tetrachloride, chloroform, methylene chloride, ethanol, methanol and N,N-dimethylformamide. Partially soluble in benzene and acetonitrile. Insoluble in ether, acetone and water. **7**: yield 52%; m.p. 170°C; ^{31}P NMR 36.6 ppm. Anal. calcd for $C_{27}H_{29}BrN_3P$: C, 64.04; H, 5.77; N, 8.30. Found: C, 63.75; H, 5.77; N, 8.31. Soluble in ethanol and methanol. Partially soluble in chloroform. Insoluble in carbon tetrachloride, benzene, ether, acetone, acetonitrile and water. **8**: yield 48%; m.p. 259–261°C; ^{31}P NMR 20.3 ppm. Anal. calcd for $C_{24}H_{23}BrN_3P$: C, 62.09; H, 4.99; N, 9.05. Found: C, 64.35; H, 5.10; N, 9.25. Soluble in N,N-dimethylformamide. Partially soluble in chloroform, methylene chloride, ethanol, methanol, acetonitrile and water. Insoluble in carbon tetrachloride, benzene and ether.

Reactions of primary amines with $[Ph_2X_2P]^+Br^-$. Synthesis of Bis(alkylamino/arylamino)diphenylphosphonium compounds $(RNH)_2(C_6H_5)_2PX$ (R = n-C_3H_7 (**9**), i-C_3H_7 (**10**), n-C_4H_9 (**11**), s-C_4H_9 (**12**), n-C_6H_{13} (**13**), c-C_6H_{11} (**14**), $C_6H_5CH_2$ (**15**)). Compounds of this series were prepared similarly to **6**, described above, using $(C_6H_5)_2PCl$ instead of $(C_6H_5)PCl_2$ as a starting material. The approximate reflux periods were 6 h for **9**, **10** and **15**; 7.5, 4, 11 and 20 h for **11**, **12**, **13** and **14**, respectively. Benzene was used as the solvent in all experiments. Compound **9** was recrystallized from a mixture of ethanol-ethyl acetate, compounds **10** and **14** from acetonitrile. All other compounds were obtained as oils. **9**: yield 63%; m.p. 158–159°C; ^{31}P NMR 38.2 ppm. Anal. calcd for $C_{18}H_{26}BrN_2P$: C, 56.70; H, 6.87; N, 7.35. Found: C, 56.95; H, 7.00; N, 7.26. Soluble in chloroform, ethanol, methanol and water. Insoluble in benzene. **10**: yield 75%; m.p. 208–210°C; ^{31}P NMR 34.7 ppm. Anal. calcd for $C_{18}H_{26}BrN_2P$: C, 56.70;

H, 6.87; N, 7.35. Found: C, 57.98; H, 7.20; N, 7.60. Soluble in chloroform, ethanol, and methanol. Partially soluble in acetonitrile. Insoluble in benzene. **11**: oil. ^{31}P NMR 39.9 ppm. No anal. obtained. Soluble in chloroform, ethanol and methanol. Partially soluble in acetone, acetonitrile and water. Insoluble in benzene and ether. **12**: oil. ^{31}P NMR 36.7 ppm. No anal. obtained. Soluble in chloroform, ethanol and methanol. Partially soluble in acetonitrile. Insoluble in benzene. **13**: oil. ^{31}P NMR 38.8 ppm. No anal. obtained. Soluble in chloroform, ethanol and methanol. Partially soluble in benzene and acetonitrile. Insoluble in water. **14**: yield 87%; m.p. 196–200°C; ^{31}P NMR 35.7 ppm. Anal. calcd for $C_{24}H_{34}BrN_2P$: C, 62.48; H, 7.43; N, 6.07. Found: C, 54.29; H, 8.30; N, 7.40. Soluble in ethanol and methanol. Partially soluble in acetonitrile. Insoluble in benzene and acetone. **15**: oil. ^{31}P NMR 39.9 ppm. Anal. calcd for $C_{26}H_{26}BrN_2P$: C, 65.41; H, 5.49; N, 5.87. Found: C, 64.02, H, 5.63; N, 5.07. Soluble in ether, ethanol and methanol. Partially soluble in benzene and acetonitrile. Insoluble in water.

Reactions of primary amines with $[Ph_3XP]^+Br^-$. Synthesis of (alkylamino/arylamino)triphenylphosphonium bromides $(RNH)(C_6H_5)_3PBr$ (R = n-C_3H_7 (**16**), i-C_3H_7 (**17**), n-C_4H_9 (**18**), s-C_4H_9 (**19**), n-C_6H_{13} (**20**), c-C_6H_{11} (**21**), $C_6H_5CH_2$ (**22**), C_6H_5 (**23**)). Compounds of this series were prepared as described for **6**, above, using $(C_6H_5)_3P$ as the starting phosphine. The approximate reflux period was 6 h for all reactions. Benzene was used as the solvent in all experiments. Compound **16** was recrystallized from water, compounds **17** and **21** from acetonitrile, **18** from acetone, **22** and **23** from chloroform-ether. **16**: yield 90%; m.p. 182–184°C; ^{31}P NMR 38.2 ppm. Anal. calcd for $C_{21}H_{23}BrNP$: C, 63.01; H, 5.79; N, 3.50. Found: C, 60.71; H, 5.66; N, 3.29. Soluble in chloroform, acetone, ethanol, methanol, DMF and acetonitrile. Partially soluble in benzene, dichloromethane and water. Insoluble in carbon tetrachloride and ether. **17**: yield 52%; m.p. 237–240°C; ^{31}P NMR 36.2 ppm. Anal. calcd for $C_{21}H_{23}BrNP$: C, 63.01; H, 5.79; N, 3.50. Found: C, 62.94; H, 5.71; N, 3.37. Soluble in chloroform, methylene chloride, ethanol, methanol and N,N-dimethylformamide. Partially soluble in carbon tetrachloride, acetonitrile and water. Insoluble in benzene, ether and acetone. **18**: no information on yield due to only partial crystallization of oil obtained as product; m.p. 140–142.5°C; ^{31}P NMR 38.2 ppm. Anal. calcd for $C_{22}H_{25}BrNP$: C, 63.78; H, 6.08; N, 3.38. Found: C, 64.26; H, 6.07; N, 3.33. Soluble in chloroform, acetone, ethanol and methanol. Partially soluble in benzene. Insoluble in ether and water. **19**: oil; ^{31}P NMR 36.8 ppm. No anal. obtained. Soluble in chloroform, methylene chloride, acetone, ethanol and methanol. Partially soluble in ether. Insoluble in benzene and water. **20**: oil; ^{31}P NMR 38.3 ppm. No anal. obtained. Soluble in benzene, chloroform, acetone and acetonitrile. Partially soluble in ether. **21**: yield 48%; m.p. 118–120°C; ^{31}P NMR 36.1 ppm. Anal. calcd for $C_{24}H_{27}BrNP$: C, 65.45; H, 6.18; N, 3.18. Found: C, 63.21; H, 7.23; N, 4.59. Soluble in benzene, chloroform, methylene chloride, ethanol, methanol and N,N-dimethylformamide. Partially soluble in acetone and acetonitrile. Insoluble in carbon tetrachloride, ether and water. **22**: yield 65%; m.p. 193–195°C; ^{31}P NMR 39.2 ppm. Anal. calcd for $C_{25}H_{23}BrNP$: C, 66.98; H, 5.17; N, 3.12. Found: C, 66.51; H, 4.99; N, 3.23. Soluble in ethanol, methanol, N,N-dimethylformamide and water. Partially soluble in carbon tetrachloride, benzene, chloroform, methylene chloride, acetone and acetonitrile. Insoluble in ether. **23**: yield 82%; m.p. 201–202°C; ^{31}P NMR 33.4 ppm. Anal. calcd for $C_{24}H_{21}BrNP$: C, 66.37; H, 4.87; N, 3.22. Found: C, 65.05; H, 4.73; N, 2.98. Soluble in methylene chloride, ethanol, methanol, N,N-dimethylformamide and acetonitrile. Partially soluble in benzene, chloroform, acetone and water. Insoluble in carbon tetrachloride and ether.

Reactions of $(s\text{-}C_4H_9NH)(C_6H_5)_3PBr$, **19**, *an oil, with* $NaB(C_6H_5)_4$. Synthesis of $(s\text{-}C_4H_9NH)(C_6H_5)_3PB(C_6H_5)_4$ (**24**). Several milliliters of oil **19** were dissolved in ethanol with stirring. A second solution of $NaB(C_6H_5)_4$ in ethanol-water was added to the former insuring an excess of moles of boron over moles of phosphonium bromide. After several hours of stirring and heating to reflux, a large amount of white solid had appeared. Recrystallized from ethanol-water. **24**: m.p. 175°C (dec); ^{31}P NMR 36.8 ppm. Anal. calcd for $C_{46}H_{45}BNP$: C, 84.52; H, 6.94; N, 2.14. Found: C, 80.25; H, 6.63; N, 1.92.

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