

solid-state structure with respect to possible exchange routes in solution. The two transition-state structures considered most likely for rearrangement in these H_4ML_4 complexes are (a) a T_d-43m symmetry model of interpenetrating tetrahedra and (b) an $S_4(\bar{4})$ symmetry model where the four phosphorus and molybdenum atoms are coplanar, with the hydrogen tetrahedron staggered with respect to the P atoms. The observed structure is nearly midway between a planar MoP_4 and a regular tetrahedral MoP_4 configuration; it is slightly closer to the S_4 planar model based on rms deviations from the idealized transition states. Hence, based on the solid-state evidence both transition states are about equally accessible. In fact, it was not possible even with all the available data to establish unequivocally the rearrangement mechanism operating in these complexes (discussed in ref 17),

although the T_d model is certainly preferred on steric grounds.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2295.

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Reactions of Ammonia and Ammonia-Chloramine Mixtures with Monochloroarsines and Diarsines and X-Ray Crystallographic Study of 2,2,4,4,6,6-Hexaphenylcyclotriarsazene, $[(C_6H_5)_2AsN]_3$

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It has been shown that ammonia and deuterated ammonia react with dimethylchloroarsine to give the respective arseno-ammonium chloride. The dialkylchloroarsines and diarsines react with ammonia-chloramine mixtures to form $R_4As_2N_2 \cdot HCl$ ($R = CH_3$ or C_2H_5) and $[(C_6H_5)_2AsN]_3 \cdot HCl$. Physical properties and mass spectral data suggest that $(CH_3)_4As_2N_2 \cdot HCl$ is a hydrochloride intermediate to an arsenonitrile, while $(C_2H_5)_4As_2N_2 \cdot HCl$ is a multiple arsenic-nitrogen bonded polymer containing arsenic-chlorine bonds. The results of the diarsine reactions suggest that arsenic-arsenic bonds are cleaved and give the same products as those obtained by the analogous reaction with dimethyl- or diphenylchloroarsines. The formation of tris(diethylarsino)amine is difficult to explain by an acceptable reaction path. The crystal structure of 2,2,4,4,6,6-hexaphenylcyclotriarsazene, $[(C_6H_5)_2AsN]_3$, has been determined from three-dimensional X-ray data collected with an automated diffractometer by use of nickel-filtered copper radiation. The compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a = 9.713$ (1) Å, $b = 11.825$ (2) Å, $c = 15.645$ (2) Å, $\alpha = 67.72$ (1)°, $\beta = 93.49$ (1)°, $\gamma = 105.79$ (1)°, and $Z = 2$. The observed and calculated densities are 1.51 and 1.515 g/cm³, respectively. The structure was refined by least-squares calculations to a conventional R index of 0.061 for 3818 independent intensities. The As_3N_3 ring of the molecule is slightly puckered. The six As-N bond distances appear to be equivalent with an average value of 1.758 (4) Å. The structure is discussed relative to that of $[(C_6H_5)_2AsN]_4$. The mass spectral data for $[(C_6H_5)_2AsN]_4$ show As_4N_4 ring opening with formation of $[(C_6H_5)_2AsN]_3$. The possible fragmentation mechanisms suggested by the metastable peaks are discussed.

Introduction

Reichle¹ prepared the arsenonitrilic tetramer $[(C_6H_5)_2AsN]_4$, mp 316–317°, by pyrolyzing the reaction product of diphenylchloroarsine with lithium azide. The tetramer was also synthesized by Haque and Din² by mixing $(C_6H_5)_2AsCl_3$, NH_4Cl , and liquid NH_3 at -35° for 2 hr. Glick³ has shown that this tetramer has $S_4-\bar{4}$ symmetry with a tub-like configuration and two nonequivalent types of arsenic-nitrogen bonds, 1.67 ± 0.03 and 1.79 ± 0.03 Å. The arsenonitrilic trimer $[(C_6H_5)_2AsN]_3$, mp 155–157°, was prepared by the ammonolysis of $(C_6H_5)_2AsCl_3$.⁴ The reaction of ammonia-chloramine mixtures with diphenylchloroarsine gives a product which upon heating and recrystallizing from dimethylformamide (DMF) yields the DMF adduct of the trimer,

$[(C_6H_5)_2AsN]_3 \cdot DMF$.⁴ Whereas analytical and infrared data for the trimer and adduct were given, no molecular weight data were cited to substantiate the postulated molecular formula. We have reinvestigated these latter two reactions in an attempt to isolate and characterize completely the pure trimer. In addition, we have determined the crystal structure of this compound to obtain details of the stereochemistry of the molecule and to give useful bond distance information for comparison with other known arsenic-nitrogen bond distances.^{3,5,6}

The preparation of the trimer *via* the chloramination reaction is analogous to the ammonolysis and chloramination of chlorophosphines^{7,8} to give diamminophosphonium chlorides which undergo self-condensation to yield phosphonitriles.

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Similarly, chloramination of diphosphines,⁹ in the presence of ammonia, has resulted in the cleavage of phosphorus-phosphorus bonds with the ultimate formation of the phosphonitriles. Chloramination of dimethylarsine in the presence of ammonia yielded a product with an elemental analysis suggesting the dihydrochloride of the arsenonitrilic tetramer, $[(CH_3)_2AsN]_4 \cdot 2HCl$, or possible mixtures of products such as equimolar mixtures of $[(CH_3)_2AsN]_4$ and $[(CH_3)_2AsN]_4 \cdot 4HCl$.¹⁰ This reaction was postulated to occur by the initial formation of the tetramethyldiarsine with subsequent chloramination in a manner analogous to that of the diphosphine.⁹ We have carried out the reactions of dialkylchloroarsines and diarsines with ammonia-chloramine mixtures to determine if the alkyl-substituted arsenonitriles could be obtained by this route.

Cullen and Emeleus¹¹ ammonolyzed dimethylchloroarsine at -46° but were unsuccessful in isolating and characterizing the arsenic-containing product. Upon mixing the bis(trifluoromethyl)chloroarsine with varying amounts of ammonia, they obtained $(CF_3)_2AsNH_2$ and/or $[(CF_3)_2As]_2NH$.¹¹ The reaction of diphenylchloroarsine with ammonia has been shown to give aminodiphenylarsine.¹² In the present study we have investigated the reactions of ammonia and deuterated ammonia with dimethylchloroarsine to determine if the aminoarsine can be obtained as the initial reaction product.

Experimental Section

Materials. All solvents used were dried and stored over calcium hydride. Dimethylarsenic acid and magnesium nitride were obtained from K and K Laboratories, and were used as obtained. Tetraethyllead was obtained from the Ethyl Corp. and used as obtained. Ethyl iodide and arsenic trichloride were obtained from Baker Chemical Co. Deuterium oxide, hexadeuteriodimethyl sulfoxide, deuteriochloroform, and hexadeuteriobenzene were obtained from Stohler Isotope Chemicals.

All storing and transferring of the arsenic-containing starting materials and experimental purification work were conducted in a dry nitrogen atmosphere in a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-93 Dri-Train. Because of the high reactivity of the arsines toward oxygen, special reaction conditions were used. The ammonia and deuterated ammonia reactions were carried out in an all-glass vacuum line. The materials to be chloraminated were added to a reaction flask equipped with a large cold finger and adapters for connection to the chloramine generator and vacuum line. The flask was attached to the generator, the connecting tubes were flushed with dry nitrogen, the stopcocks on the reaction flask were opened, and the chloramine-ammonia-nitrogen mixture from the generator was bubbled through the reaction solution for the desired length of time. The nitrogen and excess ammonia passed from the reaction flask into a continually flowing nitrogen stream.

Analyses. Elemental analyses were carried out by Schwarzkopf and Galbraith Microanalytical Laboratories of Woodside, N. Y., and Knoxville, Tenn., respectively. 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 or IR-20A 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 . Infrared absorption peaks of the reaction products are listed in Table I.

Nuclear Magnetic Resonance Spectra. The proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer. Tetramethylsilane and the sodium salt of 3-(trimethylsilyl)propane-sulfonic acid were used as internal standards in the respective instances.

Mass Spectra. The mass spectra, using a direct-probe inlet system, were recorded with a Perkin-Elmer Hitachi RMU 6E mass spectrometer at the ionizing voltages indicated for the respective spectra. The mass spectral data are given in Tables II–VI.

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Table I.^a Infrared Absorption Data (cm^{-1})

$[(CH_3)_2AsNH_3]Cl$, Mull	
3120 s, 3040–2900 s, b, 2260 w, 2210 m, 1750 w, 1435 w, 1405 vs, 1255 m, 1230 m, 1135 m, 902 s, 872 s, 842 s, 800 w, 755 w, sh, 732 m, 670 m, 590 s, 545 vs, 315 w, 262 w	
$[(CH_3)_2AsND_3]Cl$, Mull	
2990 m, 2910 m, 2310 vs, 2250 vs, 2180 s, 1660 w, b, 1405 m, 1255 s, 1230 vw, 1120 m, 1060 vs, 905 s, 890 s, 860 s, 838 m, 810 m, 732 m, 670 w, 600 m, 590 s, 580 s, 510 vs	
$(CH_3)_3As_2N_2HCl$, Mull	
2980 s, 2960 s, 2940 s, 2900 s, 2540 m, 1420 w, sh, 1405 m, 1380 w, sh, 1268 m, 1000 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	
$(C_2H_5)_4As_2N_2HCl$, Mull	
3070 sh, 3030 sh, 2930 s, 2870 s, 2830 sh, 2520 m, 2190 w, 1475 m, 1460 sh, 1450 s, 1405 m, 1370 m, 1350 sh, 1340 sh, 1310 w, 1250 sh, 1220 m, 1075 sh, 1020 m, 940 s, 700 s, 725 s, 670 s, 600 m, 545 s, 350 m, 330 sh, 305 sh	
$[(C_2H_5)_2As]_2N$, Film	
2950 vs, 2920 s, 2900 s, 2870 s, 2810 w, 2720 w, 1460 sh, 1450 m, 1420 w, 1410 w, 1370 m, 1355 sh, 1210 w, 1080 m, 1020 m, 955 m, 930 sh, 755 vs, b, 680 ms, 550 ms, 530 m, 510 sh, 345 w	
$[(C_6H_5)_2AsN]_3 \cdot HCl$, Mull	
3080 w, 3020 w, 2670 w, b, 2450 m, b, 2280 w, 1485 m, 1445 s, 1310 w, 1280 w, 1185 w, 1160 w, 1082 s, 1065 sh, 1025 w, 995 w, 920 vs, b, 848 w, 770 m, 735 s, 688 s, 620 m, 605 w, 470 s, 460 m, 450 m	

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

Synthesis of Chloramine. The gaseous mixture of chloramine and ammonia was prepared by the gas-phase reaction of chlorine with ammonia.¹³

Synthesis of Deuterated Ammonia. Deuterated ammonia was prepared by the reaction of magnesium nitride with deuterium oxide. The deuterated ammonia was passed through a column of magnesium nitride to ensure the removal of all water vapor and condensed into a flask on the vacuum line.

Preparation of the Arsines. Dimethylchloroarsine, bp 106.5° (760 mm), was prepared by the reaction of dimethylarsenic acid with sodium hypophosphite and hydrochloric acid according to the procedure described by Steinkopf and Mieg.¹⁴ Ethyldichloroarsine, bp 88–90° (100 mm), was prepared by the reaction of tetraethyllead with arsenic trichloride by the procedure described by Kharasch, Jensen, and Weinhouse.¹⁵ Diethylchloroarsine, bp 73–76° (73 mm), was prepared by the reaction of ethyldichloroarsine with ethyl iodide according to the procedure of Banks.¹⁶ Tetramethyldiarsine was prepared by the direct action of dimethylchloroarsine on zinc dust as described by Bunsen.¹⁷ Tetraphenyldiarsine, mp 128–129°, was prepared by the reaction of diphenylchloroarsine with tri-*n*-butylphosphine as reported earlier.¹⁸ $(C_6H_5)_2AsCl_3$ was prepared by the reaction of diphenylchloroarsine with chlorine according to the procedure of Wiberg and Moedritzer.¹⁹

Reaction of Ammonia with Dimethylchloroarsine, $(CH_3)_2AsCl + NH_3 \rightarrow [(CH_3)_2AsNH_3]Cl$. Dimethylchloroarsine (22 mmol) was added to a reaction flask containing 25 ml of diethyl ether. Dry ammonia (22 mmol) was condensed into the reaction flask at -196° and the reaction mixture was warmed to room temperature. As soon as the ether melted, a white solid formed. After the temperature of the reaction flask reached room temperature, all the highly volatile materials were distilled from the flask. The white solid product was vacuum sublimed at 60° and 10^{-4} mm. The product did not melt at atmospheric pressure, but sublimed. *Anal.* Calcd for $[(CH_3)_2-$

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Table II. Mass Spectral Data for $(\text{CH}_3)_4\text{As}_2\text{N}_2\text{HCl}^a$

<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment
476	1.6	$(\text{CH}_3)_6\text{As}_4\text{N}_4$	166	0.9		122	100	$(\text{CH}_3)_2\text{AsNH}_3$	59	2.6	
461	1.0	$(\text{CH}_3)_7\text{As}_4\text{N}_4$	165	1.8		121	3.2	$(\text{CH}_3)_3\text{AsNH}_2$	52	4.2	$\text{CH}_3^{37}\text{Cl}$
432	0.2	$(\text{CH}_3)_8\text{As}_4\text{N}_4\text{H}$	164	1.0		114	10.4	$\text{H}_2\text{As}^{37}\text{Cl}$	50	13.3	$\text{CH}_3^{35}\text{Cl}$
418	0.2	$(\text{CH}_3)_4\text{As}_4\text{N}_4\text{H}_2$	162	2.4		113	4.4	HAS^{37}Cl	44	81.7	
403	0.1	$(\text{CH}_3)_3\text{As}_4\text{N}_4\text{H}_2$	160	3.6		112	24	$\text{H}_2\text{As}^{35}\text{Cl}, \text{As}^{37}\text{Cl}$	43	6.3	
396	0.6		158	18.8	$(\text{CH}_3)_2\text{AsNH}_2^{37}\text{Cl}$	111	11.7	HAS^{35}Cl	42	5.8	<i>b</i>
357	2.7	$(\text{CH}_3)_6\text{As}_3\text{N}_3$	156	60.5	$(\text{CH}_3)_3\text{AsNH}_2^{35}\text{Cl}$	110	2.1	As^{35}Cl	41	127	<i>b</i>
342	5.2	$(\text{CH}_3)_7\text{As}_3\text{N}_3$	155	1.5		108	67	$(\text{CH}_3)_2\text{AsH}_3$	40	84	<i>b</i>
314	1.2	$(\text{CH}_3)_3\text{As}_3\text{N}_3\text{H}_2$	154	1.3		107	14.1	$(\text{CH}_3)_2\text{AsH}_2$	39	36	<i>b</i>
313	2.2	$(\text{CH}_3)_3\text{As}_3\text{N}_3\text{H}$	150	2.0		106	36	$(\text{CH}_3)_2\text{AsH}$	38	38	$\text{H}^{37}\text{Cl} + \text{b}$
300	4.6	$(\text{CH}_3)_2\text{As}_3\text{N}_3\text{H}_3$	149	4.7	$\text{As}^{37}\text{Cl}_2$	105	3.9	$(\text{CH}_3)_2\text{As}$	37	2.9	^{37}Cl
289	0.5		147	6.4	$\text{As}^{35}\text{Cl}^{37}\text{Cl}$	104	29.2		36	67	H^{35}Cl
243	4.9	$(\text{CH}_3)_4\text{As}_2\text{N}_2\text{H}_5$	145	9.4	$\text{As}^{35}\text{Cl}_2$	103	6.0		35	8	^{35}Cl
233	3.5		143	5.5	$(\text{CH}_3)_2\text{AsH}^{37}\text{Cl}$	102	10.4		32	2	
228	2.5	$(\text{CH}_3)_4\text{As}_2\text{NH}_4, (\text{CH}_3)_3\text{As}_2\text{N}_2\text{H}_5$	142	16	$(\text{CH}_3)_2\text{As}^{37}\text{Cl}$	101	3.3		31	8.7	
218	2.7		141	16.6	$(\text{CH}_3)_2\text{AsH}^{35}\text{Cl}$	100	1.3		30	1.3	
214	1.5	$(\text{CH}_3)_3\text{As}_2\text{NH}_5, (\text{CH}_3)_2\text{As}_2\text{N}_2\text{H}_6$	140	48	$(\text{CH}_3)_2\text{As}^{35}\text{Cl}$	94	11.1	$\text{CH}_3\text{AsH}_4, \text{AsNH}_5$	29	7.6	
212	1.1	$(\text{CH}_3)_3\text{As}_2\text{NH}_3, (\text{CH}_3)_2\text{As}_2\text{N}_2\text{H}_4$	139	2.0		93	8.3	$\text{CH}_3\text{AsH}_3, \text{AsNH}_4$	28	67	<i>b</i>
211	1.5	$(\text{CH}_3)_3\text{As}_2\text{NH}_2, (\text{CH}_3)_2\text{As}_2\text{N}_2\text{H}_3$	138	9.4		92	89.6	$\text{CH}_3\text{AsH}_2, \text{AsNH}_3$	27	8	<i>b</i>
202	0.4		137	1.7		91	23.3	$\text{CH}_3\text{AsH}, \text{AsNH}_2$	26	3.6	<i>b</i>
198	1.1	$(\text{CH}_3)_2\text{As}_2\text{NH}_4$	128	22.3	$\text{CH}_3\text{AsH}^{37}\text{Cl}$	90	93.2	$\text{CH}_3\text{As}, \text{AsNH}$	25	2	<i>b</i>
196	2.4	$(\text{CH}_3)_2\text{As}_2\text{NH}_2$	127	3.4		89	26.9	AsN	18	71	NH_4
195	2.7	$(\text{CH}_3)_2\text{As}_2\text{NH}$	126	67	$\text{CH}_3\text{AsH}^{35}\text{Cl}$	88	4.7		17	95	NH_3
187	6.3		125	3.6		78	1.4	AsH_3	16	78	NH_2
185	6.7		124	7.2		77	6.5	AsH_2	15	14	$\text{NH} + \text{b}$
180	1.4	$\text{CH}_3\text{As}_2\text{NH}, (\text{CH}_3)_2\text{As}_2$	123	20.8	$(\text{CH}_3)_2\text{AsNH}_4$	76	6.0	AsH	14	7	<i>b</i>
171	7.3					75	17.5	As			
169	7.2					60	6.2				

^a Ionizing voltage 70 eV. ^b Peaks are probably due to CH_3CN and its fragments, since this was the solvent of recrystallization: J. L. Franklin, Y. Wada, P. Natalis, and P. M. Hierl, *J. Phys. Chem.*, **70**, 2353 (1966); F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

Table III. Mass Spectral Data for $(\text{CH}_3)_4\text{As}_2\text{N}_2\text{HCl}^a$

<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment
476	1.4	$(\text{CH}_3)_8\text{As}_4\text{N}_4$	156	66.5	$(\text{CH}_3)_2\text{AsNH}_2^{35}\text{Cl}$	91	20	$\text{CH}_3\text{AsH}, \text{AsNH}_2$
461	0.5	$(\text{CH}_3)_7\text{As}_4\text{N}_4$	150	38.0		90	66	$\text{CH}_3\text{As}, \text{AsNH}$
357	2.3	$(\text{CH}_3)_6\text{As}_3\text{N}_3$	143	6.9	$(\text{CH}_3)_2\text{AsH}^{37}\text{Cl}$	78	3.8	AsH_3
342	5.0	$(\text{CH}_3)_7\text{As}_3\text{N}_3$	142	29	$(\text{CH}_3)_2\text{As}^{37}\text{Cl}$	77	5.8	AsH_2
300	1.9	$(\text{CH}_3)_2\text{As}_3\text{N}_3\text{H}_3$	141	15	$(\text{CH}_3)_2\text{AsH}^{35}\text{Cl}$	74	5.3	
243	6.6	$(\text{CH}_3)_4\text{As}_2\text{N}_2\text{H}_5$	140	88.4	$(\text{CH}_3)_2\text{As}^{35}\text{Cl}$	60	12.7	
232	11.2		138	13		59	6.6	
227	4.6	$(\text{CH}_3)_4\text{As}_2\text{NH}_3, (\text{CH}_3)_3\text{As}_2\text{N}_2\text{H}_3$	128	30.5	$\text{CH}_3\text{AsH}^{37}\text{Cl}$	57	4.8	
226	3.0	$(\text{CH}_3)_4\text{As}_2\text{NH}_2, (\text{CH}_3)_3\text{As}_2\text{N}_2\text{H}_2$	126	88	$\text{CH}_3\text{AsH}^{35}\text{Cl}$	56	4.9	
223	3.6		124	6.6		45	5.3	
220	2.8		123	44.7	$(\text{CH}_3)_2\text{AsNH}_4$	44	18.3	
218	7.1		122	83.8	$(\text{CH}_3)_2\text{AsNH}_3$	43	4.1	
214	2.0	$(\text{CH}_3)_3\text{As}_2\text{NH}_5, (\text{CH}_3)_2\text{As}_2\text{N}_2\text{H}_6$	114	7.2	$\text{H}_2\text{As}^{37}\text{Cl}$	42	7.6	<i>b</i>
212	3.6	$(\text{CH}_3)_3\text{As}_2\text{NH}_3, (\text{CH}_3)_2\text{As}_2\text{N}_2\text{H}_4$	112	14.7	$\text{H}_2\text{As}^{35}\text{Cl}, \text{As}^{37}\text{Cl}$	41	198	<i>b</i>
211	2.0	$(\text{CH}_3)_3\text{As}_2\text{NH}_2, (\text{CH}_3)_2\text{As}_2\text{N}_2\text{H}_3$	111	4.6	HAS^{35}Cl	40	70	<i>b</i>
208	3.0		108	83.8	$(\text{CH}_3)_2\text{AsH}_3$	39	18	<i>b</i>
206	1.6		107	14	$(\text{CH}_3)_2\text{AsH}_2$	38	7.4	$\text{H}^{37}\text{Cl} + \text{b}$
202	2.1		106	50.8	$(\text{CH}_3)_2\text{AsH}$	36	20.3	H^{35}Cl
195	2.3	$(\text{CH}_3)_2\text{As}_2\text{NH}$	105	4.9	$(\text{CH}_3)_2\text{As}$	31	3.8	
187	19.9		104	39.6		29	3	
185	17.8		103	6		28	22.4	<i>b</i>
171	18.3		102	7.4		18	69	NH_4
169	19.9		94	7.4	CH_3AsH_4	17	100	NH_3
159	20.0		93	4.4	CH_3AsH_3	16	31	NH_2
			92	45.6	CH_3AsH_2			

^a Ionizing voltage 15 eV. ^b See footnote *b* of Table II.

AsNH_3Cl : C, 15.25; H, 5.76; N, 8.90; As, 47.58; Cl, 22.51. Found: C, 15.48; H, 5.98; N, 8.45; As, 47.37; Cl, 22.18. The infrared spectral data are given in Table I. The proton magnetic resonance spectrum was measured using $\text{DMSO-}d_6$ as the solvent and the DMSO peak (-149 Hz relative to the sodium salt of 3-(trimethylsilyl)propanesulfonic acid) as the internal reference. The spectrum consisted of two single peaks having the τ values 2.68 and 8.78 corresponding to the NH_3 and $(\text{CH}_3)_2\text{As}$ protons, respectively. The area ratios under these peaks were 1:1.8, respectively. The yield of dimethylarsenoammonium chloride was 2.67 g (80% of theory based upon the dimethylchloroarsine used).

Reaction of Deuterated Ammonia with Dimethylchloroarsine, $(\text{CH}_3)_2\text{AsCl} + \text{ND}_3 \rightarrow [(\text{CH}_3)_2\text{AsND}_3]\text{Cl}$. The reaction procedure using 22 mmol of $(\text{CH}_3)_2\text{AsCl}$ and 22 mmol of ND_3 was identical with that used in the ammonia- $(\text{CH}_3)_2\text{AsCl}$ reaction. The white

solid product was purified by vacuum sublimation at 60° and 10^{-4} mm. *Anal.* Calcd for $[(\text{CH}_3)_2\text{AsND}_3]\text{Cl}$: C, 14.97; N, 8.73; As, 46.69; Cl, 22.09. Found: C, 15.20; N, 8.67; As, 47.15; Cl, 21.35. The infrared spectral data are given in Table I. The yield of $[(\text{CH}_3)_2\text{AsND}_3]\text{Cl}$ was 2.7 g (80% of theory based upon the dimethylchloroarsine used).

Reaction of an Ammonia-Chloramine Mixture with Dimethylchloroarsine. Dimethylchloroarsine (2.1 g, 15 mmol) was dissolved in 50 ml of 20–40° boiling petroleum ether or diethyl ether in a reaction flask. The flask was connected to the chloramine generator and the effluent gases from the generator were bubbled through the solution for 25 min (42 mmol of NH_2Cl) at room temperature. A white solid precipitated immediately. After 6 min, the white solid appeared to liquefy and form a dense oil immiscible with petroleum ether. After the chloramination process was completed, the reaction flask

Table IV. Mass Spectral Data for $[(C_2H_5)_2As]_3N^a$

<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment
363	1		139	13		78	56	AsH ₃
356	0.7	(C ₂ H ₅) ₄ As ₃ NH	134	10	(C ₂ H ₅) ₂ AsH	77	14	AsH ₂
350	0.9		122	7.4	(C ₂ H ₅)AsNH ₄	59	9.3	C ₄ H ₁₁
333	0.9		121	54	(C ₂ H ₅)AsNH ₃	57	17.4	C ₄ H ₉
306	0.6		119	35	(C ₂ H ₅)AsNH ₂	56	13	C ₄ H ₈
299	1.6		118	37	(C ₂ H ₅)AsNH	55	11	C ₄ H ₇
291	0.9		113	5		52	11	
282	1.4	(C ₂ H ₅) ₄ As ₂ NH ₂	112	6		51	11	
281	0.9	(C ₂ H ₅) ₄ As ₂ NH	111	14		50	9	
270	3		110	15		47	9.8	
255	1.8	(C ₂ H ₅) ₃ As ₂ NH ₄	105	27	C ₂ H ₅ AsH, C ₂ H ₃ AsH ₃	45	8.8	
254	8.5	(C ₂ H ₅) ₃ As ₂ NH ₃	104	57	C ₂ H ₅ As, C ₂ H ₃ AsH ₂	44	8.8	
242	2		103	20	C ₂ H ₃ AsH	43	39.7	
226	2.5	(C ₂ H ₅) ₂ As ₂ NH ₄	102	12	C ₂ H ₃ As	42	20.5	
225	1.4	(C ₂ H ₅) ₂ As ₂ NH ₃	101	14		41	2.7	
224	7.3	(C ₂ H ₅) ₂ As ₂ NH ₂	94	3	H ₃ AsNH ₂	39	17	
198	2.9	(C ₂ H ₅)As ₂ NH ₅	93	17	H ₃ AsNH	32	23.7	
170	7.8	As ₂ NH ₆	92	5.8	H ₂ AsNH	31	20.3	
168	23.5	As ₂ NH ₄	90	6.8	AsN	29	47.9	C ₂ H ₅
163	6.2		85	7.5		28	100	C ₂ H ₄ , N ₂
150	23	As ₂ , (C ₂ H ₅) ₂ AsNH ₃	84	7.5		27	39.7	
142	3.7		83	11.6		18 ^b		NH ₄
141	4.7		82	9.4		17 ^b		NH ₃
140	11		79	7.5		16 ^b		NH ₂

^a Ionizing voltage 70 eV. ^b Off scale.

Table V. Mass Spectral Data for (C₂H₅)₄As₂N₂HCl^a

<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment
413	5	(C ₂ H ₅) ₅ As ₃ N ₃ H	170	32	(C ₂ H ₅) ₂ As ³⁷ Cl
385	10	(C ₂ H ₅) ₄ As ₃ N ₃ H ₂	169	5	(C ₂ H ₅) ₂ As ³⁵ ClH
384	7	(C ₂ H ₅) ₄ As ₃ N ₃ H	168	100	(C ₂ H ₅) ₂ As ³⁵ Cl
358	2	(C ₂ H ₅) ₃ As ₃ N ₃ H ₄	142	10	(C ₂ H ₅)As ³⁷ ClH
357m			141	8	(C ₂ H ₅)As ³⁷ Cl
356	0.6	(C ₂ H ₅) ₃ As ₃ N ₃ H ₂	140	32	(C ₂ H ₅)As ³⁵ ClH
330m			139	21	(C ₂ H ₅)As ³⁵ Cl
328	0.4	(C ₂ H ₅) ₂ As ₃ N ₃ H ₃	133	13	(C ₂ H ₅) ₂ As
300	0.6	(C ₂ H ₅)As ₃ N ₃ H ₄	132	7	
298	2	(C ₂ H ₅) ₄ As ₂ N ₂ H ₄	120	4	
283	3	(C ₂ H ₅) ₄ As ₂ NH ₃	119m		
282	28	(C ₂ H ₅) ₄ As ₂ NH ₂	117m		
269	2.3	As ₃ N ₃ H ₅ , (C ₂ H ₅) ₃ As ₂ N ₂ H ₄	113	2	HA ³⁷ Cl
254	7	(C ₂ H ₅) ₃ As ₂ NH ₃	112	7	As ³⁷ Cl
253	16	(C ₂ H ₅) ₃ As ₂ NH ₂	111	5	HA ³⁵ Cl
228m			110	22	As ³⁵ Cl
226	2	(C ₂ H ₅) ₂ As ₂ NH ₄	106	13	C ₂ H ₅ AsH
225	24	(C ₂ H ₅) ₂ As ₂ NH ₃	105	43	C ₂ H ₅ As
200m			104	5	
197	10	(C ₂ H ₅)As ₂ NH ₄	78	16	AsH ₃
172m			29	19	C ₂ H ₅
171	2	(C ₂ H ₅) ₂ As ³⁷ ClH	17	24	NH ₃

^a Ionizing voltage 70 eV.

was warmed to room temperature under a stream of dry nitrogen. As the ammonia evolved, the immiscible lower layer slowly crystallized to yield a white solid. The solvent was then distilled from the reaction flask. The remaining tacky, white solid was taken into the dry-box and extracted with acetonitrile. The infrared spectrum of the white residue insoluble in acetonitrile was identical with that of ammonium chloride.

A white solid (I) was obtained when the acetonitrile solution was cooled or added to diethyl ether. The proton magnetic resonance spectrum of this solid obtained using D₂O as the solvent and the sodium salt of 3-(trimethylsilyl)propanesulfonic acid as the internal standard gave a single proton resonance at τ 8.23 (attributed to the (CH₃)₂As group). The proton magnetic resonance spectrum obtained using DMSO-*d*₆ as the solvent and the sodium salt of 3-(trimethylsilyl)propanesulfonic acid as the internal standard gave two single peaks at τ 8.22 [(CH₃)₂As protons] and 2.53 (possible NH protons); mp 217–219° dec. *Anal.* Calcd for (CH₃)₄As₂N₂HCl (I): C, 17.49; H, 4.78; N, 10.21; As, 54.60; Cl, 12.92. Found: C, 17.68; H, 4.70; N, 10.45; As, 54.62; Cl, 13.27. A density of 1.96 g/cm³ for a crystal of I was obtained using a solvent mixture of 1,2-dibromoethane and CCl₄. The infrared spectral data are given in Table I. The mass spectral data at ionizing voltages of 70 and 15 eV are given in Tables II and III. The infrared spectrum, nmr spectra, analyses, and mass

spectral data suggested I might be formulated as an arsenonitrilic hydrochloride. The yield of I was 1.53 g (75% of theory based upon the amount of dimethylchloroarsine put into the reaction).

No more than traces of ammonium chloride or the appropriate amine hydrochloride were obtained when I was added to liquid ammonia or to a variety of primary, secondary, or tertiary amines, and I was recovered essentially quantitatively with no other arsenic-nitrogen compound being observed.

Reaction of an Ammonia-Chloramine Mixture with Diethylchloroarsine. Diethylchloroarsine (5.2 g, 31 mmol) was dissolved in 75 ml of diethyl ether in a reaction flask. The flask was then connected to the generator and chloraminated for 30 min (50 mmol of NH₂Cl). A white precipitate formed immediately. Ammonia was then passed through the solution until all the solvent had evaporated. The remaining tacky, white solid was extracted with petroleum ether. Evaporation of the petroleum ether solution yielded 1.0 g of a clear colorless oil. The oil was purified using a sublimation technique. When first heating to 95° at 10⁻³ mm, a trace amount of NH₄Cl was obtained on the cold finger and identified by infrared spectroscopy. Further heating of the oil at 150° and 10⁻³ mm gave a clear, colorless "sublimate." A very small quantity of dark residue remained in the sublimation flask. The melting point of the "sublimate" was 33–35°. *Anal.* Calcd for [(C₂H₅)₂As]₃N: C, 34.86; H, 7.32; N, 3.39; As,

Table VI. Mass Spectral Data for $[(C_6H_5)_2AsN]_3^a$

<i>m/e</i>	<i>I, %</i>	Fragment	<i>m/e</i>	<i>I, %</i>	Fragment
973	28	$[(C_6H_5)_2AsN]_4H$	475	2	$(C_6H_5)_4As_2NH_3$
972	55	$[(C_6H_5)_2AsN]_4$	474	2	$(C_6H_5)_4As_2NH_2$
971	54		473	2	$(C_6H_5)_4As_2NH$
896	54	$(C_6H_5)_7As_2N_4H$	460	2	$(C_6H_5)_4As_2H_2$
895	100	$(C_6H_5)_7As_2N_4$	459	6	$(C_6H_5)_4As_2H$
882	0.8	$(C_6H_5)_7As_2N_3H$	447m		
881	1.3	$(C_6H_5)_7As_2N_3$	438m		
867m			413	2	$(C_6H_5)_3As_2N_2H_4$
825m			411	2	$(C_6H_5)_3As_2N_2H_2$
820	18	$(C_6H_5)_6As_2N_4H_2$	398	3	$(C_6H_5)_3As_2NH_3$
819	32	$(C_6H_5)_6As_2N_4H$	335	2	$(C_6H_5)_2As_2N_2H_3$
808	17	$(C_6H_5)_6As_2N_3H_2$	334	2	$(C_6H_5)_2As_2N_2H_2$
807	32	$(C_6H_5)_6As_2N_3H_3$	323	3	$(C_6H_5)_2As_2NH_5$
805	12	$(C_6H_5)_6As_2N_3H$	322	12	$(C_6H_5)_2As_2NH_4$
745	10	$(C_6H_5)_6As_2N_3H_2$	307	2	$(C_6H_5)_2As_2H_3$
731	12	$(C_6H_5)_6As_2N_3H_2$	247	1.5	$(C_6H_5)_2AsNH_4$
730	19	$(C_6H_5)_6As_2N_3H$	246	2	$(C_6H_5)_2AsNH_3$
729	32	$[(C_6H_5)_2AsN]_3$	245	2	$(C_6H_5)_2AsNH_2$
717m			244	2	$(C_6H_5)_2AsNH$
690m			243	1.5	$(C_6H_5)_2AsN$
666m			232	7	$(C_6H_5)_2AsH_3$
655	21	$(C_6H_5)_5As_3N_3H_3$	231	34	$(C_6H_5)_2AsH_2$
654	33	$(C_6H_5)_5As_3N_3H_2$	230	3	$(C_6H_5)_2AsH$
653	78	$(C_6H_5)_5As_3N_3H$	229	9	$(C_6H_5)_2As$
594m			170	1	$(C_6H_5)AsNH_4$
585m			169	2	$(C_6H_5)AsNH_3$
578	12	$(C_6H_5)_4As_3N_3H_3$	168	1	$(C_6H_5)AsNH_2$
577	40	$(C_6H_5)_4As_3N_3H_2$	167	6	$(C_6H_5)AsNH$
565	3	$(C_6H_5)_4As_3N_2H_2$	156	1.5	$(C_6H_5)AsH_4$
563	3	$(C_6H_5)_4As_3N_2H_2$	155	6	$(C_6H_5)AsH_3$
549m			154	1.5	$(C_6H_5)AsH_2, C_{12}H_{10}$
521m			153	10	$(C_6H_5)AsH$
502	2	$(C_6H_5)_3As_3N_3H_4$	151	2	
489	2	$(C_6H_5)_3As_3N_2H_5, (C_6H_5)_4As_2N_2H_3$	79	2	C_6H_7
487	2	$(C_6H_5)_3As_3N_2H_3, (C_6H_5)_4As_2N_2H$	78	1	C_6H_6

^a Ionizing voltage 15 eV.

54.43; mol wt 413. Found: C, 35.04; H, 7.43; N, 3.42; As, 54.26; mol wt 400 (in benzene). The nmr spectrum obtained using CCl_4 as the solvent and TMS as the internal standard showed a complex quartet (-109 to -85 Hz) and a complex triplet (-81 to -55 Hz). The infrared spectrum of the sublimate (Table I) was identical with that of the original oil, thereby indicating that a small quantity of impurity present in the oil was responsible for the NH_4Cl . The mass spectral data for $[(C_2H_5)_2As]_3N$ are given in Table IV. The yield of crude $[(C_2H_5)_2As]_3N$ was 1.0 g.

The tacky white solid, insoluble in petroleum ether, was extracted with boiling benzene. The remaining white solid residue was shown by infrared spectroscopy to be ammonium chloride. Ten milliliters of triethylamine was added to the benzene extract and the resulting solution was refluxed for 12 hr. The solution was evaporated to dryness giving 2.06 g of white solid residue. Absence of triethylamine hydrochloride was indicated by the complete solubility of the white solid in CCl_4 . Recrystallization of the white solid using boiling CCl_4 gave a 30% recovery of a white needlelike solid. The melting point data were as follows: 70° , shrinks; 80° , takes on a wet appearance; 105 – 108° , melts to a clear, colorless liquid. Anal. Calcd for $(C_2H_5)_4As_2N_2 \cdot HCl$: C, 29.05; H, 6.41; N, 8.48; As, 45.35; Cl, 10.72. Found: C, 29.50; H, 6.70; N, 8.52; As, 45.42; Cl, 10.64. The infrared spectral data are given in Table I. The mass spectral data are given in Table V. The nmr spectrum obtained in C_6H_6 using TMS as the internal standard shows a quartet (-140 to -111 Hz) and a triplet (-86 to -61 Hz) attributed to the methylene and methyl protons, respectively.

Reaction of an Ammonia-Chloramine Mixture with Tetramethyldiarsine. Tetramethyldiarsine (1.3 g, 6.2 mmol) was dissolved in 40 ml of dry benzene and chloraminated in the presence of ammonia on the generator. A white precipitate formed immediately. The chloramination was continued for 25 min. The solid product was extracted with hot acetonitrile to give a white crystalline material on standing; mp 220 – 221° . Anal. Calcd for $(CH_3)_4As_2N_2 \cdot HCl$: C, 17.49; H, 4.78; N, 10.21; As, 54.60; Cl, 12.92. Found: C, 17.40; H, 4.69; N, 10.51; As, 54.18; Cl, 12.74. The melting point, infrared spectra, and proton magnetic resonance spectra of this material were identical with those of the product obtained by the reaction of dimethylchloroarsine with an ammonia-chloramine mixture; yield 1.0 g.

Reaction of an Ammonia-Chloramine Mixture with Tetraphenyldiarsine. Tetraphenyldiarsine (1.07 g, 2.3 mmol) was dissolved in 40 ml of benzene and allowed to react with the gaseous ammonia-chloramine mixture from the chloramine generator for 15 min. The solid product was extracted with hot benzene. Evaporation of the benzene solution gave a solid residue weighing 1.10 g. A portion of this material was recrystallized twice with a benzene-ether mixture; mp 206 – 208° . Anal. Calcd for $[(C_6H_5)_2AsN]_3 \cdot HCl$: C, 56.45; H, 4.08; N, 5.49; As, 29.35; Cl, 4.63. Found: C, 55.75; H, 4.19; N, 5.40; As, 29.77; Cl, 5.18. The infrared spectral data are given in Table I. The nmr spectrum in $CDCl_3$ showed only highly split phenyl resonances.

When a benzene solution of $[(C_6H_5)_2AsN]_3 \cdot HCl$ was treated with triethylamine, a white solid precipitated which was then filtered, washed with benzene, and dried *in vacuo*. The infrared spectrum and melting point of this material were identical with those of a pure sample of triethylamine hydrochloride. The filtrate was evaporated under reduced pressure to give a white powder, mp 159 – 160° . The melting point reported for $[(C_6H_5)_2AsN]_3$ is 155 – 157° .⁴ The infrared spectrum of this material was the same as that reported for the trimer.⁴

Reaction of an Ammonia-Chloramine Mixture with Diphenylchloroarsine. The chloramination of diphenylchloroarsine was carried out on the generator using the general procedure described above. The resulting solid product was extracted with boiling acetonitrile. Upon cooling of the acetonitrile solution, colorless, triclinic crystals, mp 158 – 160° , were obtained. Anal. Calcd for $[(C_6H_5)_2AsN]_3$: C, 59.25; H, 4.14; N, 5.77; As, 30.83; mol wt 729. Found: C, 59.04; H, 4.34; N, 5.81; As, 30.81; mol wt 713 (in benzene). Prolonged heating of the acetonitrile solution gave upon cooling a crystalline material containing triclinic and tetragonal crystals. Evaporation of the acetonitrile solution gave more triclinic and tetragonal crystals and a tacky, slightly colored material. The tacky material was not characterized. X-Ray data showed that the triclinic crystals were those of the trimer $[(C_6H_5)_2AsN]_3$, whereas the tetragonal crystals were those of the tetramer $[(C_6H_5)_2AsN]_4$. The mass spectral data for $[(C_6H_5)_2AsN]_4$ are given in Table VI.

Ammonolysis of $(C_6H_5)_2AsCl_3$. A 5.28-g (0.02-mol) sample of $(C_6H_5)_2AsCl_3$ was allowed to react with 1 mol of ammonia in a stain-

less steel bomb at room temperature. The white solid product was extracted with boiling acetonitrile. When the solution was cooled, white, triclinic crystals, mp 158–160°, were obtained. The infrared spectrum was identical with that of $[(C_6H_5)_2AsN]_3$.⁴ Heating the acetonitrile solution for 1 hr or more, followed by cooling, produced a white, crystalline material containing triclinic and tetragonal crystals. These were shown to be $[(C_6H_5)_2AsN]_3$ and $[(C_6H_5)_2AsN]_4$, respectively.

X-Ray Structural Study of 2,2,4,4,6,6-Hexaphenylcyclotriarsazene, $[(C_6H_5)_2AsN]_3$. Platelike crystals of $[(C_6H_5)_2AsN]_3$ were obtained by slowly cooling a hot acetonitrile solution of the compound. Since the crystals are sensitive to moisture, they were stored under mineral oil. Crystals for use in the X-ray analysis were transferred along with mineral oil into Lindemann glass capillaries. Weissenberg and oscillation photographs showed that the crystals are triclinic. We assumed that the space group is $P\bar{1}$, and this assumption was corroborated by the structure analysis. A crystal with approximate dimensions of $0.4 \times 0.3 \times 0.2$ mm was mounted along its a axis on a Picker FACS-1 diffractometer. Cell dimensions, which were determined by a least-squares analysis of the 2θ values for 13 high-angle reflections (Cu $K\alpha_1$, λ 1.54051 Å; $23 \pm 3^\circ$) are $a = 9.713$ (1) Å, $b = 11.825$ (2) Å, $c = 15.645$ (2) Å, $\alpha = 67.72$ (1)°, $\beta = 93.49$ (1)°, and $\gamma = 105.79$ (1)°. The experimentally determined density, 1.51 g/cm³, as measured by flotation in benzene and 1,2-dibromoethane, compares well with that of 1.515 g/cm³ calculated for two formula units per cell.

Intensity data were collected with the diffractometer using Ni-filtered Cu $K\alpha$ radiation and the θ - 2θ technique with a scanning speed of 2°/min in 2θ . Background measurements of 10 sec were made at each terminus of a scan. Measurements were started with a 2θ limit of 128° for the $h > 0, k > 0, l > 0$ sector of the reciprocal space. Since there were only a few reflections with appreciable intensities beyond 100°, the 2θ limit for the rest of the data collection was lowered to 100°. A total of 3818 independent intensities were obtained. The intensities of two reference reflections (040 and 005) which were monitored periodically during the data collection process decreased continuously to about 93% of their original values. The check reflection intensities were used to calculate a scale factor as a function of crystal exposure time. The measured intensities of all reflections were then scaled to what their values would have been at the beginning of the intensity measurements. The reflections were assigned intensity values and standard deviations according to the formulas

$$I = S - 0.5(B_1 + B_2)(T_s/T_b)$$

$$\sigma(I) = [S + 0.25(B_1 + B_2)(T_s/T_b)^2 + (0.03S)^2]^{1/2}$$

with S being the total scan count, B_1 and B_2 the background counts, T_s the scan time, and T_b the counting time for each background. Reflections that had scan counts below background levels were assigned intensity values of 0.0 and were included in all subsequent calculations. The intensities and their variances were corrected for Lorentz and polarization factors, and absorption corrections were applied by using the program ORABS.²⁰ The calculated transmission factors ranged from 0.41 to 0.51. The absorption corrections did not include contributions of the glass capillary or the mineral oil that surrounded the crystal.

The phase determination was carried out using the symbolic addition method^{21,22} as applied by Long²³ based on 258 reflections with $E \geq 1.70$. Of the 16 solutions generated by assigning arbitrary signs to 7 reflections, one was outstanding, converging the most rapidly (9 cycles) and having the highest consistence index (0.99). An E map based on this solution revealed the locations of the three arsenic atoms. A structure factor calculation based on the arsenic atoms resulted in an R index of 0.35 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). The nitrogen and carbon atoms were located in a difference Fourier map that was phased with the arsenic atoms. The trial structure was refined by use of a modified version of the full-matrix least-squares program ORFLS.²⁴ The quantity minimized was $\sum w(F_o^2 - F_c^2/k^2)^2$, where k is a scale factor and the weight w is equal to $1/\sigma^2(F_o^2)$. Scattering

factors for the neutral nonhydrogen atoms were from ref 25, and hydrogen atom scattering factors were from Stewart, Davidson, and Simpson.²⁶ Both real and imaginary anomalous dispersion corrections from Cromer and Liberman²⁷ were applied to the atomic scattering factors for arsenic, nitrogen, and carbon. Final cycles of refinement included the positional parameters and anisotropic temperature factors for the nonhydrogen atoms. Hydrogen atom positions were calculated assuming sp^2 bonding and a C-H distance of 0.9 Å. These parameters were included in the structure factor calculations, but not in the refinement. In the last cycle the average shift/deviation ratio was 1:3 and the largest ratio was 1:2 for the β_{33} temperature factor of atom As(1). R and R_w ($R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4]^{1/2}$) had final values of 0.061 and 0.123, respectively. A final three-dimensional difference map showed several peaks and troughs ranging from -0.7 to 0.5 e/Å³. The heavy-atom parameters are listed in Table VII; hydrogen parameters are given in Table VIII. A table of observed and calculated structure factors is available upon request.²⁸

X-Ray Structural Study of $[(C_6H_5)_2AsN]_4$. $[(C_6H_5)_2AsN]_4$ crystallizes from acetonitrile in the form of well-developed tetragonal prisms. The space group $P4_21c$ was indicated by the following systematic absences of reflections in Weissenberg photographs: $h0l$ for l odd and $h00$ for h odd. A needle fragment with approximate dimensions of 0.2, 0.2, and 0.5 mm was sealed in a Lindemann glass capillary. Cell dimensions determined as described for the case of $[(C_6H_5)_2AsN]_3$ are $a = 14.968$ (1) Å and $c = 9.702$ (1) Å (Cu $K\alpha_1$, λ 1.54051 Å; $23 \pm 3^\circ$). X-Ray work with the tetramer was discontinued when we discovered that the crystal structure had been determined earlier by Glick.³ The values for the cell constants which Glick determined by photographic methods are $a = 14.96$ (3) Å and $c = 9.76$ (2) Å.

Discussion

The results of this study show that dimethylchloro- and diethylchloroarsines react with chloramine, in the presence of ammonia, to give compounds having the empirical formula $R_4As_2N_2HCl$ ($R = CH_3$ or C_2H_5). Furthermore, cleavage of the arsenic-arsenic bond occurs when chloramine reacts with tetramethyldiarsine in the presence of ammonia to give the $(CH_3)_4As_2N_2HCl$ species. The infrared spectra of these compounds show very strong and broad absorption bands in the 1000–900-cm⁻¹ region. Reichle¹ previously assigned the broad, intense infrared absorption peak observed at 943 cm⁻¹ for $[(C_6H_5)_2AsN]_4$ to the As=N vibrational mode. A similar peak was observed by Sisler and Stratton⁴ for $[(C_6H_5)_2AsN]_3$. Even though analogous empirical formulas are obtained for the methyl- and ethyl-substituted products, they are not analogous compounds as indicated by their physical properties and respective mass spectra. The mass spectra of $(CH_3)_4As_2N_2HCl$ (I) and $(C_2H_5)_4As_2N_2HCl$ (II) at 70-eV ionizing voltage are given in Tables II and V, respectively. Neither spectrum shows a molecular ion peak for these compounds.

I is insoluble in nonpolar organic solvents and only slightly soluble in hot chloroform and acetonitrile. II is very soluble in nonpolar and polar organic solvents.

Table II shows that the most intense peak in the spectrum is assignable to $(CH_3)_2AsNH_3^+$. Furthermore, many peaks are assignable to fragments containing arsenic-nitrogen bonds, and the As-N containing fragments comprise about 32% of the total ions in the spectrum. Fragments containing arsenic-chloride bonds account for 16.2%; peaks assignable to HCl and Cl account for 7.6%; and peaks assignable to NH_4 , NH_3 , and NH_2 account for 24% of the total ions. It is reasonable

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(28) See paragraph at end of paper regarding supplementary material.

Table VII. Heavy-Atom Parameters and Their Standard Deviations^a

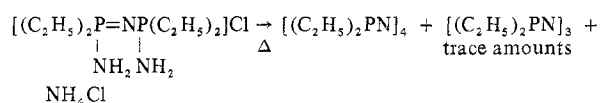
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As(1)	914 (1)	7,238 (1)	854 (1)	111 (1)	66 (1)	32 (1)	23 (1)	-4 (1)	-18 (1)
As(2)	1574 (1)	5,091 (1)	2476 (1)	110 (1)	60 (1)	37 (1)	25 (1)	-2 (1)	-18 (1)
As(3)	909 (1)	7,268 (1)	2754 (1)	114 (1)	68 (1)	36 (1)	31 (1)	-8 (1)	-24 (1)
N(1)	1197 (7)	5,715 (5)	1304 (4)	188 (10)	73 (6)	46 (3)	60 (6)	-18 (5)	-26 (4)
N(2)	1439 (7)	5,850 (5)	3227 (4)	197 (10)	82 (6)	38 (3)	67 (6)	-14 (4)	-26 (4)
N(3)	897 (7)	8,095 (5)	1566 (4)	182 (10)	83 (6)	39 (3)	44 (6)	-5 (4)	-30 (4)
C(1)	-834 (7)	7,054 (6)	212 (4)	87 (9)	83 (7)	41 (4)	24 (6)	-4 (5)	-21 (4)
C(2)	-1552 (8)	5,909 (7)	159 (5)	130 (11)	104 (8)	57 (4)	12 (8)	1 (6)	-40 (5)
C(3)	-2780 (9)	5,797 (8)	-320 (6)	135 (13)	142 (11)	81 (6)	4 (10)	-2 (7)	-60 (7)
C(4)	-3329 (9)	6,822 (10)	-748 (6)	133 (13)	187 (13)	76 (6)	42 (11)	-13 (7)	-70 (8)
C(5)	-2609 (10)	7,970 (9)	-718 (6)	173 (14)	174 (12)	88 (6)	81 (11)	-51 (8)	-71 (8)
C(6)	-1342 (9)	8,107 (8)	-252 (6)	153 (13)	126 (10)	77 (6)	47 (9)	-28 (7)	-56 (6)
C(7)	2327 (7)	8,323 (6)	-125 (4)	89 (9)	81 (7)	44 (4)	20 (6)	-5 (5)	-12 (5)
C(8)	2872 (10)	9,569 (8)	-259 (7)	170 (14)	109 (10)	89 (6)	3 (10)	-7 (8)	-20 (7)
C(9)	3940 (12)	10,313 (10)	-1022 (9)	202 (18)	131 (12)	112 (9)	-23 (12)	-2 (10)	-16 (9)
C(10)	4341 (10)	9,783 (13)	-1557 (7)	123 (14)	217 (18)	77 (7)	69 (13)	6 (8)	-17 (9)
C(11)	3758 (11)	8,559 (11)	-1416 (7)	173 (16)	198 (16)	71 (6)	81 (13)	18 (8)	-12 (8)
C(12)	2746 (10)	7,814 (8)	-718 (5)	207 (15)	131 (10)	43 (4)	52 (10)	13 (7)	-13 (6)
C(13)	3491 (7)	4,900 (6)	2531 (5)	105 (10)	74 (7)	48 (4)	21 (7)	-4 (5)	-28 (5)
C(14)	3880 (9)	3,940 (7)	3261 (6)	127 (12)	102 (9)	86 (6)	36 (8)	-21 (7)	-47 (6)
C(15)	5279 (11)	3,838 (9)	3284 (7)	154 (15)	132 (11)	113 (8)	64 (10)	-22 (9)	-62 (8)
C(16)	6275 (10)	4,718 (11)	2592 (8)	150 (15)	185 (14)	111 (8)	62 (12)	-20 (9)	-99 (9)
C(17)	5901 (10)	5,693 (11)	1896 (7)	146 (16)	211 (15)	87 (7)	-14 (12)	29 (8)	-87 (9)
C(18)	4512 (9)	5,800 (8)	1852 (5)	110 (12)	146 (10)	58 (5)	-8 (9)	1 (6)	-40 (6)
C(19)	366 (7)	3,387 (6)	2991 (5)	96 (9)	77 (7)	44 (4)	12 (6)	6 (5)	-19 (5)
C(20)	60 (8)	2,670 (7)	2449 (6)	122 (12)	86 (8)	83 (6)	27 (8)	5 (6)	-31 (6)
C(21)	-808 (10)	1,400 (8)	2820 (8)	155 (14)	84 (9)	112 (8)	24 (9)	10 (8)	-32 (7)
C(22)	-1293 (12)	927 (9)	3720 (9)	239 (19)	87 (10)	115 (9)	2 (11)	1 (11)	-9 (8)
C(23)	-1026 (16)	1,665 (11)	4241 (8)	410 (29)	151 (14)	77 (7)	-52 (16)	43 (12)	-14 (8)
C(24)	-170 (10)	2,906 (9)	3871 (6)	211 (16)	146 (12)	70 (6)	-50 (11)	33 (8)	-33 (7)
C(25)	2194 (7)	8,430 (6)	3223 (4)	104 (10)	73 (7)	33 (3)	25 (6)	-5 (5)	-14 (4)
C(26)	3279 (8)	8,075 (7)	3776 (5)	151 (12)	129 (9)	61 (5)	30 (9)	-8 (6)	-55 (6)
C(27)	4256 (9)	8,939 (9)	4087 (6)	156 (13)	163 (12)	66 (5)	15 (10)	-8 (7)	-58 (7)
C(28)	4104 (10)	10,148 (8)	3838 (6)	190 (15)	118 (10)	53 (5)	-31 (10)	10 (7)	-33 (6)
C(29)	2961 (11)	10,486 (7)	3307 (6)	246 (18)	80 (8)	72 (6)	1 (10)	-9 (8)	-31 (6)
C(30)	2021 (9)	9,634 (7)	3007 (5)	198 (14)	85 (8)	58 (5)	29 (8)	-22 (6)	-25 (5)
C(31)	-927 (7)	6,986 (6)	3312 (4)	102 (10)	69 (7)	42 (4)	28 (7)	-6 (5)	-22 (4)
C(32)	-1330 (8)	6,012 (7)	4167 (5)	113 (12)	123 (9)	46 (4)	32 (8)	-12 (6)	-28 (6)
C(33)	-2635 (9)	5,819 (8)	4605 (6)	145 (14)	128 (10)	61 (5)	35 (9)	-4 (7)	-31 (6)
C(34)	-3522 (10)	6,568 (9)	4173 (6)	150 (14)	150 (11)	76 (6)	41 (11)	2 (8)	-40 (7)
C(35)	-3133 (10)	7,523 (9)	3301 (6)	177 (16)	141 (11)	76 (6)	64 (10)	5 (8)	-32 (7)
C(36)	-1820 (9)	7,730 (7)	2877 (6)	135 (12)	89 (8)	71 (5)	40 (8)	-5 (7)	-27 (6)

^a The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + \dots + 2k\beta_{23})]$. All values have been multiplied by 10^4 .

to postulate that I contains few, if any, As-Cl bonds. If the Cl is present as Cl^- in I, then As-Cl containing fragments could easily arise from recombination mechanisms within the mass spectrometer. Physical properties and mass, nmr, and infrared spectral data would suggest that I is an arsenic-nitrogen bonded compound, probably polymeric with As-N multiple bonding, and could reasonably be postulated to be a hydrochloride salt. A hydrochloride salt would not be unexpected, since chloramination of tetraphenyldiarsine yields a hydrochloride, $[(\text{C}_6\text{H}_5)_2\text{AsN}]_3 \cdot \text{HCl}$. In the phenyl-substituted case, the HCl could be successfully removed by reaction with triethylamine and the pure arsenonitrile trimer isolated.

The mass spectral data suggest that under the mass spectrometry conditions I gives dimethyl-substituted arsenonitrilic compounds. Tables II and III show peaks at m/e values of 476 and 357 assignable to $[(\text{CH}_3)_2\text{AsN}]_4$ and $[(\text{CH}_3)_2\text{AsN}]_3$, respectively, and associated peaks corresponding to fragments wherein CH_3 groups are successively lost from the tetramer and trimer. The occurrence of arsenonitrilic species in the mass spectrum of I would not be unexpected if I is assumed to be a hydrochloride salt of an arsenic-nitrogen polymer containing no As-Cl bonds. Such a polymer could cyclize with loss of NH_4Cl and resultant formation of $[(\text{CH}_3)_2\text{AsN}]_4$ and $[(\text{CH}_3)_2\text{AsN}]_3$. This type of reaction is well known for the pyrolysis of phosphorus-nitrogen intermediates obtained

from ammonia-chloramine reactions with dialkylchlorophosphines and tetraalkyldiphosphines^{8,29}



Since no metastable peaks are observed in the spectrum of I, a fragmentation mechanism cannot be supported by mass spectral data.

I is identical in its properties and spectral data with the compound reported earlier from the ammonia-chloramine reaction with dimethylarsine.¹⁰ The data could agree with the previously speculated structure of $[(\text{CH}_3)_2\text{AsN}]_4 \cdot 2\text{HCl}$, but not the equimolar mixture of $[(\text{CH}_3)_2\text{AsN}]_4$ and $[(\text{CH}_3)_2\text{AsN}]_3 \cdot 4\text{HCl}$. A structural formula is difficult to propose from the available data, but I is speculated to be a hydrochloride intermediate of the dimethylarsenonitrile tetramer.

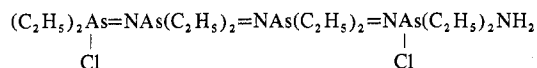
Table V (compound II) shows that the most intense peak can be assigned to the $(\text{C}_2\text{H}_5)_2\text{As}^{35}\text{Cl}^+$ fragment. Fragments containing As-Cl bonds account for 49.4% of the total ions in the spectrum. The spectrum also contains many peaks assignable to fragments containing As-N bonds (21.5% of total ions). There is a complete absence of peaks assignable to HCl or Cl and that assignable to NH_3 is of low per cent

Table VIII. Hydrogen Atom Parameters^a

Atom	x	y	z
H(C2)	-180	545	79
H(C3)	-352	515	13
H(C4)	-414	658	-38
H(C5)	-320	818	-42
H(C6)	-159	831	24
H(C8)	338	949	28
H(C9)	471	1050	-65
H(C10)	532	990	-145
H(C11)	464	816	-119
H(C12)	309	719	-29
H(C14)	329	323	315
H(C15)	526	306	318
H(C16)	660	437	227
H(C17)	607	550	140
H(C18)	417	568	134
H(C20)	96	259	233
H(C21)	-18	92	282
H(C22)	-94	29	404
H(C23)	-56	123	475
H(C24)	74	276	421
H(C26)	378	779	347
H(C27)	510	904	374
H(C28)	493	1070	346
H(C29)	356	1106	275
H(C30)	204	1003	238
H(C32)	-64	625	455
H(C33)	-236	605	514
H(C34)	-370	694	455
H(C35)	-296	829	346
H(C36)	-136	855	272

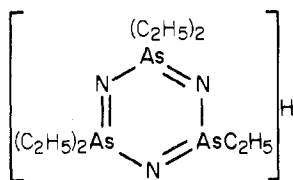
^a The positional parameters are multiplied by 10^3 . All hydrogen atoms were assigned an isotropic temperature factor of 3.0 \AA^2 .

abundance (4.8%). These data would suggest that II contains both As-N and As-Cl bonds and that no mechanism is available for the formation of NH_4Cl . The physical properties and mass and infrared spectral data would suggest that II is an arsenic-nitrogen bonded compound, probably polymeric with multiple As-N bonding, that it contains As-Cl bonds, and that it is not a hydrochloride salt. A possible structural formula would be



although other polymeric species are possible.

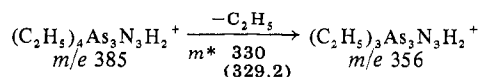
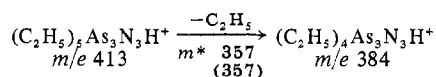
The mass spectral data for II show no peaks assignable to either the arsenonitrilic tetramer or trimer. It is tempting to assign the weak peak at m/e to the species



although an open-chain arsenic-nitrogen bonded species is possible. The lack of an arsenonitrilic tetramer and trimer in the mass spectrum of II would be consistent with the assumption of a covalently bonded arsenic-nitrogen polymer containing As-Cl bonds. A cyclized As-N polymer observed in the mass spectrum should contain As-Cl bonds or be a fragment showing a loss of Cl. This would be analogous to known pyrolysis reactions involving P-N polymers containing P-Cl bonds.⁹

The metastable peaks at 357 and 330 correspond to the transitions $413^+ \rightarrow 384^+ + 29$ and $385^+ \rightarrow 356^+ + 29$. The following fragmentation mechanisms and ion structures are

assumed for the genesis of these ions (calculated m^* given in parentheses)



Other metastable peaks in the mass spectrum of II suggest possible fragmentation mechanisms. Metastable ions were detected for m/e values of 228, 200, 172, 119, and 117. These correspond to the following transitions: $282^+ \rightarrow 253^+ + 29$; $254^+ \rightarrow 225^+ + 29$; $226^+ \rightarrow 197^+ + 29$; $170^+ \rightarrow 141^+ + 29$; $168^+ \rightarrow 139^+ + 29$. All such transitions involve the loss of an ethyl group from an As-N or an As-Cl species.

In addition to $(C_2H_5)_4As_2N_2HCl$, an appreciable amount of $[(C_2H_5)_2As]_3N$ was obtained in the ammonia-chloramine-diethylchloroarsine reaction. The existence of the tris(diethylarsino)amine is indicated by analytical, molecular weight, nmr, and infrared data. The absence of a multiple As-N bond is indicated by the lack of a strong infrared absorption peak in the $1200\text{--}800\text{-cm}^{-1}$ region. A very strong absorption peak is observed at 755 cm^{-1} , which is probably assignable to the As-N stretching mode. This assignment is not unreasonable since the P-N stretching mode appears between 750 and 1000 cm^{-1} depending upon the substituents on the nitrogen.³⁰ The existence or formation of this species in the presence of excess chloramine would not be expected. Instead, the attack of chloramine on the tertiary arsine to give possibly an arsenic-nitrogen polymer as a final reaction product would be postulated. The tris(diethylarsino)amine was always obtained when diethylchloroarsine was chloraminated on the generator. No acceptable reaction path has been postulated to explain the formation of this species.

The mass spectrum of $[(C_2H_5)_2As]_3N$ shows no molecular ion peak but does show peaks which may be assigned to expected fragments of such a compound. The only peak suggesting three arsenics bonded to one nitrogen atom is found at m/e 356 and can be assigned as $(C_2H_5)_4As_3NH^+$. Most other assignments are for As-N-As or As-N type species.

The ammonolysis of $(C_6H_5)_2AsCl_3$ and reaction of ammonia-chloramine mixtures with diphenylchloroarsine gives triclinic crystals of $[(C_2H_5)_2AsN]_3$. The molecular weight and the results of the X-ray structure determination confirmed the formation of the trimer reported earlier by Sisler and Stratton.⁴ Figure 1 shows the trimer molecule as viewed approximately perpendicular to the plane through the three arsenic atoms. Bond distances and angles involving the atoms of the central ring are given in Tables IX and X, respectively. The As-N distances vary from 1.742 (6) to 1.771 (6) Å with a mean bond length of 1.758 (4) Å. The scatter for the As-N bond lengths as calculated by $s = [\sum_i \Delta_i^2 / (n - 1)]^{1/2}$ (with Δ_i the i th deviation from the mean and $n = 6$) is 0.010 Å. This value is comparable with the values for the individual esd's of 0.006 Å for the As-N bond distances (Table IX). Therefore we conclude that all As-N bonds are equivalent. This is in contrast to the tetrameric compound $[(C_6H_5)_2AsN]_4$ where the X-ray crystallographic results suggest an alternating pattern of As-N bond distances with the two types of bonds displaying lengths of 1.67 (3) and 1.79 (3) Å.³ In both the trimer and the tetramer, the As-N bond distances appear to be shorter than one would expect for an As-N

(30) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1960, p 324.

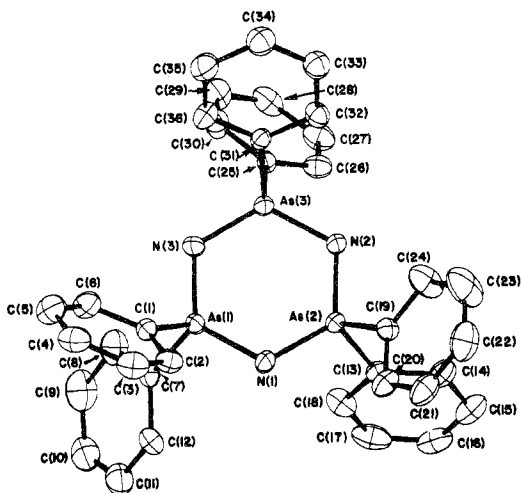


Figure 1. A molecule of $[(C_6H_5)_2AsN]_3$. Atoms are represented by thermal ellipsoids which are defined by the principal axes of thermal vibration and are scaled to include 25% probability.

Table IX. Selected Bond Distances in $[(C_6H_5)_2AsN]_3$ (Å)

As(1)-N(1)	1.760 (6)	As(1)-C(1)	1.922 (7)
As(1)-N(3)	1.771 (6)	As(1)-C(7)	1.919 (7)
As(2)-N(1)	1.755 (6)	As(2)-C(13)	1.929 (7)
As(2)-N(2)	1.757 (6)	As(2)-C(19)	1.919 (7)
As(3)-N(2)	1.763 (6)	As(3)-C(25)	1.925 (7)
As(3)-N(3)	1.742 (6)	As(3)-C(31)	1.923 (7)

Table X. Selected Bond Angles in $[(C_6H_5)_2AsN]_3$ (deg)

As(1)-N(1)-As(2)	118.2 (4)	N(1)-As(2)-C(13)	107.4 (3)
N(1)-As(2)-N(2)	121.5 (3)	N(1)-As(2)-C(19)	107.1 (3)
As(2)-N(2)-As(3)	117.2 (5)	N(2)-As(2)-C(13)	107.4 (3)
N(2)-As(3)-N(3)	122.5 (3)	N(2)-As(2)-C(19)	107.7 (3)
As(3)-N(3)-As(1)	116.4 (4)	C(13)-As(2)-C(19)	104.6 (3)
N(3)-As(1)-N(1)	121.7 (3)	N(2)-As(3)-C(25)	105.5 (3)
N(1)-As(1)-C(1)	105.1 (3)	N(2)-As(3)-C(31)	108.5 (3)
N(1)-As(1)-C(7)	108.7 (3)	N(3)-As(3)-C(25)	105.8 (3)
N(3)-As(1)-C(1)	110.7 (3)	N(3)-As(3)-C(31)	109.1 (3)
N(3)-As(1)-C(7)	106.1 (3)	C(25)-As(3)-C(31)	103.9 (3)
C(1)-As(1)-C(7)	103.0 (3)		

single bond. The single-bond distance calculated from Pauling's covalent single-bond radii³¹ is 1.87 Å if one applies the Schomaker-Stevenson correction.³² This value of 1.87 Å has been confirmed by an X-ray structure investigation of the adamantane-type compound $As_4(NCH_3)_6$.⁵ A slightly shorter average value of 1.83 Å has been determined for the cyclic compound $[ClAsNCH_3]_3$.⁶ As in the phosphonitriles, the relative shortening of bonds in $[(C_6H_5)_2AsN]_3$ and $[(C_6H_5)_2AsN]_4$ can be explained in terms of π bonding that is delocalized in the trimer but localized in the tetramer.

The As_3N_3 ring is slightly puckered. The maximum deviation of an atom from the least-squares plane passing through the ring is about 0.1 Å (Table XI). A slight but lesser puckering has also been observed for the P_3N_3 ring in $[(C_6H_5)_2PN]_3$.³² All three N-As-N ring angles are larger than 120° [range 121.5 (3)-122.5 (3)°, mean 121.9 (3)°] and the three As-N-As ring angles are less than 120° [range 116.4 (4)-118.2 (4)°, mean 117.3 (5)°]. This distribution of ring angles is different from that in the corresponding phosphorus compound, $[(C_6H_5)_2PN]_3$, where the ranges and mean values are 117.4 (3)-118.2 (3) and 117.8 (2)° for the N-P-N angles and 121.3 (4)-123.0 (4) and 122.1 (5)° for the P-N-P angles.

The C-C bond lengths of the phenyl groups vary from

Table XI. Deviations from the Least-Squares Plane through the Central Ring^a

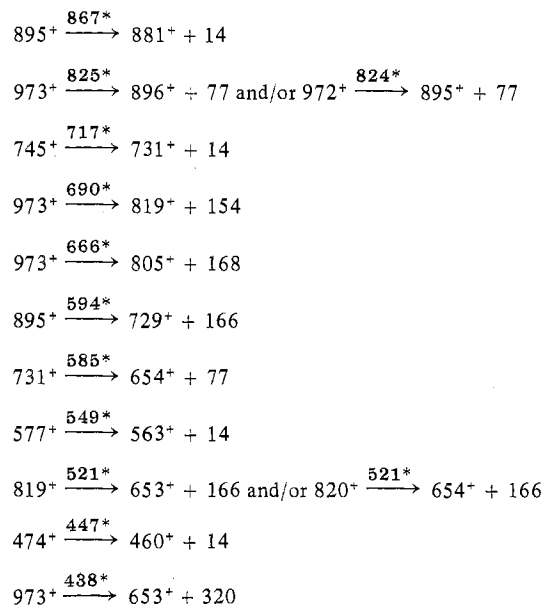
Atom	Dev, Å	Atom	Dev, Å
As(1)	0.00	N(1)	-0.08
As(2)	0.06	N(2)	0.04
As(3)	-0.12	N(3)	0.10

^a All atoms were given equal weight in the calculation.

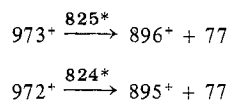
1.338 (19) to 1.460 (17) Å with a mean value of 1.382 (4) Å. The standard error calculated from the spread of the 36 C-C bond distances is 0.022 Å and the average of the individual esd's is 0.014 Å. The corresponding values for the 36 C-C-C ring angles are as follows: range, 115.9 (1.0)-121.7 (1.2)°; mean, 120.0 (2)°; error from the scatter of the angles, 1.1°; average of the individual esd's, 0.9°.

Prolonged heating of an acetonitrile solution of the trimer followed by cooling produces a mixture of trimer and tetramer and a small amount of tacky material. This suggests that ring opening occurs when the trimer is heated. Recyclization then occurs to give tetrameric or tetrameric and trimeric oligomers. The tacky material is believed to be a mixture of higher arsenic-nitrogen polymers. Such behavior of arsenonitriles is not unexpected, since phosphonitriles are known to undergo polymerization-depolymerization reactions at high temperatures.

The mass spectrum of $[(C_6H_5)_2AsN]_4$ (Table VI) shows the molecular ion peak of moderate intensity at m/e 972. The metastable peaks (867, 825d, 717, 690, 666, 594, 585, 549, 521, 448, 438) correspond to the transitions



The most intense metastable peak observed in the spectrum, 825, was broad and merged with the peak observed at 820. This broad peak might result from the overlap of the metastable ions for the transitions of



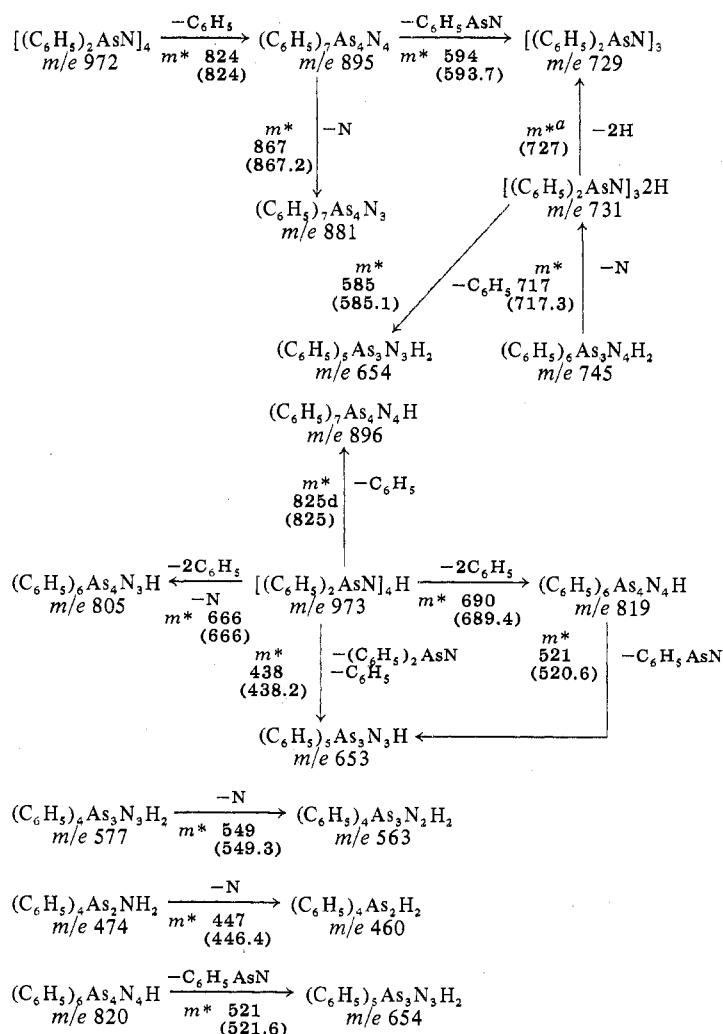
These transitions suggest the possible fragmentation mechanisms shown in Scheme I for the molecular ion M^+ , $M^+ + 1$, and other fragments.

The mass spectral data show that opening of the As_4N_4 ring occurs with the formation of the As_3N_3 species. The very intense and broad metastable peak at 825 suggests that

(31) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 221-230.

(32) V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

Scheme I



^a The metastable peak at 727 appears to be present because of the unsymmetrical nature of the m/e peak at 729.

loss of a phenyl group by the tetramer and $[(C_6H_5)_2AsN]_4H$ occurs quite readily with the formation of $(C_6H_5)_7As_4N_4$ (most intense peak in the spectrum) and $(C_6H_5)_7As_4N_4H$. The $(C_6H_5)_7As_4N_4$ species, through loss of a C_6H_5AsN group, forms the trimer. Fragments containing the As_4N_4 and As_3N_3 backbones appear to be stable. The As_4N_4 ions account for 42% and the As_3N_3 ions for 31% of the total ions in the spectrum. Fragments containing the As_4N_3 backbone make up 8.5% of the total ions. The remainder of the ions can be accounted for in terms of $As_2N_2^-$, As_2N^- , AsN^- , and As-substituted species.

This study also shows that ammonia and deuterated ammonia react with dimethylchloroarsine in a 1:1 mole ratio to give the respective arsenoammonium salts. The area ratios obtained by nuclear resonance measurements for the CH and NH protons indicate that the nitrogen atom is tetracoordinate in these species.

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Registry No. $[(CH_3)_2AsNH_3]Cl$, 40907-40-2; $[(CH_3)_2AsND_3]Cl$, 40907-41-3; $(CH_3)_4As_2N_2HCl$, 39322-80-0; $(C_2H_5)_4As_2N_2HCl$, 40907-42-4; $[(C_2H_5)_2As]_3N$, 40907-43-5; $[(C_6H_5)_2AsN]_3 \cdot HCl$, 40907-44-6; $[(C_6H_5)_2AsN]_3$, 13401-15-5; $[(C_6H_5)_2AsN]_4$, 13275-03-1; ND_3 , 13550-49-7; $(C_6H_5)_2AsCl_3$, 29165-89-7; dimethylchloroarsine, 557-89-1; ammonia, 7664-41-7; chloramine, 10599-90-3; diethylchloroarsine, 686-61-3; tetramethyldiarsine, 471-35-2; tetraphenyldiarsine, 2215-36-3; diphenylchloroarsine, 712-48-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2304.