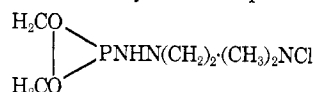


position temperature, the appearance of the P=O absorption in the infrared spectrum after heating, and the change in solubility properties.

The reaction with ammonia also indicates the presence of a reactive species. The decrease in the amount of transamination with time may be caused by conversion to the oxide form which is inert¹⁵ to transamination under the conditions of the experiment. Alternatively, the extent of transamination may be related to the crystallite size, the larger crystallites being less reactive. A slow rate of crystallization has been demonstrated in the reaction of 2-(*N,N*-dimethylhydrazino)-1,3,2-dioxophospholane with dimethylchloramine.⁸ The product of this reaction is a viscous liquid which crystallizes with difficulty. The crystalline form melts at 165–167°; its analysis corresponds to the formula



Although dialkylaminophospholanes and arsolanies are known^{16,17} to undergo transamination with ammonia and amines, 2-(*N,N*-dimethylhydrazino)-1,3,2-dioxophospholane does not react with excess ammonia under the same conditions which result in dimethylhydrazine evolution from the 1:1 addition product.

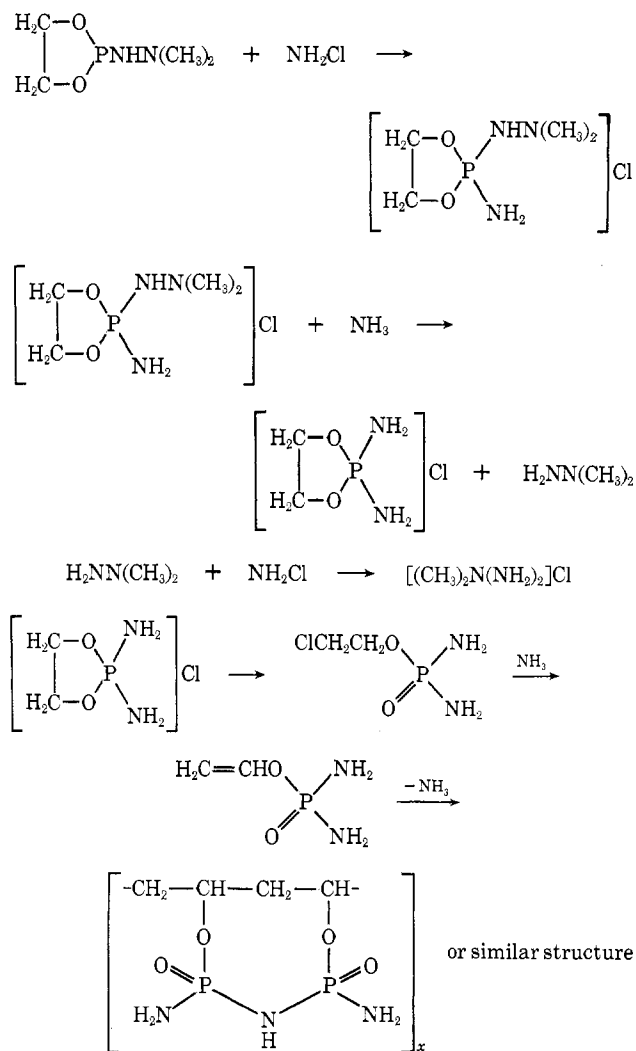
These considerations lead us to postulate the following sequence of reactions to describe the reaction of 2-(*N,N*-dimethylhydrazino)-1,3,2-dioxophospholane with chloramine and ammonia (see Scheme I). The products in this sequence which we have isolated are amino-2,2-dimethylhydrazinodioxophosphonium chloride, 1,1-dimethylhydrazine, 2,2-dimethyltriazanium chloride, and an intractable phosphorus-containing material with a P:N ratio of 2:3.

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SCHEME I



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Reactions of Dimethylchloramine and Ammonia-Free Chloramine with Trialkylarsines and Phenarsazines

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The reactions of a series of trialkylarsines with chloramine and dimethylchloramine yield in every case examined the corresponding aminoarsonium chlorides. Chloramination of some 5,10-dihydrophenarsazines demonstrates that the preferred site for amination is the arsenic atom rather than the nitrogen atom. Some theoretical implications of these results are discussed.

It has been established¹ in this laboratory that chloramine reacts with triphenylarsine and trimethylarsine to give good yields of the respective aminoarsonium chlorides. Other investigations^{2,3} have shown that

dimethylchloramine reacts with tertiary phosphines to give the respective aminophosphonium salts whereas dialkylphosphonates⁴ and tris(dimethylamino)phosphine² behave differently, the latter forming $(\text{R}_2\text{N})_3\text{PCl}^+\text{Cl}^-$. Other dialkylchloramines⁵ react with tris(diethylamino)phosphine to give the chlorophospho-

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nium chlorides. Vetter and Nöth⁶ have demonstrated that dimethylchloramine reacts with tris(dimethylamino)arsine to give the tetrakis(dimethylamino)arsonium chloride.

We thought it of interest to study the reactions of dimethylchloramine and of ammonia-free chloramine with trialkylarsines in order to compare the relative reactivity of these two chloramines with arsines and to examine further the range of application of the chloramine reaction with the arsines.

Chloramine reacts with tertiary phosphines containing the P-N bond to give the expected aminophosphonium chlorides.^{2,3,7-10} No cleavage of the P-N bond occurs in these reactions. We were interested in the reactivity of tertiary arsines containing the As-N bond toward chloramine but observed that, in the presence of ammonia, breaking of the As-N bond occurs as a result of transamination type reactions occurring with =As-NR₂. Therefore, in these simple aminoarsines we could not determine whether the chloramine molecule preferentially attacks the arsenic atom or the nitrogen atom. In order to answer this question the chloramination of some phenarsazines was studied. The phenarsazines contain arsenic and nitrogen atoms connected by a conjugated system, a structure which precludes the possibility of transamination.

Experimental Section

Materials.—All solvents were obtained as reagent grade materials and were dried, distilled, and stored over calcium hydride.

Analyses.—Elemental analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nitrogen analyses were carried out using the Kjeldahl method except where otherwise noted. Melting points were determined using the Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared Spectra.—Infrared spectra were recorded on a Beckman IR-10 spectrometer. The spectra were obtained on the solids in the form of KBr 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 . A summary of the spectral bands of materials used and produced in this study is found in Table I.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were measured on a Varian Model A-60 nmr spectrometer. Tetramethylsilane and the sodium salt of 3-trimethylsilylpropanesulfonic acid were used as internal standards when the solvents were CDCl₃ and DMSO-*d*₆, respectively. A summary of the nmr data for the materials used and produced in this study not listed in the literature is found in Table II.

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

Preparation of Chloramine and Dimethylchloramine.—Chloramine was prepared by the anhydrous method developed by Mattair and Sisler.¹¹ The method of obtaining and handling the ammonia-free chloramine in the vacuum line was analogous to the procedure developed in this laboratory and previously described.¹² Dimethylchloramine was prepared by a procedure analogous to the Raschig synthesis of chloramine.¹³ The pure

TABLE I^aINFRARED ABSORPTION DATA (CM⁻¹)

HN(C₆H₄)₂AsCl, Mull
3340 vs, 3040 w, 1900 w, 1601 vs, 1580 w, 1570 vs, 1510 m, 1480 s, 1465 vs, 1438 s, 1360 w, 1325 w, 1278 w, 1255 w, 1232 m, 1160 m, 1130 m, 1065 s, 1020 w, 895 w, 445 m, 750 vs, 740 vs, 715 s, 590 s, 440 s, 400 m.

HN(C₆H₄)₂AsCH₃, Mull
3380 vs, 3050 w, 2980 w, 2910 w, 1900 w, 1590 s, 1570 s, 1500 w, 1480 m, 1460 vs, 1440 s, 1410 m, 1322 s, 1280 w, 1255 s, 1230 m, 1160 m, 1130 w, 1120 w, 1060 w, 1030 w, 970 w, 930 w, 880 m, 860 w, 845 s, 835 m, 760 vs, 745 s, 722 vs, 670 w, 650 m, 595 w, 550 s, 535 s, 450 s

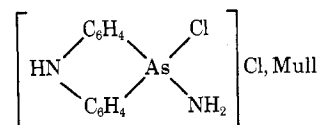
[(CH₃CH₂)₃AsNH₂]Cl, Mull
3140 vs, 2920 vs, 2870 vs, 2800 vs, 1485 w, 1440 s, 1410 m, 1380 m, 1260 s, 1240 w, 1090 s, 1040 s, 1020 s, 970 m, 800 m, 770 w, 750 m, 730 s, 690 s, 605 m, 545 m

[(CH₃CH₂CH₂)₃AsNH₂]Cl, Mull
3190 vs, 3180 vs, 3140 vs, 3100 vs, 3090 vs, 2950 vs, 2930 vs, 2870 vs, 1450 s, 1410 m, 1350 m, 1300 w, 1214 m, 1080 s, 1050 m, 840 m, 720 s, 695 s

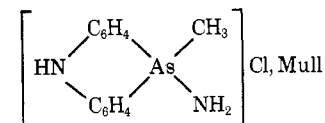
[(CH₃)₃AsN(CH₃)₂]Cl, Mull
2990 vs, 2900 m, 2860 m, 2800 m, 1460 vw, 1452 w, 1448 w, 1420 w, 1312 w, 1305 w, 1273 m, 1250 w, 1160 s, 1105 m, 1055 s, 942 vs, 915 vs, 860 m, 795 w, 712 vw, 650 w, 643 m, 610 m, 568 vs, 354 vw, 320 m

[(CH₃CH₂)₂AsN(CH₃)₂]Cl, Mull
2960 m, 2930 vs, 2805 m, 1460 s, 1382 w, 1312 w, 1250 m, 1150 s, 1040 m, 930 vs, 825 w, 794 w, 757 s, 605 m, 596 m, 360 w

[(CH₃CH₂CH₂)₂AsN(CH₃)₂]Cl, Mull
2960 vs, 2920 vs, 2870 s, 2810 m, 1450 m, 1410 w, 1370 w, 1310 w, 1250 w, 1220 w, 1210 w, 1160 m, 1060 s, 1037 w, 940 vs, 838 w, 790 vs, 723 m, 645 vw, 595 vw, 345 vw



3230 m, 3140 s, 3040 s, 3000 s, 2830 m, 1607 s, 1582 m, 1565 w, 1510 w, 1460 vs, 1439 s, 1405 s, 1362 w, 1322 w, 1275 w, 1245 m, 1240 sh, 1230 m, 1155 w, 1138 w, 1065 m, 1024 m, 967 m, 922 s, 890 w, 847 m, 830 w, 800 w, 742 vs, 720 m, 670 s, 640 w, 590 w, 570 w, 530 w, 440 s, 338 w, 340 s



3240 s, 3150 vs, 3050 vs, 2980 vs, 2930 vs, 2850 s, 1610 vs, 1585 vs, 1575 s, 1520 s, 1470 w, 1455 s, 1445 s, 1410 m, 1360 m, 1245 m, 1165 m, 1140 m, 1110 w, 1075 m, 1030 m, 860 s, 752 vs, 720 m, 690 w, 645 w, 620 w, 597 w, 535 w, 450 m, 390 w, 340 w

^a Key: s, strong; m, medium; w, weak; v, very; sh, shoulder.

dimethylchloramine (bp 43°) was then diluted with ether to give the solution used in these experiments.

Preparation of Trialkylarsines.—Trimethylarsine, triethylarsine, and tri-*n*-propylarsine were prepared by the reaction of arsenic(III) oxide with the respective trialkylaluminum compound according to the procedure described by Stamm and Breindel.¹⁴

Preparation of 10-Chloro-5,10-dihydrophenarsazine (HN-(C₆H₄)₂AsCl).—10-Chloro-5,10-dihydrophenarsazine was prepared by the reaction of arsenic trichloride with diphenylamine according to the procedure of Burton and Gibson.¹⁵ No nmr spectrum of the material synthesized was obtained because of the low solubility of the product in common deuterated solvents.

Preparation of 10-Methyl-5,10-dihydrophenarsazine (HN-

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TABLE II
¹H NMR SPECTRAL DATA

Compd	Group	Chem shift, τ	Solvent	Int std	Area ratio
[(CH ₃) ₃ AsN(CH ₃) ₂]Cl	N(CH ₃) ₂	7.37	CDCl ₃	CHCl ₃	$\frac{\text{As}(\text{CH}_3)_3}{\text{N}(\text{CH}_3)_2} = \frac{1.44}{1}$
	As(CH ₃) ₃	7.68			
[(CH ₃ CH ₂) ₃ AsN(CH ₃) ₂]Cl	CH ₂	7.30 (av)	CDCl ₃	CHCl ₃	$\frac{(\dots\text{CH}_2)_3\text{As} + \text{N}(\text{CH}_3)_2}{(\text{CH}_3\dots)_3\text{As}} = \frac{1.3}{1}$
	N(CH ₃) ₂	7.34			
	CH ₃	8.82 (av)			
[(CH ₃ CH ₂ CH ₂) ₃ AsN(CH ₃) ₂]Cl	α -CH ₂	7.08 (av)	CDCl ₃	TMS	$\frac{(\dots\text{CH}_2)_3\text{As} + \text{N}(\text{CH}_3)_2}{(\dots\text{CH}_2\dots)_3\text{As}} = \frac{1.96}{1}$
	N(CH ₃) ₂	7.18			
	β -CH ₂	8.25 (av)			
	CH ₃	8.88 (av)			
[HN(C ₆ H ₄) ₂ As(CH ₃)(NH ₂)]Cl	NH	-0.80	DMSO- <i>d</i> ₆	3-(Trimethylsilyl)-propanesulfonic acid	NH:C ₆ H ₄ :CH ₃ = 1:8.05:3.04
	C ₆ H ₄	2.93 (av)			
	NH ₂	3.13 (av)			
	CH ₃	7.97			
HN(C ₆ H ₄) ₂ AsCH ₃	NH	0.77	DMSO- <i>d</i> ₆	3-(Trimethylsilyl)-propanesulfonic acid	NH:C ₆ H ₄ :CH ₃ = 1:8.05:3.04
	C ₆ H ₄	2.77 (av)			
	CH ₃	8.95			

TABLE III
SUMMARY OF CHLORAMINE AND DIMETHYLCHLORAMINE REACTIONS

Reactants		Mole ratio	Product	Yield, %
A	B	A:B		
(C ₂ H ₅) ₃ As	NH ₂ Cl	1:1	[(C ₂ H ₅) ₃ AsNH ₂]Cl ^a	80
(<i>n</i> -C ₃ H ₇) ₃ As	NH ₂ Cl	1:1	[(<i>n</i> -C ₃ H ₇) ₃ AsNH ₂]Cl ^a	40
(CH ₃) ₃ As	(CH ₃) ₂ NCl	1:7.6	[(CH ₃) ₃ AsN(CH ₃) ₂]Cl ^b	46
(C ₂ H ₅) ₃ As	(CH ₃) ₂ NCl	1:8:8	[(C ₂ H ₅) ₃ AsN(CH ₃) ₂]Cl ^b	40
(<i>n</i> -C ₃ H ₇) ₃ As	(CH ₃) ₂ NCl	1:1	[(<i>n</i> -C ₃ H ₇) ₃ AsN(CH ₃) ₂]Cl ^b	65
HN(C ₆ H ₄) ₂ AsCl	NH ₂ Cl	1:1	[HN(C ₆ H ₄) ₂ As(Cl)(NH ₂)]Cl·49.3% (CH ₃ CH ₂) ₂ O	89
HN(C ₆ H ₄) ₂ AsCH ₃	NH ₂ Cl	1:2.6	[HN(C ₆ H ₄) ₂ As(CH ₃)(NH ₂)]Cl	90

^a White solid product formed immediately upon melting of the diethyl ether. ^b White solid product slowly formed as the reaction mixture warmed to room temperature.

TABLE IV
ANALYTICAL DATA

Compd	Mp, °C	Analyses, %									
		C		H		As		N		Cl	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[(C ₂ H ₅) ₃ AsNH ₂]Cl	63 dec	33.75	33.83	8.02	8.18	35.08	35.11	6.56	6.50	16.60	16.57
[(<i>n</i> -C ₃ H ₇) ₃ AsNH ₂]Cl	92-94 dec	42.28	42.21	9.07	9.29	29.30	29.08	5.48	5.20	13.87	13.97
[(CH ₃) ₃ AsN(CH ₃) ₂]Cl	184-186 dec	30.09	30.12	7.58	7.95	37.54	38.01	7.02	5.35 ^a	17.77	18.67
[(C ₂ H ₅) ₃ AsN(CH ₃) ₂]Cl	107-110 solid darkens; 128-129 melts	39.76	39.54	8.76	8.75	31.00	30.83	5.80	6.01	14.67	14.96
[(<i>n</i> -C ₃ H ₇) ₃ AsN(CH ₃) ₂]Cl	105-107	46.54	46.63	9.60	9.69	26.42	26.33	4.94	4.94	12.50	12.72
[HN(C ₆ H ₄) ₂ As(Cl)(NH ₂)]Cl·49.3% (CH ₃ CH ₂) ₂ O	208 turns dark green; 212 viscous; 250 black; 263 vigorous bubbling	45.91	45.41	4.39	4.26	20.49	20.49	7.66	7.25	19.39	18.04
[HN(C ₆ H ₄) ₂ As(CH ₃)(NH ₂)]Cl	140 shrinkage; 150 turns tan; 168-170 solid expands and turns yellow; 176 melts with dec	50.27	51.29	4.57	5.27	24.27	23.65	9.11	8.66	11.48	11.20

^a Combustion nitrogen. Note: When nitrogen analysis by the combustion method is carried out on an arsenic-nitrogen compound, the results are commonly lower than expected because of the formation of highly condensed As-N species which are difficult to decompose.

(C₆H₄)₂AsCH₃.—The methyl-substituted phenarsazine was prepared by the reaction of methylmagnesium bromide with 10-chloro-5,10-dihydrophenarsazine according to the procedure of Gibson and Johnson.¹⁶

Procedure for the Dimethylchloramine and Ammonia-Free Chloramine Reactions.—The concentration of the ether solution of chloramine was determined after the solution had been distilled into a graduated tube in the vacuum line. The concentration of chloramine in the solution was determined by allowing aliquot samples of the solution to react with an acidified potassium iodide solution, the iodine being titrated with a standard sodium thio-sulfate solution. The appropriate amount of arsine was added to the reaction flask inside the drybox and then was degassed on the vacuum line. The chloramine solution was condensed onto the arsine and the reaction mixture was allowed to warm to

room temperature. It was vigorously stirred by means of a magnetic stirrer. After the appropriate length of time all readily volatile materials were distilled from the reaction mixture. The residue was taken into the drybox and purified.

The respective reactions are summarized in Table III and the analytical data are given in Table IV.

Discussion

The products of the reactions of the trialkylarsines with chloramine and dimethylchloramine have been found, in all cases, to be the aminoarsonium salts. These aminoarsonium salts are the direct analogs of the products of the corresponding amine and phosphine reactions with chloramine.

Compared with the infrared spectra of the trialkyl-

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arsine starting materials, the infrared spectra of the respective products show, in each case, a new peak of medium to strong intensity in the 700–850-cm⁻¹ region. This peak is probably assignable to the As–N stretching mode. This assignment is reasonable since the absorption peak for the P–N stretching mode appears between 750 and 1000 cm⁻¹,¹⁷ depending upon the substituents on the nitrogen atom. The absence of a new infrared absorption peak in the region expected for the As–Cl stretching vibration, 300–450 cm⁻¹,¹⁸ supports the assumption of an aminoarsonium chloride structure, [R₃AsNR₂']Cl, rather than a structure having a pentacoordinate arsenic.

The chloraminations of the triethyl- and tri-*n*-propylarsines proceed instantaneously in ether at low temperatures. Sisler and Stratton¹ observed that trimethylarsine reacts with chloramine instantaneously at a low temperature, but triphenylarsine does not react at a measurable rate at –79°. Assuming that the chloramination reaction proceeds *via* an S_N2 type of bimolecular reaction mechanism with chloramine acting as the electrophile, an increase in electron density on arsenic would be expected to increase the reaction rate. The triethyl- and tri-*n*-propylarsine reactions are in agreement with this postulate on the basis of the electron densities on the arsenic atoms in aliphatic arsines being higher than in aromatic arsines and the rates of chloramination being therefore higher for the aliphatic compounds.

The dimethylchloramine reactions do not occur instantaneously at –79° as was found to be the case in the analogous chloramine reactions but proceed slowly even at room temperature. In fact, 100% conversion of the arsine to the arsonium salt was never obtained, even when the dimethylchloramine was in a 10:1 molar excess. By analogy with chloramine, one might expect these reactions to proceed by a S_N2 mechanism with dimethylchloramine acting as an electrophile. The methyl groups on the nitrogen are electron donating, thereby increasing the electron density

on the nitrogen atom and consequently decreasing its electrophilic character. Therefore, dimethylchloramine should be a weaker electrophile than chloramine. Neglecting steric factors, its reactions, in comparison with those of chloramine, should proceed more slowly. This, indeed, appears to be the case.

The reactions of chloramine with 10-chloro-5,10-dihydrophenarsazine and 10-methyl-5,10-dihydrophenarsazine provided the opportunity to observe which of the two potential Lewis base sites—nitrogen or arsenic—would be attacked by chloramine. The chloramination products show no reducing properties (negative reaction toward iodate). If a hydrazonium salt had been formed by amination of the nitrogen atom, the product should have had reducing properties. Also, the infrared spectra of the amino phenarsazonium salts show the appearance of a new band in the 700–850-cm⁻¹ region; the same band appeared in the chloramination products of the simple tertiary arsines. These data strongly indicate the existence of an As–N bond in the reaction product. Thus, neglecting any stereochemical arguments, it would appear that the arsenic atom is more susceptible to electrophilic attack than is the nitrogen atom. The ability of the arsenic atom to utilize its vacant 4d orbitals in forming a dπ–pπ bond with nitrogen may influence the formation of the aminoarsonium salt. Also, the electron cloud of the arsenic atom in the 10 position should be more diffuse than that of the nitrogen in the 9 position. The arsenic should, therefore, be more readily polarized than the nitrogen and the transition state, As···NH₂···Cl, should have a lower energy of formation than the transition state N···NH₂···Cl, thus favoring the chloramination of the arsenic atom. The infrared spectrum of the methyl derivative shows no absorption peak for an As–Cl stretching mode. Therefore, pentacoordinate arsenic can probably be ruled out in this reaction product.

Acknowledgment.—The authors are pleased to acknowledge the partial 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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