Although this criterion for alane extraction from tetrahydridoaluminates and borane extraction from tetrahydridoborates has not been widely investigated in transition metal compounds, it probably applies here as well. For example, contrary to published reports, bis(triphenylphosphine)tetrahydridoboratocopper(I) is unstable in pyridine and decomposes to copper metal, hydrogen, and pyridine–borane. Also attempts to prepare the very stable $[(C_6H_5)_3P]_2CuBH_4$ complex from copper hydride and pyridine–borane in the presence of phosphine were not successful.[28]

While the nature of the hydride species as a result of alane extraction is important, it is probably not the sole determining factor. If it were, the reaction of trimethylamine with $NaAlH_4$ might be expected to yield Na_3AlH_6.[29] The lack of reaction is probably best explained in terms of the ionic model for $NaAlH_4$ mentioned earlier.

Acknowledgment.—We are pleased to acknowledge partial support of this work by the National Aeronautics and Space Administration (Grant NGL 11-002-018). The authors also gratefully acknowledge interesting and helpful discussions with Professor D. F. Shriver on the infrared spectra of complex aluminum hydrides.

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Reactions of Some Trialkyls of Phosphorus, Arsenic, or Antimony with Some Organohalophosphines, -arsines, or -stibines

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Received June 30, 1969

The reactions of a series of alkyl- and arylphosphines, -arsines, or -stibines with a variety of halo- and haloalkyl- (or haloaryl-) phosphines, -arsines, or -stibines have been studied. It has been shown that in most instances the formation of adducts of the general formula $R_nMX_{3-n}\cdot yM'R'_3$ occurs and that in many instances these adducts decompose to give M–M bonded compounds plus $R'_3M'X_2$. It was further shown by electrical conductance and proton magnetic resonance data that a number of these adducts are ionic in solution.

Introduction

Reactions of the trialkyls of phosphorus, arsenic, and antimony with organohalophosphines, -arsines, and -stibines have been studied by several investigators.[1-10] In some of the reactions, adducts of the type $R_nMX_{3-n}\cdot yM'R'_3$, where $y = 1$ or 2, were obtained. In others, compounds containing M–M bonds and compounds of the type $R'_3M'X_2$ were obtained. The nature of the bonding and structure of these adducts have not been determined nor have the parameters which influence the type of product obtained.

In most instances, reactions of trialkylphosphines with diorganohalophosphines and -arsines yield stable phosphino- and arsinophosphonium salts of the type $[R_2MPR'_3]X$.[5,6,10] The reaction of triethylphosphine with diphenylchlorophosphine yields the adduct $[(C_6H_5)_2PP(C_2H_5)_3]Cl$.[6] Tri-*n*-butylphosphine, however, brings about oxidative coupling as it reacts with diphenylchlorophosphine to give tetraphenylbiphosphine and tri-*n*-butyldichlorophosphorane.[7]

Studies from this laboratory have shown that tri-*n*-butylphosphine reacts with phenyldichlorophosphine and methyldichlorophosphine to abstract chlorine and give oxidative coupling according to

$$5P(C_4H_9)_3 + 5C_6H_5PCl_2 \longrightarrow (C_6H_5P)_5 + 5(C_4H_9)_3PCl_2$$[7,11]

$$5P(C_4H_9)_3 + 5CH_3PCl_2 \longrightarrow (CH_3P)_5 + 5(C_4H_9)_3PCl_2$$[9]

However, the reactions of triethylphosphine with phenyldichlorophosphine and methyldichlorophosphine at $-20°$ give the adducts $C_6H_5PCl_2\cdot P(C_2H_5)_3$ and $CH_3PCl_2\cdot P(C_2H_5)_3$, respectively; upon warming to room temperature, these adducts decompose according to[9]

$$5C_6H_5PCl_2\cdot P(C_2H_5)_3 \longrightarrow (C_6H_5P)_5 + 5(C_2H_5)_3PCl_2$$

$$5CH_3PCl_2\cdot P(C_2H_5)_3 \longrightarrow (CH_3P)_5 + 5(C_2H_5)_3PCl_2$$

Reactions of tri-*n*-butylphosphine with organodihaloarsines yield only 1:1 adducts.[8] Attempts to convert these adducts to products containing As–As bonds by heating failed. Conductance measurements in nitromethane indicate that these adducts can best be written as $[R(X)AsP(C_4H_9)_3]X$.[8] However, in deu-

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terated chloroform, the proton magnetic resonance data were interpreted as indicating that they are nonionic.[8]

The trihalides of phosphorus, arsenic, and antimony have been found to react with the trialkyls of phosphorus, arsenic, and antimony according to[2-4,9]

$$MX_3 + yM'R_3 \longrightarrow MX_3 \cdot yM'R_3 \longrightarrow M + R_3M'X_2$$

The product represented by M contains variable amounts of halogen or other impurities and undoubtedly consists of a three-dimensional network of M atoms with some X atoms included. It is thus best considered as an impure sample of the free element. For example, phosphorus trichloride and antimony trichloride react with trimethylphosphine to give 1:2 adducts $MCl_3 \cdot 2P(CH_3)_3$. However, no adducts of trimethylstibine have been isolated; only the M–M bonded products have been obtained.[4] Holmes and Bertaut have studied a number of similar reactions and have concluded that the order of reducing strengths of the nitrogen family trimethyl compounds is: $(CH_3)_3Sb > (CH_3)_3As > (CH_3)_3P$.[4]

The purpose of the studies reported here was twofold: (1) to determine the type of bonding and general structural features of the adduct types $RMX_2 \cdot yM'R'_3$ and $MX_3 \cdot yM'R'_3$ and (2) to determine the factors influencing the stabilities of the adduct intermediates relative to the corresponding M–M bonded products.

Experimental Section

All reactants and solvents were stored and manipulated in a moisture-free, oxygen-free atmosphere provided by a Vacuum Atmosphere Model HE-43 inert-atmosphere box equipped with a Model HE-93B Dri-Train. All solvents, except the absolute ethanol, were dried and stored over calcium hydride.

Materials.—Trimethylphosphine, triethylphosphine, and methyldichlorophosphine were obtained from K & K Laboratories, tri-*n*-butylstibine and triphenylstibine were from M & T Chemicals, Inc., methyldiiodoarsine, phenyldichloroarsine, phenyldiiodoarsine, and phosphorus trifluoride were from Peninsular ChemResearch, methyldichlorophosphine was from the FMC Co., and phenyldichlorophosphine was from the Eastern Chemical Co. Trimethylarsine,[12,13] trimethylstibine,[14] triethylstibine,[12] diphenyliodoarsine,[15] dimethylchloroarsine,[16] and phenyldichlorostibine[17] were prepared as reported in the literature.

Analyses.—Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points were determined in sealed tubes using a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were recorded on a Varian Model A-60-A spectrometer. The compounds were run in deuterated chloroform, deuterated acetone, and deuterated DMSO with TMS as internal standard.

Conductance Measurements.—The specific conductances in nitromethane were measured by using an Industrial Instruments, Inc., Model RCM 15B1 Serfass conductivity bridge. A constant temperature of 25.0° was maintained by a water bath regulated by a Sargent Thermonitor, Model SW.

Reaction Procedure.—The reaction data reported in this study are presented in Table I and the analyses for the new products are presented in Table II.

Experimental procedures for most of the reactions are similar. The typical procedure consisted of weighing the trialkyl derivatives into a flask containing solvent and then adding the halogen compounds dropwise with constant stirring. The adducts were obtained either by immediate precipitation or by crystallization from solution. All of the adducts are solids. The M–M bonded products obtained when adducts could not be isolated were identified by a comparison of their physical properties, *i.e.*, melting points, infrared spectra, and nmr spectra, with the literature values of these properties. The trialkyldihalostibanes generally were not isolated, since they are all viscous oils and difficult to purify.

The reactions of tri-*n*-butylstibine with methyldichloroarsine and ethyldichloroarsine yielded in each case small amounts of a red solid and a brown solid, respectively, and a viscous yellow oil. These solids were analyzed for carbon and hydrogen, but the analyses varied significantly from preparation to preparation. The viscous oils presumably contain cyclic polyarsines, $(RAs)_5$, and tri-*n*-butyldichlorostibane, both of which are viscous liquids.

The reaction of triethylstibine and methyldichlorophosphine is exothermic. The reaction product is a viscous oil which we could not separate into its pure components. The very complex proton magnetic resonance spectra of this oil suggested that these components were triethyldichlorostibane and $(CH_3P)_5$.

In certain cases, the proton magnetic resonance spectrum of the reaction mixture was identical with the summation of the spectra of the reactants. In these cases, it was assumed that no reaction had occurred.

Conductance and Magnetic Resonance Results and Discussion

Conductivity Measurements.—Specific conductance values are listed in Table III. Only two trimethylphosphine adducts of the type $MX_3 \cdot yP(CH_3)_3$ were either sufficiently soluble or sufficiently stable in nitromethane to have their conductances measured. These were the two iodides $AsI_3 \cdot 2P(CH_3)_3$ and $SbI_3 \cdot P(CH_3)_3$. The specific conductance of the former is considerably larger than that of the latter and suggests that in solution they exist as the ionic species $[I_2SbP(CH_3)_3]I$ and $[IAs \cdot 2P(CH_3)_3]I_2$.[18] The trimethylarsine adducts $AsI_3 \cdot As(CH_3)_3$ and $SbI_3 \cdot As(CH_3)_3$ are considerably more conducting than the corresponding chlorides, $AsCl_3 \cdot As(CH_3)_3$ and $SbCl_3 \cdot As(CH_3)_3$. The latter are probably best written as molecular species in solution.

The specific conductances of adducts of the type $RMX_2 \cdot M'(CH_3)_3$ indicate that the iodides are often considerably more dissociated than are the corresponding chlorides and that the iodides probably exist as $[R(I)MM'(CH_3)_3]I$ in solution. The trimethylphosphine adducts of CH_3AsCl_2 and $C_6H_5AsCl_2$ are probably best written as $[CH_3(Cl)AsP(CH_3)_3]Cl$ and $[C_6H_5(Cl)AsP(CH_3)_3]Cl$, but the corresponding trimethylarsine adducts are best written as molecular species in solution.

Magnetic Resonance Measurements.—The proton magnetic resonance data are summarized in Tables IV and V. Unfortunately, many of the adducts of

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TABLE I

SUMMARY OF REACTION DATA FOR THE GENERAL REACTION

$R_nMX_{3-n} + yM'R'_3 \rightarrow R_nMX_{3-n} \cdot yM'R'_3 \rightarrow$ OXIDATION–REDUCTION PRODUCTS

No.	Reactants: A, R_nMX_{3-n}	Reactants: B, $M'R'_3$	A:B mole ratio	Solvent	Products (% yield)
1	PCl_3	$P(CH_3)_3$	1:2	$(C_2H_5)_2O$	$PCl_3 \cdot 2P(CH_3)_3$[a]
2	PBr_3	$P(CH_3)_3$	1:2	$(C_2H_5)_2O$	$PBr_3 \cdot 2P(CH_3)_3$ (51)[a]
3	PBr_3	$P(C_4H_9)_3$	1:3	$(C_2H_5)_2O$	Unstable adduct[a]
4	PBr_3	$P(CH_3)_3$	2:3	Neat, CH_3CN	$(CH_3)_3PBr_2$, P_x
5	PCl_3	$P(CH_3)_3$	2:3	CH_3CN	$(CH_3)_3PCl_2$, P_x
6	PF_3	$P(CH_3)_3$	1:2	Neat	White solid → brown solid[b]
7	AsF_3	$P(C_2H_5)_3$	2:3	Neat	$(C_2H_5)_3PF_2$ (90), As[c]
8	$AsCl_3$	$P(CH_3)_3$	1:2	$(C_2H_5)_2O$	$AsCl_3 \cdot 2P(CH_3)_3$ (67)[a]
9	$AsCl_3$	$P(CH_3)_3$	2:3	Neat, CH_3CN	$(CH_3)_3PCl_2$, As
10	$AsCl_3$	$P(C_2H_5)_3$	1:2	$(C_2H_5)_2O$	Unstable adduct[a]
11	SbF_3	$P(C_2H_5)_3$	2:3	Neat	$(C_2H_5)_3PF_2$ (95), Sb[d]
12	$SbCl_3$	$P(CH_3)_3$	1:2	C_2H_5OH	$SbCl_3 \cdot 2P(CH_3)_3$ (52)
13	$SbCl_3$	$P(C_2H_5)_3$	1:2	$(C_2H_5)_2O$	Unstable adduct[a]
14	SbI_3	$P(CH_3)_3$	1:2	C_2H_5OH	$SbI_3 \cdot P(CH_3)_3$ (70)
15	SbI_3	$P(C_4H_9)_3$	1:1	Acetone	Unstable adduct
16	$AsCl_3$	$As(CH_3)_3$	1:1	Neat, $(C_2H_5)_2O$, CH_3CN	$AsCl_3 \cdot As(CH_3)_3$ (60)
17	AsI_3	$As(CH_3)_3$	1:1	Neat, $C_6H_5CH_3$, CH_3CN	$AsI_3 \cdot As(CH_3)_3$ (81)
18	$SbCl_3$	$As(CH_3)_3$	1:1	C_2H_5OH	$SbCl_3 \cdot As(CH_3)_3$ (70)
19	SbI_3	$As(CH_3)_3$	1:1	C_2H_5OH	$SbI_3 \cdot As(CH_3)_3$ (80)
20	AsI_3	$Sb(CH_3)_3$	2:3	$C_6H_5CH_3$	$(CH_3)_3SbI_2$, As
21	SbI_3	$Sb(CH_3)_3$	1:1	Neat, C_2H_5OH, CH_3CN	$SbI_3 \cdot Sb(CH_3)_3$ (89)
22	SbI_3	$Sb(C_4H_9)_3$	1:1	C_2H_5OH	Unstable adduct
23	CH_3PCl_2	$As(CH_3)_3$	1:1	Neat, CH_3CN	No reaction
24	CH_3PCl_2	$As(C_4H_9)_3$	1:1	Neat	No reaction
25	CH_3PCl_2	$Sb(C_2H_5)_3$	1:1	Neat	$(CH_3P)_5$, $(C_2H_5)_3SbCl_2$
26	CH_3PCl_2	$Sb(C_6H_5)_3$	1:1	Neat	No reaction
27	$C_6H_5PCl_2$	$As(CH_3)_3$	1:1	Neat, CH_3CN	No reaction
28	$C_6H_5PCl_2$	$As(C_4H_9)_3$	1:1	Neat	No reaction
29	$C_6H_5PCl_2$	$Sb(C_2H_5)_3$	1:1	Neat	$(C_6H_5P)_5$ (87), $(C_2H_5)_3SbCl_2$
30	$C_6H_5PCl_2$	$Sb(C_4H_9)_3$	1:1	Neat	$(C_6H_5P)_5$, $(C_4H_9)_3SbCl_2$
31	CH_3AsCl_2	$P(CH_3)_3$	1:2	Acetone	$CH_3AsCl_2 \cdot P(CH_3)_3$ (83)
32	CH_3AsCl_2	$As(CH_3)_3$	1:1	Neat	$CH_3AsCl_2 \cdot As(CH_3)_3$ (56)
33	CH_3AsCl_2	$Sb(C_4H_9)_3$	1:1	Neat	Oil and red solid
34	CH_3AsI_2	$P(CH_3)_3$	1:2	C_6H_6	$CH_3AsI_2 \cdot 2P(CH_3)_3$ (87)
35	CH_3AsI_2	$As(CH_3)_3$	1:1	Neat	$CH_3AsI_2 \cdot As(CH_3)_3$ (58)
36	CH_3AsI_2	$Sb(C_2H_5)_3$	1:1	Neat	$(CH_3As)_n$ (70), $(C_2H_5)_3SbCl_2$ (85)
37	CH_3AsI_2	$Sb(C_4H_9)_3$	1:1	Neat	$(CH_3As)_n$ (85), $(C_4H_9)_3SbI_2$ (65)
38	$C_2H_5AsCl_2$	$P(CH_3)_3$	1:1	C_6H_6	$C_2H_5AsCl_2 \cdot P(CH_3)_3$ (85)
39	$C_2H_5AsCl_2$	$As(CH_3)_3$	1:1	C_6H_6	$C_2H_5AsCl_2 \cdot As(CH_3)_3$ (43)
40	$C_2H_5AsCl_2$	$Sb(C_4H_9)_3$	1:1	Neat	Oil and brown solid
41	$C_6H_5AsCl_2$	$P(CH_3)_3$	1:1	Acetone	$C_6H_5AsCl_2 \cdot P(CH_3)_3$ (98)
42	$C_6H_5AsCl_2$	$As(CH_3)_3$	1:1	$(C_2H_5)_2O$	$C_6H_5AsCl_2 \cdot As(CH_3)_3$ (35)
43	$C_6H_5AsCl_2$	$Sb(C_4H_9)_3$	1:1	Neat	$(C_6H_5As)_6$ (59), $(C_4H_9)_3SbCl_2$
44	$C_6H_5AsI_2$	$P(CH_3)_3$	1:1	Neat	$C_6H_5AsI_2 \cdot P(CH_3)_3$ (59)
45	$C_6H_5AsI_2$	$As(CH_3)_3$	1:1	Neat	$C_6H_5AsI_2 \cdot As(CH_3)_3$ (52)
46	$C_6H_5AsI_2$	$As(C_4H_9)_3$	1:1	Neat	$C_6H_5AsI_2 \cdot As(C_4H_9)_3$ (62)
47	$C_6H_5AsI_2$	$Sb(C_4H_9)_3$	1:1	Neat	$(C_6H_5As)_6$ (54), $(C_4H_9)_3SbI_2$
48	$C_6H_5SbCl_2$	$P(CH_3)_3$	1:1	$(C_2H_5)_2O$	$C_6H_5SbCl_2 \cdot P(CH_3)_3$ (71)
49	$C_6H_5SbCl_2$	$Sb(C_4H_9)_3$	1:1	Neat	See text
50	$(C_6H_5)_2PCl$	$As(CH_3)_3$	2:1	Neat, CH_3CN	No reaction
51	$(C_6H_5)_2PCl$	$As(C_4H_9)_3$	2:1	Neat	No reaction
52	$(C_6H_5)_2PCl$	$Sb(C_4H_9)_3$	2:1	Neat	$(C_6H_5)_2PP(C_6H_5)_2$ (86), $(C_4H_9)_3SbCl_2$
53	$(CH_3)_2AsCl$	$P(CH_3)_3$	1:1	Acetone	$(CH_3)_2AsCl \cdot P(CH_3)_3$ (82)
54	$(CH_3)_2AsCl$	$As(CH_3)_3$	2:1	Neat	No reaction
55	$(CH_3)_2AsCl$	$As(C_4H_9)_3$	2:1	Neat	No reaction
56	$(CH_3)_2AsCl$	$Sb(C_4H_9)_3$	2:1	Neat	$(CH_3)_2As(C_4H_9)$ (79), $(C_4H_9)_2SbCl$, $C_4H_9SbCl_2$[e]
57	$(CH_3)_2AsCl$	$Sb(C_6H_5)_3$	2:1	Neat	No reaction
58	$(C_2H_5)_2AsCl$	$As(CH_3)_3$	1:1	$(C_2H_5)_2O$	No reaction
59	$(C_6H_5I)_2AsI$	$As(CH_3)_3$	2:1	Neat, CH_3CN	No reaction
60	$(C_6H_5)_2AsI$	$As(C_4H_9)_3$	2:1	Neat	No reaction
61	$(C_6H_5)_2AsI$	$Sb(C_4H_9)_3$	2:1	$(C_2H_5)_2O$	$(C_6H_5)_2AsAs(C_6H_5)_2$ (82), $(C_4H_9)_3SbI_2$

[a] Reaction temperature −20°. [b] White solid was obtained at liquid N_2 temperature, but it decomposed to a brown, sticky solid at room temperature. [c] Refluxed 12 hr. [d] Refluxed 72 hr. [e] Refluxed 64 hr.

TABLE II
ANALYTICAL DATA

Compound	Mp, °C	Analyses, % C Calcd	C Found	H Calcd	H Found	P Calcd	P Found	As Calcd	As Found	Sb Calcd	Sb Found	Halide Calcd	Halide Found
$PBr_3 \cdot 2P(CH_3)_3$	Dec[a]	17.04	17.09	4.28	4.57	22.00	22.54					56.70	56.43
$AsCl_3 \cdot 2P(CH_3)_3$	Dec[a]	21.62	22.04	5.44	5.84	18.28	18.12	22.44	22.52			31.90	31.44
$AsI_3 \cdot 2P(CH_3)_3$	Dec[a]	11.84	11.47	2.98	3.10	10.19	10.14	12.31	12.17			62.64	62.29
$SbI_3 \cdot P(CH_3)_3$	120–128 dec	6.11	6.02	1.53	1.81	5.36	5.18					65.85	66.72
$AsCl_3 \cdot As(CH_3)_3$	Dec[a]	11.95	11.84	3.01	2.94			49.79	50.07			35.24	35.07
$AsI_3 \cdot As(CH_3)_3$	140–144 dec	6.26	6.42	1.58	1.61			26.07	26.16			66.13	66.48
$SbCl_3 \cdot As(CH_3)_3$	148–150	10.35	10.29	2.61	2.94					34.97	35.10	30.55	30.40
$SbCl_3 \cdot 2P(CH_3)_3$	162–175 dec											27.89	27.66
$SbI_3 \cdot As(CH_3)_3$	145 dec	5.81	5.99	1.44	1.45							61.15	62.78
$SbI_3 \cdot Sb(CH_3)_3$	91–92	5.38	5.20	1.36	1.48					36.38	36.33	56.97	56.76
$(C_2H_5)_3PF_2$	[Liq bp (59–61° (41 mm)]	46.20	46.46	9.68	9.82	19.87	19.94					24.23	24.05
$CH_3AsI_2 \cdot 2P(CH_3)_3$	Dec[a]	16.96	16.68	4.27	4.24	14.51	14.40	15.18	15.35			51.19	51.00
$CH_3AsCl_2 \cdot P(CH_3)_3$	Dec[a]	20.28	20.34	5.11	5.03							29.93	29.54
$C_2H_5AsCl_2 \cdot P(CH_3)_3$	Dec[a]	23.93	24.08	5.62	5.94	12.33	11.43	29.85	30.23			28.25	28.46
$C_6H_5AsCl_2 \cdot P(CH_3)_3$	115 dec	36.15	36.35	4.75	5.00							23.71	23.65
$C_6H_5AsI_2 \cdot P(CH_3)_3$	120–128	22.43	22.76	2.93	2.77							52.67	52.56
$C_6H_5SbCl_2 \cdot P(CH_3)_3$	161–165	31.26	30.93	4.08	4.10	8.95	8.74			35.21	34.94	20.50	20.45
$CH_3AsCl_2 \cdot As(CH_3)_3$	94–97	17.11	16.83	4.30	4.13								
$CH_3AsI_2 \cdot As(CH_3)_3$	108	10.35	10.58	2.61	2.65			32.29	32.17			54.70	54.95
$C_2H_5AsCl_2 \cdot As(CH_3)_3$	112	19.97	19.89	4.78	4.62			50.87	50.66			24.38	24.22
$C_6H_5AsCl_2 \cdot As(CH_3)_3$	89–95	31.53	31.82	4.12	3.65			43.74	43.71			20.71	20.80
$C_6H_5AsI_2 \cdot As(CH_3)_3$	66–79	20.25	20.56	2.34	2.68								
$C_6H_5AsI_2 \cdot As(C_4H_9)_3$	67–73	33.15	32.54	4.95	4.37							38.92	38.40
$(CH_3As)_n$	204–204.5	13.35	13.49	3.34	3.32			83.33	75.62				
$(C_2H_5)_3SbI_2$		15.58	15.76	3.27	3.24					26.31	26.10	54.82	54.47
$(CH_3)_2As(C_4H_9)$	[Liq bp 133–135° (760 mm)]	44.48	44.11	9.33	9.11			46.29	46.11	0.00	0.00	0.00	0.00
$(C_4H_9)_2SbCl + C_4H_9SbCl_2$		27.65	27.53	5.22	5.74					46.72	46.15	20.41	20.71

[a] Decomposed over a wide temperature range without melting.

TABLE III
SPECIFIC CONDUCTANCES

Adduct	Specific conductances (10^{-3} M), μmho/cm	Adduct	Specific conductances (10^{-3} M), μmho/cm
$AsI_3 \cdot 2P(CH_3)_3$	117	$C_6H_5AsCl_2 \cdot P(CH_3)_3$	38.3
$SbI_3 \cdot P(CH_3)_3$	53.7	$C_6H_5AsI_2 \cdot P(CH_3)_3$	57.2
$AsCl_3 \cdot As(CH_3)_3$	5.9	$C_6H_5SbCl_2 \cdot P(CH_3)_3$	13.7
$AsI_3 \cdot As(CH_3)_3$	58.3	$CH_3AsCl_2 \cdot As(CH_3)_3$	5.6
$SbCl_3 \cdot As(CH_3)_3$	20.4	$CH_3AsI_2 \cdot As(CH_3)_3$	50.0
$SbI_3 \cdot As(CH_3)_3$	51.8	$C_6H_5AsCl_2 \cdot As(CH_3)_3$	4.9
$CH_3AsCl_2 \cdot P(CH_3)_3$	37.8	$C_6H_5AsI_2 \cdot As(CH_3)_3$	49.1
$CH_3AsI_2 \cdot 2P(CH_3)_3$	124		

TABLE IV
PROTON MAGNETIC RESONANCE DATA

No.	Compound	Solvent	τ_{CH_3}	$\tau_{R'}$	J_{PCH_3}, cps
1	$AsI_3 \cdot 2P(CH_3)_3$	Acetone-d_6	7.88		13.1
2	$AsCl_3 \cdot As(CH_3)_3$	Acetone-d_6	8.71		
3	$SbCl_3 \cdot As(CH_3)_3$	Acetone-d_6	8.91		
4	$SbCl_3 \cdot Sb(CH_3)_3$	Acetone-d_6	7.92		
5	$(C_2H_5)_3PF_2$	$CDCl_3$		8.01, 8.84[a]	
6	$(C_2H_5)_3SbCl_2$	$CDCl_3$		7.31 triplet 8.42 quartet	
7	$(CH_3)_2AsC_4H_9$	$CDCl_3$	9.11	8.57[b]	
8	$[(CH_3)_2AsP(CH_3)_3]Cl$	DMSO-d_6	8.07	8.58	14.4
9	$Sb(CH_3)_3$	$CDCl_3$	8.91		

[a] The spectrum consists of two partially superimposed multiplets centered at these values. [b] Unresolved multiplets centered at this value.

TABLE V
PROTON MAGNETIC RESONANCE DATA OF $RMX_2 \cdot M(CH_3)_3$ ADDUCTS

No.	Compound	τ_{CH_3} $CDCl_3$	τ_{CH_3} Acetone-d_6	τ_R $CDCl_3$	τ_R Acetone-d_6	J_{PCH_3},[a] cps
1	$P(CH_3)_3$	9.02	9.04			2.0
2	$As(CH_3)_3$	9.10	9.08			
3	$C_6H_5SbCl_2 \cdot P(CH_3)_3$	8.22	*b*	1.67[d], 2.57	*b*	13.0
4	$C_6H_5AsCl_2 \cdot P(CH_3)_3$	8.04	7.96	1.83, 2.65	1.68, 2.47	13.7
5	$C_6H_5AsCl_2 \cdot As(CH_3)_3$	8.97	8.96	2.07, 2.43	1.98, 2.40	
6	$C_6H_5AsI_2 \cdot P(CH_3)_3$	7.80	7.80	1.90, 2.58	1.89, 2.66	12.6
7	$C_6H_5AsI_2 \cdot As(CH_3)_3$	8.95	8.21	2.06, 2.66	1.89, 2.59	
8	$CH_3AsCl_2 \cdot P(CH_3)_3$	7.94	7.91	7.79	7.79	13.9
9	$CH_3AsCl_2 \cdot As(CH_3)_3$	8.63	8.56	7.72	7.72	
10	$CH_3AsI_2 \cdot 2P(CH_3)_3$	7.92	*c*	7.63	*c*	13.5
11	$CH_3AsI_2 \cdot As(CH_3)_3$	8.67	8.11	7.08	7.33	
12	$C_2H_5AsCl_2 \cdot As(CH_3)_3$	8.37	8.45	7.52, 8.54	7.50, 8.57	

[a] Determined in deuterated chloroform. [b] Decomposed in deuterated acetone. [c] Resonances are obscured by the resonances of partially deuterated acetone that is present as an impurity. [d] Braces indicate two multiplets centered at the values shown.

the type $MX_3 \cdot yM'(CH_3)_3$ are insufficiently soluble in the common deuterated solvents to be studied.

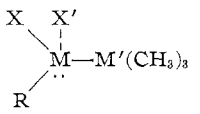
The resonances of the methyl protons of trimethylphosphine and trimethylarsine exhibit downfield shifts upon quaternization of the phosphorus and arsenic atoms.[13,19,20] For example, the methyl resonance of $As(CH_3)_3$ occurs at τ 9.10 but undergoes a downfield shift to τ 8.00 in tetramethylarsonium iodide.[13] If the adducts isolated in this study contain either quaternized phosphorus, arsenic, or antimony atoms, the methyl resonances of $M(CH_3)_3$ should be shifted to lower τ values, and the J_{PCH_3} coupling constants of the trimethylphosphine adducts should be of similar magnitude to those values observed for other phosphonium compounds. These values range from 12.0 to 14.0 cps.[13]

The proton resonance data of these adducts support

(19) S. R. Jain, W. S. Brey, and H. H. Sisler, *Inorg. Chem.*, **6**, 515 (1967).
(20) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

those structures previously assigned from the conductivity data. Downfield shifts of the methyl resonances of $P(CH_3)_3$, $As(CH_3)_3$, and $Sb(CH_3)_3$ were observed for all adducts, and the J_{PCH_3} coupling constants range from 12.6 to 13.9 cps.

The magnetic resonances of adducts of the type $RMX_2M'(CH_3)_3$ were examined in deuterated chloroform and in deuterated acetone. Generally, these resonances undergo a larger downfield shift in acetone than in chloroform. This observation can best be understood by assuming that the degree of ionization is greater in the more polar acetone than in chloroform. The general structure of an adduct of the type $RMX_2 \cdot M(CH_3)_3$ may be represented as



As X′ dissociates from M, the electron density on M decreases. As this electron density decreases, the strength of the M–M′ bond increases, resulting in a decrease of electron density on M′, and, hence, an increase in the magnitude of the downfield shift of the proton resonances of $-M'(CH_3)_3$ caused by the inductive effect of the now more electronegative M′.

A comparison of the methyl proton resonances of the trimethylphosphine and trimethylarsine adducts reveals that the phosphine resonances are shifted farther downfield than those of the corresponding arsine adducts. At least two possible explanations may be advanced for this observation. (1) It may be assumed that trimethylphosphine interacts more strongly with RMX_2 compounds than does trimethylarsine, and, hence, that there is a greater lowering of the electron density on the phosphorus atom than on the arsenic atom. (2) It may be assumed that back-donation of the lone pair of electrons on RMX_2 to a vacant d orbital on $M'(CH_3)_3$ occurs and that this effect is more important for the trimethylarsine adducts than for the trimethylphosphine adducts. Back-donation of electron density would, if it indeed occurs, result in increasing the electron density on the $M'(CH_3)_3$ moiety and would, thus, reduce the magnitude of the downfield shift.

Trimethylarsine does not react with $(C_6H_5)_2PCl$, $(C_6H_5)_2AsI$, $C_6H_5PCl_2$, or CH_3PCl_2, whereas trialkylphosphines do react with these compounds giving compounds containing M–M bonds and trialkyldihalophosphoranes. Trimethylarsine fails to form stable adducts with these halides, presumably because of the weakness of interaction between M and M′ (*vide infra*). In view of these considerations, it would seem reasonable that the greater downfield shifts of the trimethylphosphine adducts may be better explained in terms of stronger interactions between $P(CH_3)_3$ and RMX_2 than between $As(CH_3)_3$ and RMX_2, rather than in terms of differences in back-bonding.

The proton resonances of the chloride adducts might be expected to undergo larger downfield shifts than those of the corresponding iodide adducts from considerations of electronegativity differences of the halogen atoms. The greater electronegativity of chlorine than of iodine should result in the chlorine atom being more effective than iodine in lowering electron density on M of RMX_2. Thus, $RMCl_2$ is expected to interact more strongly with $M(CH_3)_3$ than RMI_2. In acetone solution, however, the methyl resonances of the iodide adducts are all shifted to lower fields than those of corresponding chloride adducts. It is interesting to note, however, that the chloride adducts are considerably less ionized than the iodide adducts, thus suggesting that the clue to this apparent paradox may be that the electronegativity effects of the halogen atoms are outweighed by the differences in the degree of ionization of the chloride and iodide adducts.

Adducts of the type $MX_3 \cdot yM'(CH_3)_3$ exhibit proton magnetic resonance spectra similar to those of the adducts just discussed. For example, the adducts $AsI_3 \cdot 2P(CH_3)_3$ and $CH_3AsI_2 \cdot 2P(CH_3)_3$ exhibit resonances at τ 7.88 and 7.92 and J_{PCH_3} of 13.1 and 13.5 cps, respectively. The adducts $AsCl_3 \cdot As(CH_3)_3$ and $CH_3AsCl_2 \cdot As(CH_3)_3$ in deuterated acetone exhibit similar τ values of 8.71 and 8.56, respectively. The proton resonances of $AsCl_3 \cdot As(CH_3)_3$ and $SbCl_3 \cdot As(CH_3)_3$ are only slightly shifted downfield in accord with the small specific conductances observed for these adducts. The methyl resonance of the adduct $SbI_3 \cdot Sb(CH_3)_3$ undergoes a considerable downfield shift to τ 7.92. From these results it may be inferred that trimethylphosphine and trimethylstibine interact more strongly with halophosphines, -arsines, and -stibines than does trimethylarsine.

The proton resonance results obtained in this study differ somewhat in their implications from previous work done in this laboratory on adducts of the type $[R(X)AsP(C_4H_9)_3]X$.[8] It was concluded in that study that in deuterated chloroform almost no change, or even an upfield shift of the butyl resonances, occurs and that these adducts are nonionic in this solvent, the positive charge on the phosphorus atom being reduced by back-donation of electron density from the arsenic atom. Whereas the results of this study have shown that smaller downfield shifts are observed in deuterated chloroform than in deuterated acetone, nevertheless, the methyl resonances of the trimethylphosphine adducts do undergo considerable downfield shifts in this solvent.

An interesting sidelight of this study is a comparison of the proton resonance spectra of triethylstibine and triethyldichlorostibane. The spectrum of triethylstibine consists of an ill-defined multiplet centered at τ 8.69, but the spectrum of triethyldichlorostibane consists of a well-defined quartet and triplet at τ 7.31 and 8.42, respectively (Figure 1).

Synthetic Results and Discussion

The studies reported herein show that

$$R_nMX_{3-n} + yM'R'_3 \xrightarrow{\text{step 1}} R_nMX_{3-n} \cdot yM'R'_3 \xrightarrow{\text{step 2}} \begin{cases}\text{oxidation–reduction}\\ \text{products containing}\\ \text{M–M bonds}\end{cases}$$

where M and M′ = P, As, or Sb; R = alkyl or aryl; R′ = alkyl; X = halogen. There is considerable difference in the various systems in the tendencies for step 2 to occur. It is reasonable to assume that the tendency for step 2 to occur depends on the relative stabilities of the initial adduct intermediates and the products of the oxidation–reduction step 2.

Reactions of the Type $MX_3 + yM'R'_3 \rightarrow MX_3 \cdot yM'R'_3 \rightarrow M + R'_3M'X_2$.—The studied reactions of nitrogen family trialkyls with nitrogen family trihalides give either adduct intermediates or the free element M (usually impure) and compounds of the type $R'_3M'X_2$. All adducts of trimethylphosphine and trihalides isolated in this study have the formula $MX_3 \cdot 2P(CH_3)_3$, except for the antimony triiodide adduct, which has the formula $SbI_3 \cdot P(CH_3)_3$.

Adducts of trimethylphosphine with phosphorus trichloride, phosphorus tribromide, or arsenic trichloride can be obtained if the reactions are run in ether at −20°. If, however, they are run in the absence of solvent or in acetonitrile at room temperature, impure elemental phosphorus or arsenic and the corresponding trimethyldihalophosphorane are obtained. The adducts that are obtained can be thermally decomposed according to

$$2[MX_3 \cdot 2P(CH_3)_3] \longrightarrow 3(CH_3)_3PX_2 + 2M + P(CH_3)_3$$

Reactions of triethylphosphine with either arsenic trifluoride or antimony trifluoride yield triethyldifluorophosphorane and the corresponding free element. The trimethylarsine adducts are all 1:1, $MX_3 \cdot As(CH_3)_3$; in no reaction studied did trimethylarsine act as a reducing agent. On the other hand, only one stable adduct of trimethylstibine was isolated, $SbI_3 \cdot Sb(CH_3)_3$. The reaction of antimony triiodide and tri-*n*-butylstibine yields an impure orange-brown solid which is probably a partially decomposed adduct.

Factors influencing the stability of the adduct relative to oxidative coupling are difficult to delineate. However, our data indicate the probable validity of the following trends. (1) The stability of the adduct increases as the size of the alkyl group R′ of $M'R'_3$ decreases. The reactions of trimethylphosphine with phosphorus trichloride and arsenic trichloride in ether at −20° yield adducts, but tri-*n*-butylphosphine reacts with these trichlorides to give tri-*n*-butyldichlorophosphorane and impure samples of the free elements.[8,9] (2) The stability of the adduct increases in the order of I > Br > Cl > F for X of MX_3. The reaction of trimethylstibine with antimony trichloride yields trimethyldichlorostibane and elemental antimony,[4] but with antimony triiodide the adduct $SbI_3 \cdot Sb(CH_3)_3$ is obtained. In ether at −20°, tri-*n*-butylphosphine reacts with phosphorus tribromide, yielding a white solid which presumably is an adduct. Unfortunately, the solid decomposed before it could be characterized. The reaction of tri-*n*-butylphosphine with phosphorus trichloride immediately gives tri-*n*-butyldichlorophosphorane and impure elemental phosphorus.[9] Triethylphosphine reacts immediately with arsenic trifluoride, yielding triethyldifluorophosphorane and elemental arsenic. (3) The stability of the adduct increases in the order Sb > As > P for M of MX_3. Antimony triiodide forms a stable adduct with trimethylstibine, but with arsenic triiodide, trimethyldiiodostibane and impure elemental arsenic are obtained. Trimethylarsine does not form a stable adduct with phosphorus trichloride but does so with arsenic trichloride. (4) The stability of the adduct decreases in the order As > P > Sb for M′ of $M'R'_3$. Only one adduct of trimethylstibine, $SbI_3 \cdot Sb(CH_3)_3$, was isolated in this study and none is reported in the literature. Arsenic trichloride forms adducts with both trimethylphosphine and trimethylarsine, but in acetonitrile, the trimethylphosphine adduct decomposes to give trimethyldichlorophosphorane and impure elemental phosphorus.

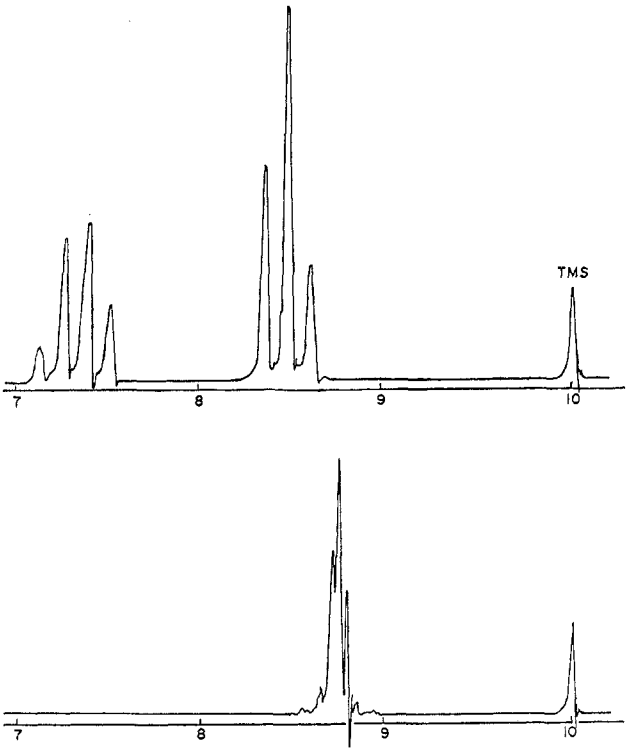


Figure 1.—The ^1H nmr spectra of (1) triethyldichlorostibane and (2) triethylstibine in the region of τ 7.0–10.0.

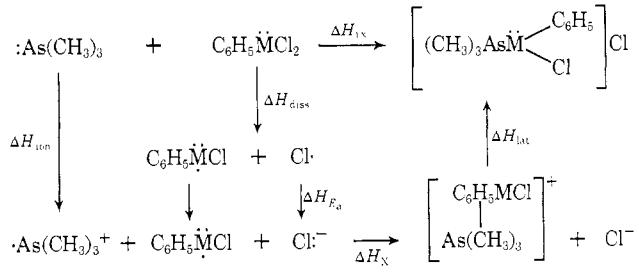
Reactions of the Types $RMX_2 + yM'R'_3 \rightarrow RMX_2 \cdot yM'R'_3 \rightarrow (1/n)(RM)_n + R'_3M'X_2$ and $R_2MX + M'R'_3 \rightarrow R_2MX \cdot M'R'_3 \rightarrow {}^1/_2R_2MMR_2 + {}^1/_2R'_3M'X_2 + {}^1/_2R'_3M'$.—All adducts of the nitrogen family trialkyls with organodihalo compounds isolated in this study have the formula $RMX_2 \cdot M'R'_3$, except the methyldiiodoarsine adduct, $CH_3AsI_2 \cdot 2P(CH_3)_3$.

Reactions of trimethylphosphine with organodihaloarsines and with phenyldichlorostibine, as well as the reactions of trialkylarsines with organodihaloarsines, yield only adducts. Trialkylarsines, however, react with neither phenyldichlorophosphine nor methyldichlorophosphine. Reactions of trialkylstibines with organodichlorophosphines and organodihaloarsines give cyclopolyphosphines and cyclopolyarsines in all reactions studied. These results are summarized in Table I.

Rationalization of the relative stabilities of adduct intermediates, relative to the formation of M–M compounds and compounds of the type $R'_3M'X_2$ or to reversion to starting materials, is a complex problem. These stabilities are undoubtedly dependent upon several parameters, and the following discussions illustrate some of the problems involved.

In no reaction studied did the trialkylarsines function as reducing agents. Trialkylstibines, on the other hand, were found to reduce the nitrogen family organodihalo compounds readily to products containing M–M bonds. The data of this study indicate that the order of the reducing strength of the nitrogen family trialkyls is $R_3Sb > R_3P > R_3As$ and not $R_3Sb > R_3As > R_3P$, as Holmes and Bertaut have reported.[4]

Reactions of trimethylarsine with halophosphines, haloarsines, or halostibines, in terms of our experience, may be expected initially to yield adducts of the type $[R_2MAs(CH_3)_3]X$ where R_2 may be X_2, R′X, or R'_2. In those instances where adducts were obtained, $-MR_2$ was Cl_2As-, I_2As-, $CH_3(Cl)As-$, $CH_3(I)As-$, $CH_3CH_2(Cl)As-$, $C_6H_5(Cl)As-$, $C_6H_5(I)As-$, Cl_2Sb-,[3] or I_2Sb-, and in those instances where no reaction occurred, $-MR_2$ was Cl_2P-,[3] $CH_3(Cl)P-$, $(C_6H_5)_2P-$, $C_6H_5(Cl)P-$, $(CH_3)_2As-$, or $(C_6H_5)_2As-$. Trimethylarsine does not react with phenyldichlorophosphine, but it forms a 1:1 adduct with phenyldichloroarsine. This difference in reactivity may be understood in terms of the following enthalpy cycle. Entropy contributions to the free energy are expected to be of similar magnitude in all systems and, therefore, can be neglected, leaving the differences in the free energy corresponding to the reactions in the two systems to be primarily a function of the changes in enthalpy



where $\Delta H_{rx} = \Delta H_{ion} + \Delta H_{diss} + \Delta H_{E_a} + \Delta H_X + \Delta H_{lat}$.

The ΔH_{ion} and ΔH_{E_a} terms are common for both the phenyldichlorophosphine and phenyldichloroarsine systems and, thus, do not affect their reactivities with trimethylarsine. In the absence of π bonding, ΔH_X is expected to be more negative for the phenyldichlorophosphine system than for the phenyldichloroarsine system. The p orbital on M of $C_6H_5MCl_2$ is more compact for phosphorus than for arsenic and, therefore, is expected to form the stronger bond with trimethylarsine. Since the cation $C_6H_5(Cl)PAs(CH_3)_3^+$ is smaller than $C_6H_5(Cl)AsAs(CH_3)_3^+$ and since lattice energy is a function of the factor $1/(r_+ + r_-)$, where r_+ and r_- are the radii of the cation and anion, respectively, the lattice energy of $[C_6H_5(Cl)PAs(CH_3)_3]Cl$ will be more negative than that of $[C_6H_5(Cl)AsAs(CH_3)_3]Cl$, and the ΔH_{lat} term for the phosphine adduct will favor the formation of this adduct over the corresponding arsine adduct. Since both the ΔH_X and ΔH_{lat} terms favor the stability of the phosphine adduct over that of the arsine adduct, the ΔH_{diss} term must be the term that determines the observed reaction behavior.

The M–Cl bond dissociation energies of phenyldichlorophosphine and phenyldichloroarsine are not available but should be of similar magnitude to the corresponding values for phosphorus trichloride (79.1 kcal/mol) and arsenic trichloride (68.9 kcal/mol).[21] This difference of approximately 10 kcal/mol may account for the difference in behavior of phenyldichloroarsine and phenyldichlorophosphine toward trimethylarsine.

The fact that arsenic trichloride and methyldichloroarsine react with trimethylarsine yielding the adducts $AsCl_3 \cdot As(CH_3)_3$ and $CH_3AsCl_2 \cdot As(CH_3)_3$ but dimethylchloroarsine fails to react is difficult to rationalize. The ΔH_{lat} terms in the energy cycles of these systems should be of similar mangitude, since methyl groups and chlorine atoms are of similar aize. The As–Cl bond dissociation energies of arsenic trichloride, methyldichloroarsine, and dimethylchloroarsine are also expected to be of similar magnitude. It would, thus, appear that the ΔH_X term may be responsible for the difference in behavior of the three systems.

An alternative explanation based on kinetic effects follows. The differences of electronegativities of the chlorine and arsenic atoms in these chloroarsines should result in the formation of partial positive charges on the arsenic atoms and partial negative charges on the chlorine atoms. As the number of chlorine atoms increases and the corresponding number of electron-releasing methyl groups decreases, the magnitude of the positive charge should increase. The greater the charge, the more susceptible to attack by trimethylarsine the arsenic atom should become. According to this approach, the failure of dimethylchloroarsine to react might be assumed to result from the arsenic atom of dimethylchloroarsine not being sufficiently positive for a successful attack by trimethylarsine.

The reaction of methyldiiodoarsine with trimethylphosphine yields the 1:2 adduct, $CH_3AsI_2 \cdot 2P(CH_3)_3$, whereas only a 1:1 adduct, $CH_3AsI_2 \cdot P(C_4H_9)_3$,[8] is obtained with tri-*n*-butylphosphine. It is possible that steric factors account for this difference. The reaction of methyldichloroarsine with trimethylphosphine yields a 1:1 adduct, $CH_3AsCl_2 \cdot P(CH_3)_3$. The failure to form a 1:2 adduct can be rationalized in terms of the As–X bond dissociation energies of the methyldihaloarsines and the lattice energies of the resulting adducts. Bond dissociation energies of methyldiiodoarsine and methyldichloroarsine are not available but should be of a magnitude similar to the corresponding values for arsenic trichloride (68.9 kcal/mol) and ar-

(21) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Oxford University Press, New York, N. Y., 1966, p 112.

senic triiodide (41.6 kcal/mol).[21] Thus it would be estimated that the difference in the As–X bond energies in the two methyldihaloarsines is approximately 27 kcal/mol. Although it is difficult to assess the parameters affecting the lattice energies of these adducts, it does seem reasonable that the lattice energy of a 1:2 adduct of methyldichloroarsine and trimethylphosphine, $[CH_3As \cdot 2As(CH_3)_3]Cl_2$, is not great enough to overcome this additional 27 kcal required for the dissociation of a second As–Cl bond. However, following this reasoning, it is surprising that the adducts of arsenic trichloride and arsenic triiodide with trimethylphosphine are both 1:2.

The reaction of methyldiiodoarsine with tri-*n*-butylstibine yields tri-*n*-butyldiiodostibane and a dark purple solid, identified by elemental analysis as $(CH_3As)_n$. The solid melts at 204–204.5° with decomposition. The products of decomposition are a red solid and a yellow oil; upon cooling, these products revert to the purple solid. The mass spectrum of this solid indicates the presence of a component of molecular weight of 450. Since the molecular weight of pentamethylcyclopentaarsine is 450 and since pentamethylcyclopentaarsine is reported to exist in both a red solid and a yellow oil modification,[22] it appears that the purple solid decomposes into these products upon melting

$$(CH_3As)_n \underset{\text{cooling}}{\overset{\text{mp}}{\rightleftharpoons}} (CH_3As)_5(l) + (CH_3As)_5(s)$$

The reaction of tri-*n*-butylstibine with dimethylchloroarsine gives dimethyl-*n*-butylarsine, a small amount of an unidentified gray solid, and a viscous liquid identified by elemental analysis as probably an equimolar ratio of di-*n*-butylchlorostibine and *n*-butyldichlorostibine. It is apparent that butyl group migration from the tri-*n*-butylstibine to the dimethylchloroarsine has occurred. The expected tetramethylbiarsine was not obtained, but when tri-*n*-butylstibine reacts with diphenyliodoarsine or diphenylchlorophosphine, the coupled products are isolated

$$Sb(C_4H_9)_3 + 2(C_6H_5)_2AsI \longrightarrow (C_6H_5)_2AsAs(C_6H_5)_2 + (C_4H_9)_3SbI_2$$

$$Sb(C_4H_9)_3 + 2(C_6H_5)_2PCl \longrightarrow (C_6H_5)_2PP(C_6H_5)_2 + (C_4H_9)_3SbCl_2$$

Butyl group migration also apparently occurs when tri-*n*-butylstibine reacts with phenyldichlorostibine. A gray solid precipitates immediately upon mixing. This solid was found by elemental analysis to contain about 85% antimony. Upon distillation of the reaction mixture after 64 hr of heating, a yellow liquid boiling at 87–89° (3 mm) was recovered. The similarity of boiling points of this yellow oil and of dibutylchlorostibine, 121–123° (10 mm),[23] suggests that it is also dibutylchlorostibine. Its proton magnetic resonance spectrum contains only butyl resonances.

The proton magnetic resonance spectrum of the residue revealed the presence of both phenyl and butyl groups with an area ratio of approximately 1:2. The phenyl proton to butyl proton ratio in phenyl-*n*-butylchlorostibine is 1:1.8. From the limited amount of data available, it is likely that the following reaction has occurred

$$Sb(C_4H_9)_3 + C_6H_5SbCl_2 \longrightarrow (C_4H_9)_2SbCl + (C_6H_5)(C_4H_9)SbCl$$

Presumably, the gray solid is a decomposition product of either dibutylchlorostibine or of both reaction products.

Acknowledgments.—We are pleased to acknowledge the support of this research by National Institutes of Health Research Project NIH-CA-08263-03 with the University of Florida. We are further pleased to acknowledge the use of materials and equipment made available through National Science Foundation Project No. GP-7863 with the University of Florida.

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