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The Reactions of Tri-*n*-butylphosphine with Haloarsines[1]

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The reactions of tri-*n*-butylphosphine with various haloarsines have been investigated. Some of these reactions lead to the formation of compounds containing As–As bonds. Other haloarsines react with tri-*n*-butylphosphine to form crystalline 1:1 addition compounds which have been shown to be arsinophosphonium halides. The new compounds obtained have been characterized by analytical, infrared, nuclear magnetic resonance, and conductivity data.

Introduction

The reactions of chloramine and dimethylchloramine, with various tertiary phosphines including tri-*n*-butylphosphine, have been investigated in detail in our laboratories.[2–6] In general, aminophosphonium chlorides are the products of these reactions. Similarly, in the majority of the published cases, compounds having a >P–X or an >As–X bond, where X is a halogen, react with tertiary phosphines resulting, except for tri-*n*-butylphosphine, in the formation of biphosphonium[7] and arsinophosphonium[8] halides, respectively. In contrast to these reactions, three interestingly different reactions of chlorophosphines with tri-*n*-butylphosphine were reported in a recent publication from this laboratory.[9] In these cases, tri-*n*-butylphosphine extracts chlorine atoms from chlorophosphines to form dichlorophosphoranes and products containing P–P bonds, as in

$$2(C_6H_5)_2PCl + (C_4H_9)_3P \longrightarrow (C_6H_5)_2P\text{–}P(C_6H_5)_2 + (C_4H_9)_3PCl_2 \quad (1)$$

$$4(C_6H_5)PCl_2 + 4(C_4H_9)_3P \longrightarrow (C_6H_5P)_4 + 4(C_4H_9)_3PCl_2 \quad (2)$$

$$2PCl_3 + 3(C_4H_9)_3P \longrightarrow 2P + 3(C_4H_9)_3PCl_2 \quad (3)$$

These reactions provide quick and simple methods of preparation of compounds containing P–P bonds.

It was of interest to examine the reactions of tri-*n*-butylphosphine with a variety of haloarsines which might provide a simple method for the synthesis of As–As bonded compounds. We have also looked for the parameters which determine the course of these reactions and which might offer information concerning their mechanisms.

The results of this investigation show that the formation of As–As bonds occurs in a few reactions of haloarsines with tri-*n*-butylphosphine; however, many haloarsines react with tri-*n*-butylphosphine to give crystalline 1:1 adducts. The new compounds obtained have been characterized by elemental analysis, electrical conductance, and infrared and nuclear magnetic resonance spectrometry.

Experimental Section

All operations were conducted in a moisture-free, oxygen-free, nitrogen atmosphere.

Materials.—Tri-*n*-butylphosphine from Peninsular ChemResearch, Inc., was fractionally distilled and the fraction boiling at 60–61° (1.2 mm) was used. Diphenylchloroarsine and methyldichloroarsine were obtained from K & K Laboratories, Inc. Phenyldichloroarsine, phenyldiiodoarsine, and methyldiiodoarsine were supplied by Peninsular ChemResearch, Inc. Dimethyliodoarsine,[10] dimethylchloroarsine,[11] and diphenyliodoarsine[12] were synthesized by previously reported procedures. The purities of these haloarsines were checked by comparing their boiling or melting points with the reported values. Dimethyliodoarsine boiled at 153–157°, the reported boiling range being 154–157°.[10] The boiling point of dimethylchloroarsine was 106–107°, as reported in the literature.[11] Diphenyliodoarsine melted at 41°, which compares well with the reported value 40.5°.[12] The proton magnetic resonance spectra of these haloarsines showed only the expected signals.

Analyses and Ir and Nmr Spectra.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories. Analytical and melting point data are reported in Table I. The infrared spectra were recorded with a Beckman Model IR-10 infrared spectrometer. The spectra of the solids were taken either in the form of pressed KBr pellets or in the form of Kel-F mulls for the range 2.5–7.5 μ and as Nujol mulls for the range 7.5–20 μ using KBr plates. Proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer. The proton magnetic resonance spectra of liquids were run as pure samples with tetramethylsilane (TMS) as internal standard and those of solids were determined in solution in deuteriochloroform with TMS as internal standard.

Conductance Data.—The equivalent conductances were determined in nitromethane solution at 25°, using a Serfass conductivity bridge, Model RCM-15B1. These data are presented in Figure 1.

Reaction of Diphenylchloroarsine with Tri-*n*-butylphosphine. Diphenylchloroarsine (0.0126 mol) was mixed with 0.064 mol of tri-*n*-butylphosphine. The exothermic reaction resulted in a viscous, homogeneous liquid which, on standing for 4 days, solidified to a thick mass. The solid mass was transferred to a filter, washed with diethyl ether, and dried under vacuum. A portion of this material was recrystallized from hot petroleum ether (ligroin, bp 60–110°) to yield white needles which melted sharply at 128–129°. The proton magnetic resonance spectrum of this compound in deuteriochloroform showed only phenyl proton signals, the highest peak being at τ 2.78 and no butyl group peaks. The melting point reported for tetraphenyldiarsine

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[1] This research was reported in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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TABLE I

ANALYTICAL AND MELTING POINT DATA

Compound	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% P Calcd	% P Found	% As Calcd	% As Found	% Cl or I Calcd	% Cl or I Found
$(C_6H_5)_2As\text{–}As(C_6H_5)_2$[a]	128–129	62.90	63.00	4.40	4.55			32.70	32.50		
$[(C_4H_9)_3P\cdot As(CH_3)_2]I$[b]	81–82	38.72	38.79	7.66	7.73	7.13	7.24	17.26	17.19	29.23	29.46
$[(C_4H_9)_3P\cdot As(C_6H_5)Cl]Cl$[a]	80–81	50.84	50.95	7.59	7.75	7.28	7.48	17.62	17.45	16.67	16.60
$[(C_4H_9)_3P\cdot As(C_6H_5)I]I$[b]	94–96	35.55	35.29	5.30	5.25	5.09	5.26	12.32	12.11	41.74	41.58
$[(C_4H_9)_3P\cdot As(CH_3)Cl]Cl$[a]	69–70	42.99	43.31	8.33	8.50	8.53	8.62	20.63	19.80	19.52	19.85
$[(C_4H_9)_3P\cdot As(CH_3)I]I$[b]	89–90	28.59	28.67	5.54	5.61	5.67	5.54	13.72	13.43	46.48	46.49
$(C_4H_9)_3PI_2$	202–204	31.60	31.49	5.97	6.02	6.79	7.08			55.64	53.25

[a] Recrystallized from petroleum ether. [b] Recrystallized from acetonitrile.

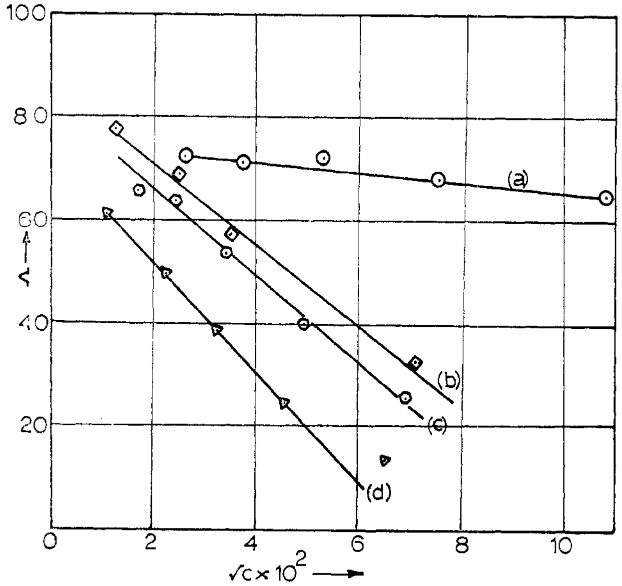

Figure 1.—Equivalent conductance of $[(C_4H_9)_3P\cdot As(CH_3)_2]I$ (a), $[(C_4H_9)_3P\cdot As(CH_3)I]I$ (b), $[(C_4H_9)_3P\cdot As(C_6H_5)Cl]Cl$ (c), and $[(C_4H_9)_3P\cdot As(CH_3)Cl]Cl$ (d) in nitromethane at 25°.

is 128–129°.[13] The elemental analysis of this material also corresponds to tetraphenyldiarsine (Table I); yield 1.25 g (43% of theory).

The presence of tributyldichlorophosphorane in the reaction products was demonstrated as follows. The ether solution and washings from the reaction were evaporated under vacuum and the residue was carefully sublimed at 120° under high vacuum. A highly hygroscopic white material was obtained on the cold finger. An alcoholic solution of the material obtained on the cold finger was added to an alcoholic solution of Reinecke's salt,[14] $NH_4[Cr(SCN)_4(NH_3)_2]\cdot H_2O$. Upon addition of water, a pink crystalline material preciptated; this material was filtered and dried under vacuum; mp 122–123°, which corresponds to the reported[15] melting point of 124–126° for the Reinecke's salt derivative of tributyldichlorophosphorane, $(C_4H_9)_3PO\cdot H[Cr(SCN)_4(NH_3)_2]$.

If the reaction mixture between tri-*n*-butylphosphine and diphenylchloroarsine is worked up in the presence of moist air, diphenylarsenic acid is obtained; this substance is known[16] to be an oxidation product of tetraphenyldiarsine.

An ethereal solution of diphenyliodoarsine reacts with tri-*n*-butylphosphine in a similar way to yield tetraphenyldiarsine.

Reaction of Arsenic Trichloride with Tri-*n* butylphosphine.—In a typical experiment, arsenic trichloride was added dropwise to tri-*n*-butylphosphine in a 2:3 mole ratio. An exothermic reaction resulted in the formation of a dark brown mass. On being shaken with acetonitrile, it became a pasty liquid from which a brown precipitate settled on standing. This dark brown powder does not melt up to 300° and does not dissolve in common organic solvents or water but reacts with nitric acid. After being washed with boiling water and being dried in the oven at 120° for 0.5 hr, it was analyzed and found to contain 89.75% As, along with 3.4% C, 0.64% H, 1.74% P, and traces of chlorine. No infrared spectrum could be recorded for this material. It is probable that the product consists of a three-dimensional network of arsenic atoms, end-stopped with alkyl groups and chlorine atoms.

The filtrate, when evaporated on the vacuum line, gave tributyldichlorophosphorane in quantitative yield; this was identified by its chlorine content (calcd, 25.95; found 25.76), its infrared spectra,[17] and the melting point of its Reinecke's salt derivative (mp 123–125°; lit.[15] mp 124–125°). The melting point of the crude tributyldichlorophosphorane was the same (134–137°) as reported in the literature;[9] however, after subliming the material twice, the melting point rose to 147–148°. The proton magnetic resonance spectrum of this compound shows three complex major bands, roughly corresponding to the area ratio 1:2:1.5 (Table II).

TABLE II

PROTON MAGNETIC RESONANCE DATA

Compound	τ_{CH_3} ±0.04	Area ratio of butyl:phenyl Calcd	Area ratio of butyl:phenyl Found	Area ratio of "butyl" resonances Calcd	Area ratio of "butyl" resonances Found
$(CH_3)_2AsCl$	8.35				
$(CH_3)AsCl_2$	7.78				
$(CH_3)_2AsI$	8.00				
$(CH_3)AsI_2$	6.87				
$[(C_4H_9)_3P\cdot As(CH_3)_2]I$	8.32			1:3:1.5	1:3.16:1.33
$[(C_4H_9)_3P\cdot As(CH_3)Cl]Cl$	7.73			1:1.33:1	1:1.40:1.12
$[(C_4H_9)_3P\cdot As(CH_3)I]I$	7.42			1:1.33:1	1:1.50:1.25
$[(C_4H_9)_3P\cdot As(C_6H_5)Cl]Cl$		5.4	5.36	1:2:1.5	1:2.15:1.4
$[(C_4H_9)_3P\cdot As(C_6H_5)I]I$		5.4	5.4	1:2:1.5	1:2.34:1.8
$(C_4H_9)_3PCl_2$				1:2:1.5	1:2.2:1.56

The reaction of arsenic triiodide dissolved in ethyl alcohol with an excess of tri-*n*-butylphosphine proceeds in an essentially similar manner. The dark brown precipitate obtained was washed with boiling water. The precipitate turned gray after drying in the oven at 120° overnight. *Anal.* Found: C, 0.51; H, 0.04; P, 1.91; I, 1.53; As, 74.6. The low percentages of elements other than arsenic indicate again that the product may be an irregular three-dimensional network of arsenic atoms, end-stopped with alkyl groups or chlorine atoms. The remaining portion of the analysis can be oxygen, which may have combined with elemental arsenic while the sample was being dried in the oven. The other product in this reaction was identified as tributyldiiodophosphorane, by making its Reinecke's salt derivative as described earlier. The derivative melted at 126–127°, which agrees well with the reported[15] melting point (124–126°) of $(C_4H_9)_3PO\cdot H[Cr(SCN)_4(NH_3)_2]$. In another experiment, when the reaction between arsenic triiodide and tri-*n*-butylphosphine was carried out in benzene, a yellowish precipitate was formed in the initial stage of the reaction, which was separated. On being washed with benzene, it became almost colorless and melted

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at 202–204°. The elemental analysis of this material corresponds to tributyldiiodophosphorane (Table I). The melting point of this material is lowered to 196–198° on recrystallization from acetonitrile. The reported melting point for tributyldiiodophosphorane is 178°,[15] which is much lower than observed in the present case. The proton magnetic resonance spectrum of this compound is identical with that of tributyldichlorophosphorane.

Reaction of Phenyldichloroarsine with Tri-*n*-butylphosphine.—Phenyldichloroarsine (0.014 mol) was added dropwise to 0.028 mol of tri-*n*-butylphosphine, resulting in an exothermic reaction. After completion of the reaction, a brownish, thick mass was obtained and was allowed to stand overnight, then filtered, washed with ether, and dried under vacuum. A portion of this material was recrystallized from hot petroleum ether, giving a white, crystalline compound which melted sharply at 80–81°. The remaining portion could be purified by subliming the material at 65–70° under approximately 1 mm pressure. An insignificant amount of dark brown residue which does not melt up to 300° was obtained. It was not characterized further. Elemental analysis of the sublimate (Table I) corresponds to the empirical formula $(C_6H_5)AsCl_2 \cdot P(C_4H_9)_3$. The area ratio of the phenyl and butyl group proton signals in the proton magnetic resonance spectrum also corresponds to the above formula. No cyclic phenylarsine was detected in the products of this reaction.

The reactions of other haloarsines with tri-*n*-butylphosphine were carried out in a similar manner and 1:1 solid crystalline adducts were obtained in all instances except that of dimethylchloroarsine. In the case of methyldiiodoarsine, which is a solid at room temperature, the reaction was carried out in ethereal solution. The yields of these 1:1 adducts varied from 60 to 94% of theory. All of these compounds are white, crystalline solids, except $[(C_4H_9)_3P \cdot As(CH_3)I]I$ and $[(C_4H_9)_3P \cdot As(C_6H_5)I]I$, which are yellow and orange, respectively.

In the case of the reaction of dimethylchloroarsine with tri-*n*-butylphosphine, a viscous liquid separated on mixing the two components in ether. Fractional distillation of the mixture gave back the reactants. The proton magnetic resonance spectrum of the viscous liquid, after evaporating the ether, shows three major complex bands which are of the same nature as observed for all 1:1 compounds and for tributyldichlorophosphorane. The observed spectrum is quite different from that of tri-*n*-butylphosphine, which shows only two major complex bands (Figure 2). The ^{31}P nmr spectrum showed a single peak at −16.2 ppm with reference to 85% phosphoric acid, which could be attributed to adduct formation, since the ^{31}P chemical shift of tri-*n*-butylphosphine is +32.3 ppm[18] and that of tributyldichlorophosphorane is −106 ppm.[19] The determination of the ^{31}P nmr spectra of numerous biphosphonium compounds of the type $[R_3PPR'_2]Cl$, where R is an alkyl and R′ an alkyl or aryl group, shows two signals in each case owing to the different natures of the two phosphorus atoms.[20] In each case the downfield signal occurs in the range −13 to −22 ppm, which is of the same order as observed in the present case (−16.2 ppm). These data indicate the formation of an adduct in solution; however, the adduct could not be isolated in the solid state.

Results and Discussion

The results obtained in the present investigation show that tri-*n*-butylphosphine reacts with various haloarsines to give two types of reactions. In one type, extraction of halogen atoms from haloarsines takes place with the formation of As–As bonded compounds as shown by

$$2(C_6H_5)_2AsX + (C_4H_9)_3P \longrightarrow (C_6H_5)_2As{-}As(C_6H_5)_2 + (C_4H_9)_3PX_2$$

$$2AsX_3 + 3(C_4H_9)_3P \longrightarrow 2As + 3(C_4H_9)_3PX_2$$

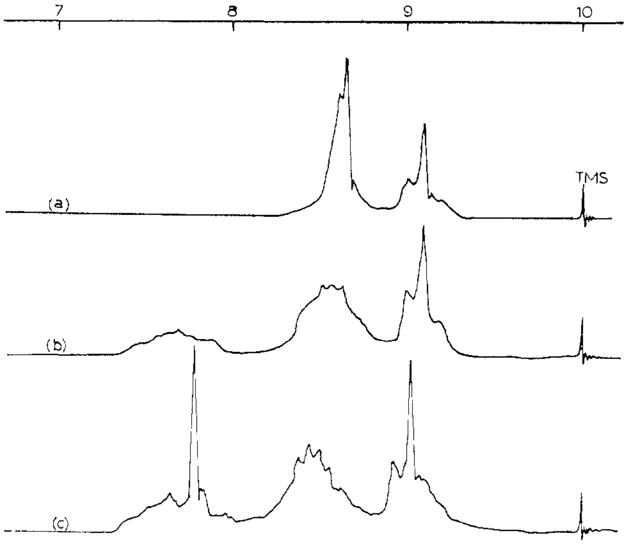

Figure 2.—Proton magnetic resonance spectra of $(n\text{-}C_4H_9)_3P$ (a), $[(C_4H_9)_3P \cdot As(C_6H_5)Cl]Cl$ (b), and $[(C_4H_9)_3P \cdot As(CH_3)Cl]Cl$ (c) in the region τ = 7.0 to 10.0.

where X = Cl or I. These reactions are analogous to those of chlorophosphines reported earlier.[9]

In the other type of reaction, the haloarsines react with tri-*n*-butylphosphine to give 1:1 addition compounds of the type $[(C_4H_9)_3P \cdot AsR_2]X$ or $[(C_4H_9)_3P \cdot AsRX]X$. Electrical conductance measurements of these compounds in nitromethane solution as shown in Figure 1 indicate that they are ionic in this solvent. As is apparent from the figure, the equivalent conductances are practically linear functions of the square roots of their molar concentrations. The value of the equivalent conductance at infinite dilution is in each case appropriate for a 1:1 electrolyte in nitromethane.[21] These reactions of tri-*n*-butylphosphine with dihaloarsines are analogous to those of tertiary phosphines with monohaloarsines, giving arsinophosphonium salts.[8] It is of particular interest to note that both diphenylhaloarsines and arsenic trihalides are reduced to tetraphenyldiarsine and elemental arsenic, respectively, on reacting with tri-*n*-butylphosphine, whereas, phenyldihaloarsines give arsinophosphonium salts. With the available data it is difficult to assess the factors determining these reactions.

The proton magnetic resonance data for the adducts, however, indicate rather strongly that they are not ionic in deuteriochloroform solution. One would expect a downfield shift of the resonances for the $-CH_3$, $-C_4H_9$, and $-C_6H_5$ groups as compared to tri-*n*-butylphosphine and the "parent" haloarsine, if these groups are contained in a cationic species. For example, methyl protons in trimethylphosphine or trimethylarsine experience a considerable downfield shift[6] on quaternization of phosphorus or arsenic as observed for $(CH_3)_4P^+I$ or $(CH_3)_4As^+I$. An examination of the chemical shift of the $-CH_3$ group in Table II and that of $-C_4H_9$ in Figure 2 in the present case indicates that there is either almost no change or an upfield shift. Infrared data on these compounds (Table III), showing

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TABLE III

INFRARED DATA (cm^{-1})[a]

$[(C_4H_9)_3P\cdot As(CH_3)_2]I$

2960 s, 2930 s, 2870 s, 1460 s, 1450 sh, 1400 w, 1385 s, 1375 sh, 1310 w, 1260 m, 1220 m, 1200 w, 1100 s, 1090 s, 1075 m, 1045 m, 910 s, 890 sh, 870 vs, 845 m, 800 s, 790 sh, 770 m, 755 m, 725 s, 715 m, 585 m, 565 m, 465 m

$[(C_4H_9)_3P\cdot As(CH_3)I]I$

2960 s, 2930 s, 2860 s, 1450 b, m, 1390 b, m, 1310 w, 1280 w, 1235 m, 1215 m, 1200 w, 1095 s, 1090 sh, 1045 w, 1002 m, 960 m, 910 s, 890 m, 850 b, m, 800 m, 750 w, 715 s, 690 m, 560 m

$[(C_4H_9)_3P\cdot As(CH_3)Cl]Cl$

2960 s, 2930 s, 2860 s, 1460 s, 1445 m, 1395 s, 1380 m, 1300 b, w, 1235 m, 1215 s, 1180 sh, 1090 s, 1000 w, 940 m, 910 m, 890 w, 850 b, m, 800 m, 755 w, 715 m, 700 sh, 565 m, 465 w

$[(C_4H_9)_3P\cdot As(C_6H_5)Cl]Cl$

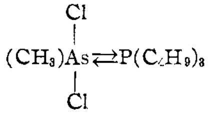
3060 b, w, 2950 s, 2930 s, 2875 s, 1460 s, 1455 sh, 1430 m, 1405 w, 1390 m, 1370 w, 1310 m, 1280 w, 1230 w, 1215 m, 1188 m, 1092 s, 1058 m, 1020 w, 997 m, 970 w, 930 w, 900 s, 800 m, 770 m, 740 vs, 720 m, 690 s, 465 m

$[(C_4H_9)_3P\cdot As(C_6H_5)I]I$

2960 s, 2930 s, 2860 s, 1460 sh, 1440 sh, 1430 b, s, 1375 b, m, 1230 w, 1200 w, 1085 s, 1062 s, 990 m, 950 w, 900 m, 780 b, m, 738 s, 718 m, 690 m, 475 sh, 460 m

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad.

almost all tri-*n*-butylphosphine vibrations unchanged or with very minor change, seem to support this result. It is possible that there may be considerable synergic bonding between the phosphorus and the arsenic atoms in these compounds, *e.g.*



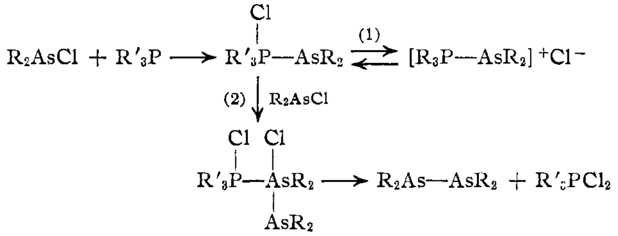
$$\mathrm{(CH_3)\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{As}}}}\rightleftarrows P(C_4H_9)_3}$$

involving the lone pairs of electrons and the empty d orbitals of the phosphorus and arsenic atoms.[22]

The proton magnetic resonance spectra of these compounds are not simple because of the presence of butyl groups. They are particularly complex in the case of methyl-substituted compounds, since the methyl proton resonance is overlapped by the butyl proton resonances. As shown in Figure 2, butyl proton resonances fall into two major bands in the case of tri-*n*-butylphosphine. However, these bands are split into three major bands in the case of arsinophosphonium compounds; *e.g.*, in the case of $[(C_4H_9)_3P\cdot As(C_6H_5)Cl]Cl$, these three bands correspond to the area ratio 1:2:1.5. In the case of methyl-substituted compounds, assuming that the methyl resonance is overlapped by one of these bands, the observed spectra can be rationalized in terms of the area ratios of the various bands, which are given in Table II.

Infrared spectra of the arsinophosphonium salts presented in Table III show almost all of the major bands of tri-*n*-butylphosphine with little or no change in the frequencies. The reported[23] characteristic band of tri-*n*-butylphosphine at 718 cm^{-1} appears almost unchanged in the arsinophosphonium compounds. Compounds having methyl substitution show the CH_3–As stretching vibration at 565 cm^{-1}, which occurs at 575 cm^{-1} in methyl-substituted arsines. The characteristic band at 1070 cm^{-1} in phenyldichloroarsine appears at 1060 cm^{-1} in the phenyl-substituted arsinophosphonium compounds. These bands in tertiary arsines are shifted to higher frequencies on "onium" salt formation and the results have been interpreted in terms of the increased strength of the As–C bonds[24] in the arsonium salts. In the present case, the shifts to lower wave numbers might mean a decrease in the strength of As–C bonds in the arsinophosphonium salts. Another band which can be readily recognized in the phenyl-substituted compounds is As–C stretch occurring at 460–465 cm^{-1}.

Among possible reaction mechanisms, including the one which assumes the attack of the phosphine on the "positive" halogen, the following seems as plausible as any



$$\mathrm{R_2AsCl + R'_3P \longrightarrow R'_3\overset{Cl}{\overset{|}{P}}{-}AsR_2 \overset{(1)}{\rightleftarrows} [R_3P{-}AsR_2]^+Cl^-}$$

$$\mathrm{(2)\ \Big\downarrow R_2AsCl}$$

$$\mathrm{R'_3\overset{Cl}{\overset{|}{P}}{-}\underset{AsR_2}{\underset{|}{\overset{Cl}{\overset{|}{As}}}}R_2 \longrightarrow R_2As{-}AsR_2 + R'_3PCl_2}$$

This mechanism assumes a pentacoordinated phosphorus as intermediate which can either proceed to form an arsinophosphonium compound or an As–As bonded compound. Reaction path 1 may be relatively more favored in the case of the reactions of a tertiary phosphine with haloarsines over those with halophosphines, because arsenic would have a somewhat lesser tendency to form the pentacoordinate intermediate than would phosphorus.

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