An analogous reaction apparently occurs between tris(tri-*n*-propylstannyl)amine and chloramine, since tri-*n*-propyltin chloride was isolated as a product from their interaction.

Results and Discussion

This report shows that chloramine cleaves the metal to nitrogen bonds in dimethyl(trialkylsilyl)amines, germylamines, and stannylamines apparently according to the following equations, where R = alkyl and M = Si, Ge, or Sn

$$3R_3MN(CH_3)_2 + 3NH_2Cl \longrightarrow 3R_3MCl + 3(CH_3)_2NH + NH_3 + N_2$$

$$3(R_3M)_2NH + 6NH_2Cl \longrightarrow 6R_3MCl + 5NH_3 + 2N_2 \quad (M \neq Si)$$

The trialkylsilicon chlorides could not be isolated because of their rapid reaction with ammonia. It should be noted that $[(n\text{-}C_4H_9)_3Si]_2NH$ was isolated instead of the expected $(n\text{-}C_4H_9)_3SiCl$ in the reaction of $(n\text{-}C_4H_9)_3SiN(CH_3)_2$. In the case of the germanium compounds, small yields of trialkylgermanium chlorides were isolated which may be the result of the relatively slow rates of reaction of trialkylgermanium chlorides with ammonia. In the case of the tin compounds, nearly quantitative yields of the trialkyltin chlorides were obtained because of their inertness toward ammonia under these conditions.

Tris(trimethylsilyl)amine and bis(trimethylsilyl)amine do not react with chloramine, but corresponding trialkylgermanium and trialkyltin compounds react readily with chloramine. It is tempting to propose an explanation for the inertness of these two silylamines toward chloramine in terms of reduced basicity caused by the silyl groups reducing the electron density on the nitrogen atoms through $d\pi$–$p\pi$ bonding. However the complexity of the phenomena observed in this investigation cannot easily be reconciled with such a simple interpretation. Other factors, such as bond strengths, reaction rates, and steric factors, may be important; however, large steric effects are not immediately apparent when, for example, the reactivity of $[(n\text{-}C_3H_7)_3Sn]_2NH$ and the reactivity of $[(CH_3)_3Si]_2NH$ are considered.

It was observed that chloramine readily cleaves the metal to nitrogen bonds in all three $R_3MN(CH_3)_2$ compounds where M = Si, Ge, or Sn, but the dimethylchloramine cleaves only the tin–nitrogen bond.

The nonreactivity of bis(triphenylgermyl)amine compared to the reactivity of the corresponding bis(triethylgermyl)amine with chloramine could be the result of an inductive effect of the phenyl groups.

All three silicon to phosphorus bonds in tris(trimethylsilyl)phosphine are cleaved by chloramine or dimethylchloramine.

The reaction of chloramine with dimethyl(trialkylstannyl)amines to produce 2,2-dimethyltriazanium chloride is of interest, since the product can be obtained in high yield in a pure state by simple filtration of the reaction mixture. A method for purification, which is more convenient than the previously reported method,[22] is recrystallization from hot acetonitrile.

Acknowledgment.—The support of this research by the National Science Foundation through grants No. GP-1600 and GP-4505 and the National Institutes of Health through grant No. CA-08263-03 is gratefully acknowledged.

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Reactions of Chloramine, Dimethylchloramine, and Chlorine with Arsine, Primary Arsines, and Secondary Arsines

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Received October 7, 1968

Chloramine and dimethylchloramine abstract hydrogen from As–H bonds, converting arsine, primary arsines, and secondary arsines to elemental arsenic, diarsines, and tetrasubstituted cyclopolyarsines, respectively. When used in less than stoichiometric quantities and in the presence of an HCl acceptor, free chlorine yields similar products. Secondary arsines react with aminoarsines of the type R_2AsNH_2 to yield tetrasubstituted diarsines. Several possible mechanisms for the chloramination reactions are discussed.

Introduction

During the past decade, the chloramination of amines, phosphines, and arsines has been extensively investigated in this laboratory.[1–8] Such chloramination has been shown to result, in the cases previously studied, in the formation of hydrazines or hydrazinium salts, aminophosphonium salts, and aminoarsonium salts, respectively. Trialkylstibines have been shown to react with chloramine to produce compounds of the type $[R_3Sb(Cl)]_2NH$.

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Highsmith and Sisler[9] have recently shown, however, that dimethylchloramine reacts with phosphine in a different manner, extracting hydrogen atoms from the phosphine molecule and forming phosphorus to phosphorus bonds as shown by

$$2PH_3 + 3(CH_3)_2NCl = (2/x)P_x + 3[(CH_3)_2NH_2]Cl$$

We were interested in determining if a similar reaction occurs in the chloramination of arsine and of primary and secondary arsines. We hoped that such a reaction with primary and secondary arsines would provide a new synthetic route to biarsines of the type R_2AsAsR_2 and to cyclopolyarsines of the type $(RAs)_n$.

Our thinking concerning the mechanism of this hydrogen-extraction reaction of chloramine led us to speculate that free halogens, if not in excess, should yield similar products. Reports in the literature[10-14] all dealt with studies in which the halogen was in excess and where, therefore, the products were haloarsines and hydrogen halides. The only exceptions are the reports of reactions of diphenylarsine and monophenylarsine[15,16] with iodine to yield $(C_6H_5)_2AsAs(C_6H_5)_2$ and $(C_6H_5As)_6$, respectively. To check this speculation, we have studied the reaction of less than stoichiometric quantities of chlorine with arsine and with some primary and secondary arsines in the presence of an HCl acceptor.

We have also studied the condensation of diphenylarsine with aminodiphenylarsine to form tetraphenylbiarsine.

Experimental Section

Materials.—All solvents used were reagent grade and were dried and stored over calcium hydride. Aluminum arsenide, sodium methylarsenate, and dimethylarsinic acid were obtained from K & K Laboratories. Benzenearsonic acid and triphenylarsine were obtained from Eastman Organic Chemicals. Benzaldehyde, zinc dust, mercuric chloride, and sodium hypophosphite were obtained from J. T. Baker Chemical Co. Lithium aluminum hydride was purchased from City Chemical Co. Hypophosphorous acid was obtained from Matheson Coleman and Bell.

Because of the high volatility of the arsines and their reactivity toward oxygen, many of the reactions were carried out in an all-glass vacuum line. All experimental purification work was conducted in a nitrogen atmosphere in a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-93 Dri-Train. All of the arsenic-containing starting materials were stored and transferred inside the Dri-Lab.

Analyses.—Elemental analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using the Thomas Hoover capillary melting point apparatus with an uncorrected thermometer.

Infrared Spectra.—Infrared spectra were recorded on a Beckman IR-10 spectrometer. The spectra were obtained on the solids in the form of Kel-F mulls using KBr plates for the range 2.5–7.5 μ and as Nujol mulls using CsI plates for the range 7.5–20 μ.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were measured on a Varian Model A-60A nmr spectrometer. Tetramethylsilane, chloroform, dimethyl sulfoxide, 3-(trimethylsilyl)propanesulfonic acid, and water were used as internal standards in the various instances.

Synthesis of Chloramine.—Chloramine was prepared in a generator by a completely anhydrous method developed by Mattair and Sisler.[17] In those cases where the vacuum line was utilized, ethereal solutions of ammonia-free chloramine were used. The ethereal solutions obtained by passing the effluent gases from the generator into diethyl ether were rendered free of ammonia by passing the resulting solution through a column of anhydrous copper sulfate.[18] The anhydrous copper sulfate not only removed all of the ammonia but also aided in the drying of the ethereal solution for later use on the vacuum line.

Synthesis of Dimethylchloramine.—Dimethylchloramine was prepared by a procedure analogous to the Raschig synthesis of chloramine.[19] Pure dimethylchloramine (bp 43°) was then diluted with diethyl ether to give the reagent used in these studies.

Preparation of the Arsines.—Arsine was prepared in the vacuum line by the acid hydrolysis of aluminum arsenide. The arsine formed was fractionally distilled and stored on the vacuum line. The infrared spectrum of the gas and the vapor pressure measurements on the liquid were identical with those reported for pure arsine.[20,21] Methylarsine was prepared by the reduction of sodium methylarsonate using hydrochloric acid and zinc–mercury amalgam according to the procedure described by Dehn.[11] The purity of the methylarsine was indicated by the presence in the nmr spectrum of only two sets of peaks at τ 9.02 (triplet) and 7.93 (quartet) having the area ratios of 1.54:1, corresponding to the CH_3As and AsH_2 protons, respectively. Dimethylarsine was prepared by reducing dimethylarsinic acid in the presence of a zinc–mercury amalgam and hydrochloric acid according to the procedure described by Dehn and Wilcox.[15] The purity of the dimethylarsine was indicated by the complete absence in the nmr spectrum of peaks other than the two sets of peaks at τ 8.93 (doublet) and 7.57 (heptet), corresponding to the $(CH_3)_2As$ and AsH protons, respectively. Phenylarsine, bp 104.5–105° (107 mm), was prepared by reducing benzenearsonic acid by means of a zinc–mercury amalgam and hydrochloric acid according to the procedure described by Goddard.[22] The purity of the phenylarsine was indicated by its nmr spectrum which showed only two sets of peaks at τ 2.70 and 6.44 (singlet) having the area ratio of 2.51:1, corresponding to the C_6H_5 and AsH_2 protons, respectively. Diphenylarsine was prepared by the reduction of diphenylchloroarsine with lithium aluminum hydride according to the procedure described by Wiberg and Mödritzer.[23] The procedure was modified by decomposing the alane–diphenylarsine complex with gaseous oxygen-free water before fractionally distilling the reaction products, bp 170–172° (22 mm) (lit.[22] bp 174° (25 mm)). Cyclopentamethylpentaarsine was prepared by the reaction of sodium methylarsonate and hypophosphorous acid according to the procedure described by Palmer and Scott.[24] The purity of the $(CH_3As)_5$ was indicated by its characteristic nmr spectrum.[25] The major *m/e* ratios (parenthetical numbers are the relative intensities using an arbitrary scale) observed in the mass spectrum of this compound were assignable as follows: CH_3As^+, 90 (23); $(CH_3)_2As^+$, 105 (97); $CH_3As_2^+$, 165 (33); $(CH_3)_3As_2^+$, 195 (28); As_3^+, 225 (53); $(CH_3)_2As_3^+$, 255 (100); $(CH_3)_3As_3^+$, 270 (100); $(CH_3)_4As_5^+$, 435 (25); $(CH_3As)_5^+$, 450 (42). Tetramethyldiarsine was prepared by the direct action of dimethylchloroarsine on zinc dust as described by

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TABLE I

SUMMARY OF CHLORAMINE AND DIMETHYLCHLORAMINE REACTIONS WITH ARSINES CONTAINING As–H BONDS

$$zR_{3-x}AsH_x + (xz/2)R'_2NCl \longrightarrow (R_{3-x}As)_z + (xz/2)R'_2NH_2Cl$$

A $R_{3-x}AsH_x$	B R_2NCl	Mole ratio A:B	$(R_{3-x}As)_z$	Yield, %	R'_2NH_2Cl	Yield, %	Other products	Yield, %
AsH_3	NH_2Cl	1:1.5	As	77	NH_4Cl	77	Arsenic hydrides	
AsH_3	$(CH_3)_2NCl$	1:1.5	As	66	$(CH_3)_2NH_2Cl$	66		
CH_3AsH_2	NH_2Cl	2:1	$(CH_3As)_5$	94	NH_4Cl	100		
CH_3AsH_2	$(CH_3)_2NCl$	2.3:1	$(CH_3As)_5$	85	$(CH_3)_2NH_2Cl$	96		
$(CH_3)_2AsH$	NH_2Cl	14.5:1	$(CH_3)_2AsAs(CH_3)_2$	96	NH_4Cl	100		
$(CH_3)_2AsH$	NH_2Cl	2.7:1	$(CH_3)_2AsAs(CH_3)_2$	10	NH_4Cl	100	$C_3H_{9.8}As_{1.4}NCl_{1.1}$[a]	8.6
$(CH_3)_2AsH$	$NH_2Cl + NH_3$	1:28.8	None		NH_4Cl	>100	$[(CH_3)_2AsN]_4 \cdot 2HCl$[b]	36
$(CH_3)_2AsH$	$(CH_3)_2NCl$	3.2:1	$(CH_3)_2AsAs(CH_3)_2$	45	$(CH_3)_2NH_2Cl$	46		
$C_6H_5AsH_2$	NH_2Cl	2:1	$(C_6H_5As)_6$	39	NH_4Cl	93		
$C_6H_5AsH_2$	$(CH_3)_2NCl$	3.1:1	$(C_6H_5As)_6$	90	$(CH_3)_2NH_2Cl$	90		
$(C_6H_5)_2AsH$	NH_2Cl	2.7:1	$(C_6H_5)_2AsAs(C_6H_5)_2$	92	NH_4Cl	100		
$(C_6H_5)_2AsH$	$(CH_3)_2NCl$	2.9:1	$(C_6H_5)_2AsAs(C_6H_5)_2$	87	$(CH_3)_2NH_2Cl$	100		

[a] Probably a mixture of condensation products of $[(CH_3)_2AsCl(NH_2)]Cl$. [b] Probably a mixture of hydrochlorides of $[(CH_3)_2AsN]_4$

TABLE II

SUMMARY OF CHLORINE REACTIONS WITH ARSINES CONTAINING As–H BONDS

$$zR_{3-x}AsH_x + (xz/2)Cl_2 + xz(CH_3CH_2)_3N \longrightarrow (R_{3-x}As)_z + xz(CH_3CH_2)_3NHCl$$

$R_{3-x}AsH_x$	Mole ratio $R_{3-x}AsH_x : Cl_2$	$(R_{3-x}As)_z$	Yield, %	$(CH_3CH_2)_3NHCl$ yield, %	Other products
AsH_3	1:1	As	20	19	Higher arsenic hydrides
CH_3AsH_2	2:1	$(CH_3As)_5$		58	$CH_{2.67}As_{2.14}$[a]
$(CH_3)_2AsH$	3.8:1	$(CH_3)_2AsAs(CH_3)_2$	49	73	None
$C_6H_5AsH_2$	1.3:1	$(C_6H_5As)_6$	73	96	As–Cl materials (traces)
$(C_6H_5)_2AsH$	1.3:1	$(C_6H_5)_2AsAs(C_6H_5)_2$	63	100	As–Cl materials (traces)

[a] Destructive distillation of this mixture yields some $(CH_3As)_5$.

Bunsen,[26] mp −6° (lit.[27] mp −6°). The major *m/e* ratios (parenthetical numbers are the relative intensities using an arbitrary scale) observed in the mass spectrum of this compound were assignable as follows: CH_3As^+, 90 (47); $(CH_3)_2As^+$, 105 (100); As_2^+, 150 (97); $CH_3As_2^+$, 165 (97); $(CH_3)_2As_2^+$, 180 (92); $(CH_3)_2As_2H^+$, 181 (37); $(CH_3)_3As_2^+$, 195 (off scale, ≫100); $(CH_3)_2AsAs(CH_3)_2^+$, 210 (off scale, ≫100). Hexaphenylcyclohexaarsine, $(C_6H_5As)_6$, mp 215–216° (lit.[28] melting points vary from 195 to 212°), was prepared by the reaction of phenylarsine with benzaldehyde according to the procedure described by Palmer and Adams.[29] The mass spectrum showed major *m/e* ratios at 77 and 152; the latter is assignable to $C_6H_5As^+$. Aminodiphenylarsine, mp 50–52° (lit.[30] mp 53°), was prepared by the reaction of chlorodiphenylarsine with ammonia as described by Ipatiew, Rasuwajew, and Stromski.[30]

General Procedure for Chloramination Reactions.—These reactions may be illustrated by

$$zR_{3-x}AsH_x + (xz/2)R'_2NCl \longrightarrow (R_{3-x}As)_z + (xz/2)R'_2NH_2Cl$$

The appropriate arsine was placed in a reaction flask on the vacuum line. Onto this was distilled a known volume of the ethereal chloramine solution having a known concentration.[8] The reaction mixture was then warmed to room temperature with constant stirring. After the reaction was complete (usually 1–2 hr), all volatile materials were distilled from the reaction flask. If the product was a liquid at room temperature, it was fractionally distilled on the vacuum line to obtain a pure product. If the product was solid, the reaction flask was taken into the drybox and the solid was extracted with the appropriate solvents to effect product separation and purification. The melting point, infrared spectra, and nmr spectra were compared with those of the known pure compounds to obtain product identification. The experimental details for the various chloramine and dimethylchloramine reactions are summarized in Table I.

General Procedure for Chlorination Reactions.—These reactions are illustrated by

$$zR_{3-x}AsH_x + (xz/2)Cl_2 + xz(CH_3CH_2)_3N \longrightarrow (R_{3-x}As)_z + xz(CH_3CH_2)_3NHCl$$

Onto an ethereal solution of the arsine in a reaction flask attached to the vacuum line was distilled a known volume of previously dried triethylamine. Onto this solution was condensed, with constant stirring at −76°, a measured quantity of gaseous chlorine. Reaction occurred immediately in all cases. The highly volatile components were distilled from the flask and the reaction products were treated in a manner analogous to that used in the respective chloramination reactions. The melting points, infrared spectra, and nmr spectra were compared with those of the known pure compounds in order to identify the products of the reactions. The experimental details for the various chlorination reactions are summarized in Table II.

The experimental procedures for those chloramination and chlorination reactions yielding arsenic-containing products other than, or in addition to, the expected $(R_{3-x}As)_z$ product are discussed below.

Reaction of Ammonia-Free Chloramine with Arsine.—This may be shown by

$$2AsH_3 + 3NH_2Cl = 2As + 3NH_4Cl$$

A 0.047 *M* solution (100 ml) of ammonia-free chloramine in diethyl ether was condensed onto 3.13 mmol of arsine at liquid nitrogen temperature on the vacuum line. After the reaction mixture had warmed to room temperature, it was noted that a white solid had formed. On standing at room temperature, the color of the solid slowly darkened until the solid was very dark brown and a silver-colored mirror had formed on the inside glass surface of the reaction flask. No unreacted chloramine remained. When a sample of the reaction product was extracted with boiling water, a water-insoluble black powder and a water-soluble mate-

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(26) R. W. Bunsen, *Ann.*, **42**, 123 (1942).
(27) See ref 22, p 51.
(28) See ref 22, p 339.
(29) C. S. Palmer and R. Adams, *J. Am. Chem. Soc.*, **44**, 1356 (1922).
(30) W. Ipatiew, G. Rasuwajew, and W. Stromski, *Ber.*, **62**, 598 (1929).

rial were obtained. The latter was shown to be ammonium chloride.

When a sample of the reaction mixture was heated in a vacuum sublimation apparatus at 110° (10^{-4} mm), a white sublimate containing traces of a yellow material was obtained on the cold finger. Arsine was evolved during the sublimation procedure and was identified by its infrared spectrum. A black solid was obtained as the residue. Resublimation of the yellow-white sublimate always gave a yellow-white sublimate, arsine gas, and a brown-black residue. The infrared spectrum of the sublimate showed that it contains major amounts of ammonium chloride. *Anal.* Found for the black residue: H, 0.31; N, 0.01; As, 88.99; Cl, 2.89. Assuming that the black powder was elemental arsenic, a 77% yield of arsenic was obtained based upon the amount of chloramine put into the reaction.

The mass spectrum of the yellow-white sublimate was obtained. The major *m/e* ratios (relative intensities using an arbitrary scale shown in parentheses) observed in the mass spectrum of the sublimate were assignable as follows: NH^+, 15 (23); NH_2^+, 16 (96); NH_3^+, 17 (100); HCl^+, 36 (53); AsH^+, 76 (25); $AsCl^+$, 110 (34); $AsCl(iso)^+$, 112 (13); $AsCl_2^+$, 145 (96); $AsClCl(iso)^+$, 147 (93); $AsCl_2(iso)^+$, 149 (28); $H_4As_2^+$, 154 (4); $H_5As_2^+$, 155 (5); $AsCl_3^+$, 180 (78); $AsCl_2Cl(iso)^+$, 182 (75); $AsClCl_2(iso)^+$, 184 (30); $AsCl_3^+$ 186 (4); $As_5H_3^{2+}$, 189 (5), $As_5H_7^{2+}$, 191 (7). Iso refers to the heavy isotope of chlorine.

This same experimental procedure was used for the reactions of dimethylchloramine and chlorine with arsine.

Reaction of Chlorine with Methylarsine in the Presence of Triethylamine.—This is shown by

$$CH_3AsH_2 + Cl_2 + (CH_3CH_2)_3N \longrightarrow \text{brick red solid} + (CH_3CH_2)_3NHCl \xrightarrow{\Delta} (CH_3As)_5 + \text{purple-black solid}$$

Onto 100 ml of diethyl ether in a reaction flask attached to the vacuum line were condensed 10 ml (liquid) of dried triethylamine and 12.3 mmol of methylarsine. Onto this solution was condensed, with constant stirring at −76°, 6.2 mmol of chlorine. The clear, colorless solution immediately turned yellow and a pale yellow solid formed. The reaction mixture was stirred for 1 hr at −76° as the solution gradually darkened. The highly volatile components were then distilled from the flask. The orange residue was washed several times with diethyl ether. Upon distilling the diethyl ether from the washings, a yellow-brown oil was obtained which immediately began to darken. A proton magnetic resonance spectrum was obtained using C_6D_6 as the solvent and tetramethylsilane as the internal standard. The spectrum showed in the region of −110 to −40 cps the presence of at least 14 different types of magnetically nonequivalent protons. This is the region for CH_3As and AsH proton peaks. This oil eventually changed to a brick red solid. The orange residue was extracted with 50-ml portions of boiling acetonitrile until no white precipitate resulted when the acetonitrile solution was added to diethyl ether. An acetonitrile-insoluble, brick red solid (I) was obtained and dried *in vacuo*. The melting point data for the brick red solid were as follows: 161–164°, solid changed from red to deep purple with some apparent decomposition; up to 254°, a liquid which readily oxidized in the air and had an arsine odor distilled from the purple solid. The infrared spectrum of this solid was completely void of absorption peaks. No proton magnetic resonance spectrum could be obtained because of the insolubility of the red solid. Mass spectra of the red solid were obtained at temperatures below and above its decomposition point. The major *m/e* ratios observed in the mass spectrum at 150° were assignable as: CH_3AsH^+, 91 (56); As_2^+, 150 (100); $(CH_3)_2As_3^+$, 255 (14); $(CH_3)_3As_3^+$, 270 (16). The major *m/e* ratios observed in the mass spectrum at 190° were assignable as: CH_3As^+, 90 (32); CH_3AsH^+, 91 (12); $(CH_3)_2As^+$, 105 (94); As_2^+, 150 (23); $CH_3As_2^+$, 165 (29); $(CH_3)_3As_2^+$, 195 (10); As_3^+, 225 (49); $(CH_3)_2As_3^+$, 255 (89); $(CH_3)_3As_3^+$, 270 (100); $(CH_3)_5As_3^+$, 300 (20); $(CH_3As)_5^+$, 450 (12). A comparison of the mass spectrum of the red solid obtained at 190° with that obtained of $(CH_3As)_5$ shows that the pentamethylpentaarsine is formed during the heating of the red solid. *Anal.* Found for I: C, 6.66; H, 1.49; As, 89.47; Cl, <0.05. This gives the empirical formula $CH_{2.67}As_{2.14}$ for I; yield, 0.2 g.

Destructive distillation of I gave a purple-black solid residue and a small amount of yellow distillate. The proton magnetic resonance spectrum of the yellow distillate was identical with that of pure cyclopentamethylpentaarsine. No yield data were obtained for the cyclopentamethylpentaarsine.

The acetonitrile solutions were added to diethyl ether to give a white solid having a melting point (253–254°) and an infrared spectrum identical with those of pure triethylamine hydrochloride.

Reaction of Dimethylarsine and Ammonia-Free Chloramine in a 2.7:1 Mole Ratio.—This is shown by

$$(CH_3)_2AsH \xrightarrow{NH_2Cl} \begin{cases} (CH_3)_2AsAs(CH_3)_2 \\ C_3H_{9.8}As_{1.4}NCl_{1.1} \\ NH_4Cl \end{cases}$$

When the general chloramination procedure was carried out using a 2.7:1 mole ratio of dimethylarsine to chloramine (ammonia-free), an orange-yellow solid was obtained in addition to a 10% yield of tetramethyldiarsine. After the removal of the volatile tetramethyldiarsine from the mixture of reaction products, the orange-yellow solid was extracted with tetrachloroethane and recrystallized from a tetrachloroethane–diethyl ether mixture. This material did not melt sharply, but began to shrink at 70°, liquefied with vigorous bubbling at 102°, and turned bright orange by 150°. The ir and nmr spectra of the material were very similar to those ascribed to $[(CH_3)_2AsN]_4 \cdot 2HCl$.[31] *Anal.* Found for the orange solid: C, 18.31; H, 5.01; N, 7.21; As, 51.92; Cl, 20.3. This corresponds to the empirical formula $C_3H_{9.8}As_{1.4}NCl_{1.1}$. This material is believed to consist of a mixture of dimethylarsenonitrilic tetramer, its hydrochlorides, and such intermediate species as $[(CH_3)_2As(NH_2)Cl]Cl$ and $[(CH_3)_2As(Cl){=}NAs(Cl)(CH_3)_2]Cl$. These species would be capable of existence in the absence of ammonia.

Reaction of an Ammonia–Chloramine Mixture with Dimethylarsine.—This is shown by

$$4(CH_3)_2AsH + 6NH_3 + 4NH_2Cl = \text{“}[(CH_3)_2AsN]_4 \cdot 2HCl\text{”} + 6NH_4Cl$$

To a reaction flask equipped with a large cold finger, an adapter for attaching the flask to the chloramine generator, and an adapter for connecting to the vacuum line was added 100 ml of 20–40° boiling petroleum ether. The flask and contents were degassed on the vacuum line and 2.3 ml of dimethylarsine (26 mmol) was condensed onto the petroleum ether. The reaction flask and contents were attached to the chloramine generator and the effluent gases from the generator were bubbled through the petroleum ether solution for 45 min (approximately 75 mmol of chloramine), while the temperature of the reaction solution was maintained at −76° to minimize the loss of the volatile dimethylarsine. A white solid formed immediately. After a few minutes, the white solid disappeared and a clear, colorless, dense layer formed which was immiscible with the petroleum ether. After the chloramination was completed, the reaction mixture was warmed to room temperature under a stream of dry nitrogen. As the ammonia evolved, the immiscible lower layer slowly turned to a white solid. The reaction flask was attached to the vacuum line and all volatile materials were distilled from the reaction flask. The remaining tacky, white solid was taken into the drybox and extracted with tetrachloroethane. The infrared spectrum of the remaining white solid was identical with that of ammonium chloride.

The tetrachloroethane solutions were added to diethyl ether. The resulting white precipitate was recrystallized from acetonitrile. The infrared spectrum of this white solid was similar

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[31] L. K. Krannich, Ph.D. Dissertation, University of Florida, June 1968.

to that of the substance believed to be the dihydrochloride $[(CH_3)_2AsN]_4 \cdot 2HCl$ obtained from the reaction of $(CH_3)_2AsCl$ with an ammonia–chloramine mixture,[31] except for an absorption peak at 970 cm^{-1}.

Peaks observed in the infrared spectrum of this material are as follows (cm^{-1}): 2980 (s), 2960 (s), 2940 (s), 2900 (s), 2540 (m), 1420 (w, sh), 1405 (m), 1380 (w, sh), 1268 (m), 1000 (s), 970 (s), 900 (s), 865 (m), 830 (m), 800 (s), 720 (m, b), 665 (w), 640 (m), 620 (m), 600 (w), 528 (m), 305 (m), 295 (w, sh).

The material melted at 170–185° with decomposition. (The melting point previously observed for $[(CH_3)_2AsN]_4 \cdot 2HCl$ was 217–218° with decomposition.[31]) This sample probably contains some other arsenic–nitrogen compounds as minor impurities. This would account for the wide melting range and the addition infrared absorption peak at 970 cm^{-1}. The product could, for example, consist of an equimolar mixture of $[(CH_3)_2AsN]_4 \cdot 4HCl$ and $[(CH_3)_2AsN]_4$ in addition to $[(CH_3)_2AsN]_4 \cdot 2HCl$. The nmr spectrum in deuterium oxide and the analysis of such a mixture would be identical with those of $[(CH_3)_2AsN]_4 \cdot 2HCl$, whereas the infrared spectrum and melting point would be different. The nmr spectrum was identical with that of $[(CH_3)_2AsN]_4 \cdot 2HCl$, having two single peaks at τ 8.22 (methyl protons attached to arsenic) and 2.53 (possibly NH protons[31]) when the spectrum was obtained using DMSO-d_6 as the solvent and the sodium salt of 3-(trimethylsilyl)propanesulfonic acid as the internal standard. *Anal.* Calcd for $[(CH_3)_2AsN]_4 \cdot 2HCl$: C, 17.49; H, 4.78; N, 10.21; As, 54.60; Cl, 12.91. Found: C, 17.67; H, 4.70; N, 10.26; As, 54.56; Cl, 13.37. The yield of "$[(CH_3)_2AsN]_4 \cdot 2HCl$" was 1.1 g (36% of theory based upon the amount of dimethylarsine put into the reaction).

The Reaction of Aminodiphenylarsine with Diphenylarsine.—This is shown by

$$(C_6H_5)_2AsNH_2 + (C_6H_5)_2AsH = (C_6H_5)_2)AsAs(C_6H_5)_2 + NH_3$$

To 0.14 g of aminodiphenylarsine (0.57 mmol) in a beaker inside the drybox was added 0.13 g of diphenylarsine (0.57 mmol). The beaker was placed inside a bell jar and the reaction mixture was maintained at 30° and a pressure of 10^{-3} mm for 6 hr. A pale yellow solid slowly formed. The reaction product was washed several times with hexane and dried *in vacuo*. The material melted at 129–130° (lit.[32] mp 120–125, 130, 130.5°). The infrared and proton magnetic resonance spectra were identical with those of tetraphenyldiarsine. The yield of tetraphenyldiarsine was 0.17 g (65% of theory based upon the amount of diphenylarsine put into the reaction).

Discussion

The Chloramine and Dimethylchloramine Reactions.—The results of this study show that arsine, primary arsines, and secondary arsines are readily converted to elemental arsenic, cyclic polyarsines, and diarsines, respectively, by reaction with chloramines. In all cases where the arsine was kept in substantial stoichiometric excess, essentially a quantitative yield of the respective arsenic–arsenic bonded compound was obtained.

Previously reported reactions of chloramines with group V bases have yielded amino-substituted "onium" chlorides, such as hydrazinium, aminophosphonium, or aminoarsonium salts.[1–7] The reactions of chloramine and dimethylchloramine with arsines containing As–H bonds

$$zR_{3-x}AsH_x + (xz/2)R'_2NCl = (R_{3-x}As)_z + (xz/2)R'_2NH_2Cl$$

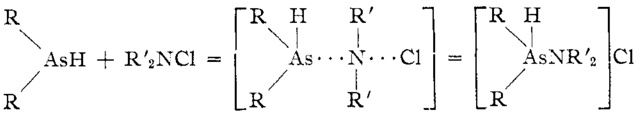
indicate that the chloramine molecules react with arsine and with primary and secondary arsines, in a different manner than that postulated for the chloramination of trisubstituted phosphines and arsines, possibly not involving initial formation of an aminoarsonium species.

The analysis of the black solid formed and the mass spectrum of the sublimate from the arsine–chloramine reaction show a complete lack of As–N-containing species. The mass spectrum shows the presence of ammonium chloride, arsenic hydrides, and chloroarsines in the sublimate. The chloroarsines could result from the interaction of HCl with the arsenic hydrides in the mass spectrometer at a temperature of 150° or could be intermediate reaction products.

The results of the study of dimethylarsine–chloramine reactions indicate that the mole ratio of dimethylarsine to chloramine is a determining factor for the type of products obtained (Table I). At high values of this ratio, the tetramethyldiarsine is the principal arsenic-containing product. As the ratio is decreased, the yield of the diarsine decreases and a material containing not only C, H, and As, but also N and Cl, results. This material is apparently a mixture of dimethylarsenonitrilic tetramer,[31] its hydrochlorides, and intermediate species. (The cyclic tetramer dimethylarsenonitrile would be the analog of the cyclic tetrameric dialkylphosphonitriles obtained by Frazier and Sisler in the chloramination of the diphosphines.[33]) When dimethylarsine was chloraminated in the presence of ammonia and a large excess of chloramine, the only arsenic-containing product recovered was the arsenonitrile. Thus, if the dimethylarsine:chloramine ratio is sufficiently low, arsenic–nitrogen compounds are formed. These species probably result from the reaction of chloramine with the initially formed diarsine in a manner analogous to that with the diphosphine.[33]

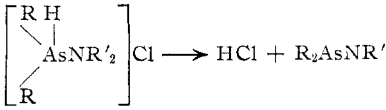
Since kinetic measurements have not been carried out, definitive statements concerning reaction mechanisms cannot be made. However, it may be useful to consider several possible mechanisms and speculate concerning their probability.

A reaction path analogous to the SN2-type displacement reaction already postulated for the chloramination of tertiary amines, phosphines, and arsines would involve nucleophilic attack by the arsine on the chloramine molecule (R′, R = hydrocarbon radical or H)



(1)

Further reaction in accordance with the equations



(2)

$$R_2AsNR'_2 + HCl \longrightarrow R_2AsCl + HNR'_2 \quad (3)$$

$$R_2AsCl + R_2AsH \longrightarrow R_2AsAsR_2 + HCl \quad (4)$$

$$HCl + HNR'_2 \longrightarrow [R'_2NH_2]Cl \quad (5)$$

would lead to the products obtained in these experiments.

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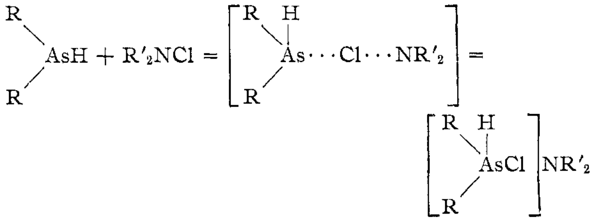
(32) F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **51**, 2272 (1929).

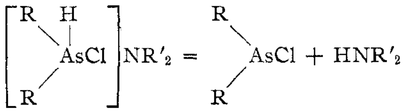
(33) S. E. Frazier and H. H. Sisler, *Inorg. Chem.*, **5**, 925 (1966).

An alternative path would be the attack of the arsine on the chlorine of the chloramine molecule



(6)

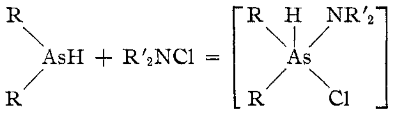
Further reaction in accordance with the equation



(7)

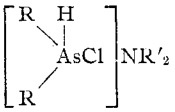
followed by eq 4 and 5 would lead to the products obtained in these experiments. This reaction path is in accordance with the known reaction of primary or secondary arsines with monohaloarsines to give compounds containing arsenic–arsenic bonds[12–14] and with the mechanism postulated by Denney and Felton[34] for the reaction of tris(dialkylamino)phosphines with dialkylchloramines to give tris(dialkylamino)dichlorophosphoranes.

Similar to the above would be a mechanism in which the initial step is the formation of a pentacoordinate arsenic derivative

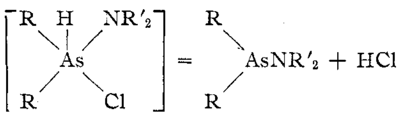


(8)

which could ionize to give the chloroarsonium derivative

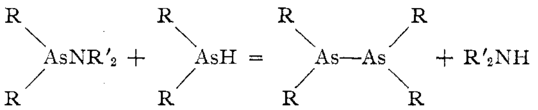


which could react as already outlined above (eq 4, 5, and 7). Another possibility would be for the pentacoordinate arsenic derivative to disproportionate to give the aminoarsine and hydrogen chloride



(9)

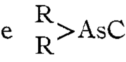
Further reaction could then occur to give the As—As bond according to the equations



(10)

$$HCl + R'_2NH = [R'_2NH_2]Cl \qquad (11)$$

This mechanism is supported by the demonstration in this study that aminoarsines react with secondary arsines to give As—As bonds. Similarly, Burg[35] has shown that $(CH_3)_2PN(CH_3)_2$ reacts with $(CH_3)_2PH$ to give $(CH_3)_2PP(CH_3)_2$. The conditions required for this mode of reaction, however, would suggest that this possible mechanism is of minor importance in our experiments.

The pentacoordinate derivative postulated above might also disproportionate to give  ${}^{R}_{R}{>}AsCl$ and HNR'_2, which then could react according to eq 4 and 5.

On the basis of data presently available, it is difficult to make a reasonable decision among the various possible reaction paths.

The results of the reactions of arsine, primary arsines, and secondary arsines with chlorine demonstrate that chlorine reacts with these substances, probably in a manner analogous to that of chloramine and substituted chloramines, and has demonstrated that elemental chlorine may be used to obtain diarsines and cyclic polyarsines from hydrogen–arsenic-bonded compounds in substantial yields. This is not in agreement with the reports of Dehn and coworkers[11,15] to the effect that chlorine reacts with primary and secondary arsines always to yield compounds having arsenic–chlorine bonds. However, it is clear that in their experiments such products resulted because chlorine was in excess. Consequently, any diarsine or polyarsine formed in their reactions would have undergone chlorination breaking the arsenic–arsenic bonds.

The arsenic–arsenic-bonded reaction product obtained from the methylarsine–chlorine reaction was not the cyclopentamethylpentaarsine as expected, but a brick red solid having the empirical formula $CH_{2.67}As_{2.14}$. The high arsenic-to-carbon ratio implies that, during the reaction, a loss of methyl groups from the arsenic occurred and that a highly condensed arsenic–arsenic-bonded product resulted. The condensed arsenic product is undoubtedly a complex species, since, prior to its final condensation, its proton magnetic resonance spectrum showed the presence of at least 14 magnetically nonequivalent methyl groups or protons. This material probably contains some of the red solid form of the cyclopentamethylpentaarsine.[36] At 161–164°, the brick red solid decomposes to give a purple-black solid and a liquid shown by our nmr spectroscopy and mass spectrometry to be the cyclopentamethylpentaarsine. Therefore, the dimethyl–chlorine reaction yields some cyclopentamethylpentaarsine and other nonchlorine-containing arsenic compounds.

The reaction of aminophenylarsine with diphenylarsine shows that an arsenic–arsenic-bonded compound can be obtained by the reaction of an aminoarsine with an arsine. The experimental conditions required to obtain a reaction suggest that the driving force of the reaction is the removal of the evolved ammonia.

Acknowledgment.—We are pleased to acknowledge the support of this research by the National Institutes of Health through Research Project No. CA-08263-03 with the University of Florida.

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[34] D. Denney and S. Felton, *Inorg. Chem.*, **7**, 99 (1968).

[35] A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).

[36] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley & Sons, Inc., Inc., New York, N. Y., 1957, p 210.