Experimental Section

Starting Materials.—DL-Methionine, DL-norleucine (Nutritional Biochemicals Corp.), and analytical grade metal salts were used without further purification.

Preparation and Characterization of the Complexes. Preparation I.—The amino acid (1.3 g) and Na_2CO_3 (0.5 g) were dissolved in 70 ml of water at 80° and the metal nitrate (hexahydrate) was added with stirring (metal:amino acid mole ratio 1:2.3). The resulting solution was concentrated under reduced pressure on a steam bath and then cooled in a refrigerator. After several hours the crystals which formed were filtered off, washed with water and ethanol, and dried *in vacuo* over P_4O_{10}.

Preparation II.—The amino acid was added to a suspension of $LiOH \cdot H_2O$ (slight excess over 1:1 mole ratio) in ethanol and stirred at 60° for 20 min. After filtration of the unreacted $LiOH \cdot H_2O$, a solution of the metal perchlorate (hexahydrate) in ethanol was added slowly. (The metal:amino acid mole ratio was 1:2 for the $M^{II}L_2$ complexes and 1:3 for the $M^{III}L_3$ and $M^{II}LClO_4$ complexes.) The precipitate which formed immediately was filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10}. For the compounds [NiMt]ClO_4, [CuMt]ClO_4, [CoNorl$_2$]$_n$, [NiNorl$_2$]$_n$, and [CuNorl$_2$]$_n$, precipitation occurred after the reaction mixture was cooled in a refrigerator for several hours. For the compounds [CrMt$_3$] and [FeMt$_3$], the reaction mixture was heated on a steam bath for 30 min, until crystallization began.

Preparation III was carried out similarly to preparation II, except that the lithium methioninato solution was added to the metal perchlorate solution (metal:methionine mole ratio 1:3).

Preparation IV was carried out according to the general method of Abderhalden and Schnitzler.[23] Freshly prepared $Cu(OH)_2$, suspended in a small volume of water, was added to a 10% aqueous solution of methionine (Cu:methionine mole ratio 1:2.2). The reaction mixture was stirred at 60° for 30 min; the deep blue crystals which formed were filtered off, washed with warm water and ethanol, and dried *in vacuo* over P_4O_{10}.

Preparation V.—A solution of sodium ethoxide in ethanol (0.12 g of sodium in 60 ml) was treated with 1.50 g of methionine and then with hydrated zinc(II) perchlorate (1.33 g) dissolved in a minimum volume of ethanol. The white precipitate which formed immediately was filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10}.

(23) E. Abderhalden and E. Schnitzler, *Z. Physik. Chem.*, **163**, 96 (1927).

Preparation VI.—Methionine (1.3 g) was dissolved in 60 ml of water, treated with $Na_2CO_3 \cdot H_2O$ (0.6 g), and heated at 80° for 20 min. Hydrated cobalt(II) perchlorate (1.1 g in 20 ml of water) was then added to the warm sodium methioninato solution, and the pale pink precipitate which formed slowly was filtered off, washed with water and ethanol, and dried *in vacuo* over P_4O_{10}.

Preparation VII.—An ethanol solution of the anhydrous metal chloride was added to a hot ethanol solution of lithium methioninato, and the mixture was refluxed for 3 hr. The resulting solution was filtered hot and on cooling gave a precipitate which was filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10}.

Preparation VIII.—An aqueous solution of the metal perchlorate hexahydrate (1.0 g in 20 ml) was added with stirring to an aqueous solution of the Li[AgMt$_2$] complex (1.0 g in 30 ml). The precipitate which formed immediately was filtered, washed with water and ethanol, and dried in air.

Preparation IX.—The [$M^{III}Mt_3$] and Li[NiMt$_3$] complexes were dissolved in ethanol and treated with an ethanol solution of silver nitrate or perchlorate. The precipitate which formed immediately was filtered off, washed with ethanol, and dried in air.

Deuterated Compounds.—The details of the preparations, analytical data, and properties of the deuterated compounds are available elsewhere.[22]

Measurements.—Analyses, magnetic susceptibility determinations, and infrared and electronic spectra and conductivity measurements were made as previously described.[24] The diffuse reflectance absorption maxima ($cm^{-1} \times 10^{-3}$) (a), and the molar conductivity values, Λ_M (ohm^{-1} cm^2 $mole^{-1}$) (b), of some complexes follow: (a) [CoMt$_2$]$_n$, 20.2, v br; 17.2 sh; [CoNorl$_2$]$_n$, 18.5; [CuMt$_2$]$_n$, 16.5; [CuNorl$_2$]$_n$, 16.5. (b) [FeMt$_3$], 1.840×10^{-3} M in water, $\Lambda_M = 223.9$; 1.690×10^{-3} M in methanol, $\Lambda_M = 74.8$; [RhMt$_3$], 1.675×10^{-3} M in water, $\Lambda_M = 55.6$; 2.100×10^{-3} M in methanol, $\Lambda_M = 5.9$; Li[NiMt$_3$], 1.190×10^{-3} M in water, $\Lambda_M = 115.0$; [NiMt]ClO_4, 1.590×10^{-3} M in acetonitrile, $\Lambda_M = 58.4$.

(24) J. V. Quagliano, J. T. Summers, S. Kida, and L. M. Vallarino, *Inorg. Chem.*, **3**, 1557 (1964).

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The Chloramination of Some Substituted Arsines

BY HARRY H. SISLER AND CEDRIC STRATTON

The reactions of triphenylarsine and diphenylchloroarsine with chloramine and with mixtures of chloramine and ammonia have been carried out and a variety of aminoarsonium chlorides and cyclic arsenonitriles prepared. Similar compounds have been derived by the ammonolysis of di- and trichlorophenylarsanes. It has been shown that chloramination, like chlorination, of phenylarsines results, under some conditions, in the fission of some of the arsenic–phenyl bonds and the elimination of chlorobenzene.

H. H. S. has previously reported that chloramine reacts with triphenylarsine to yield impure samples of triphenylaminoarsonium chloride,[1] but the pure compound was not isolated and characterized. We have

now accomplished this objective and also have studied the chloraminations of diphenylchloroarsine and tri-

(1) H. H. Sisler, XVIIth International Union of Pure and Applied Chemistry, Munich, Sept 1959.

methylarsine under a variety of conditions, both in the absence and in the presence of ammonia.

Experimental Section

Materials.—Triphenylarsine was obtained from J. T. Baker Chemical Co. and used as received. Chloramine was produced by the gas-phase chlorination of ammonia as described by Sisler, *et al.*[2] Anhydrous, ammonia-free chloramine was prepared in ethereal solution by the procedure of Gilson and Sisler.[3] All solvents were dried over calcium hydride. Trimethylarsine was prepared by the reaction of methylmagnesium iodide with arsenic-(III) chloride.[4] Diphenylchloroarsine was prepared by the dropwise addition of arsenic(III) chloride to triphenylarsine at 360°[5] and distillation of the resulting mixture, accepting only the fraction boiling at 200–210° (35 mm).

Analyses.—Most elemental analyses were carried out by Schwarzkopf Analytical Laboratory, Woodside, N. Y. Some of the nitrogen analyses were done in this laboratory using a Coleman Model 27 nitrogen analyzer. Some of the chloride analyses were done in this laboratory by the Volhard procedure.

Physical Measurements.—Infrared spectra were measured on a Perkin-Elmer Infracord Model 137 spectrophotometer. Most of the spectra were measured both in a Nujol mull and also in a Kel-F mull. Wavelength measurements were corrected by reference to a standard polystyrene spectrum. Infrared data are listed in Table I. Melting points are uncorrected. The nmr spectra were obtained using a Varian DP-60 spectrometer. All were run in deuteriochloroform and were externally referred to acetaldehyde.

Procedure.—Illustrative of the experimental procedures used in this study are the four procedures described below.

A. Direct Chloramination of Trimethylarsine at Low Pressure.—Anhydrous, ammonia-free chloramine (1.24 g, 24 mmoles) in anhydrous ether was introduced into a vacuum system (5 μ), degassed, and distilled into a degassed ethereal (25 ml) solution of trimethylarsine (1.48 g, 12 mmoles). The reaction flask was held at −78° until all of the reagent condensed. Reaction began immediately and was apparently complete in 15 min. The ether plus the excess of chloramine was distilled out, leaving 2.05 g of a white, microcrystalline solid which recrystallized unchanged from dimethylformamide and melted at 136–138° (compound XIII, Table II).

B. Chlorination of Triphenylarsine, Followed by Ammonolysis.—A stream of dry chlorine was passed into a solution of triphenylarsine (2.0 g, 6.7 mmoles) in dry ether (50 ml) at 20°. Evaporation of the solvent under reduced pressure yielded 1.2 g of white crystals of $(C_6H_5)_3AsCl_2$, mp 200°, phase change at 155° (lit. mp 204–205°, phase change at 158°). The crystals were dissolved in 50 ml of chloroform and treated with ammonia at room temperature. The chloroform-soluble portion of the product after recrystallization was a white, crystalline solid which melted at 255–260° (compound III, Figure 1).

C. Chloramination of Triphenylarsine at Atmospheric Pressure and Temperature.—The mixture of chloramine and excess ammonia obtained from the chloramine generator[2] was passed into a solution of triphenylarsine (5.75 g, 18.8 mmoles) in 100 ml of benzene for 15 min (total NH_2Cl 25 mmoles) at 20°. The resulting white precipitate was filtered and dried; it melted over an extended range up to 195° and its analysis showed a C_6H_5:As ratio of 5:2. This substance is labeled IV in Figure 1.

D. Thermal Condensation of IV.—Mixture IV was dissolved in dimethylformamide at 150°. Upon cooling, white crystals, mp 195°, were obtained (compound V, Figure 1) in good yields.

The various compounds prepared are listed with their analyses and melting points in Table II. Postulated reaction schemes are discussed in the following section and are summarized in Figures

(2) H. H. Sisler and G. Omietanski, *Inorg. Syn.*, **5**, 91 (1957).
(3) I. T. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).
(4) H. Hibbert, *Ber.*, **39**, 161 (1906).
(5) W. J. Pope and E. E. Turner, *J. Chem. Soc.*, **117**, 1447 (1920).

TABLE I
INFRARED DATA (CM^{-1})

Compound	
I	3150, 3040 s, doublet, 1980 w, 1900 w, 1820 w, 1760 w, 1530 m, 1480 s, 1440 s, 1410 m, 1335 w, 1310 w, 1180 m, 1090, 1080 s, doublet, 995 s, 965 w, 880 m, 756 s, 748 s, 740 s, 690 s
II	3150, 3050 m, doublet, 1950 w, 1900 w, 1820 w, 1750 w, 1670 s, 1560 w, 1470 m, 1430 s, 1370 m, 1330 w, 1300 m, 1250 m, 1170, 1160 m, doublet, 1090 m, 1080 s, 1020 w, 1015 w, 992 m, 970 s, b, 880 m, 865 w, 748 s, 735 s, 690 s
III	3050 m, 2950 m, 2000 s, 1930 w, 1570 w, 1480 m, 1310, 1300 m, doublet, 1185, 1175 w, doublet, 1160, 1150 w, doublet, 1080 s, 1060 m, 1010 m, 1000 m, 960 s, b, 860 w, 765 m, sh, 760 m, 740 s, 736 s, sh, 698 w, sh, 688 s
IV (mixture)	3150, 3000 s, doublet, 1720 w, 1580 w, 1510 w, 1480 s, 1440 s, 1340 w, 1310 w, 1285 m, 1270, 1265 m, doublet, 1110 m, 1090 s, 1030 m, 998 s, 930 w, 880 m, vb, 755 s, sh, 750, 744, 736 vs, triplet, 715 s, 693 vs
V	3150, 3050 s, doublet, 2580 w, 1485 m, 1440 s, 1310 w, 1185 m, 1160 w, 1085, 1075 s, doublet, 1048 w, 1020 w, 995 s, 932 w, sh, 925 w, 844 w, 748 s, sh, 740 vs, b, 722 m, sh, 685 vs, b
VII	3180, 3070 s, doublet, 1750 m, b, 1524 m, 1470 m, 1440 s, sh, 1400 s, 1330 w, 1300 w, 1180 m, 1155 m, sh, 1080, 1070 s, doublet, 1015 m, 995 s, 955 vs, b, 850, 840 w, doublet, 767, 758 s, doublet, 735 vs, b, 680 s
VIII	3180, 3070 s, doublet, 1524 m, 1470 m, 1440 s, sh, 1330 w, 1300 w, 1180 m, 1155 m, sh, 1080, 1070 s, doublet, 1015 m, 995 s, 955 vs, b, 850, 840 w, doublet, 767, 758 s, doublet, 735 vs, b, 680 s
IX	3000 s, sh, 2700 vs, b, 2270 s, 1570 m, 1470 m, 1440 s, 1330 w, 1300 w, 1190 m, 1124 w, 1080 m, 1060 sh, 1015 w, 995 m, 925 w, 845 w, 795 s, 774 s, 750 s, sh, 733 vs, b, 678 vs, b
X	3150 s, 2940 s, 2440 w, 1960 w, 1880 w, 1800 w, 1750 w, 1540 m, 1480 s, 1440 s, 1400 w, 1370 m, 1300 m, 1240 m, 1210 m, 1175 m, 1085 s, 1065 w, 1020 s, b, 990 s, 955 w, 834 m, b, 740 s, vb, 685 s
XI	(in Nujol mull only) 3100 m, sh, 3030 s (2900 s), 1950 w, 1900 w, 1810 w, 1750 vw, 1650 w, 1460 s (1450 s, sh), 1435 s (1370 s), 1300 m, 1165 m, 1155 m, sh, 1080 s, 1060 m, sh, 1020 m, 995 m, 940 vs, b, 735 s, 688 s
XII	(in Nujol mull only) 3150 s (2900 s), 1960 w, 1890 w, 1800 w, 1760 w, 1530 m, 1475 m, (1450 m, sh), 1440 s, 1400 w (1370 m), 1305 m, 1240 m, 1210 m, 1180 m, 1085 s, 1025 s, sh, 1015 s, 990 s, 955 w, 834 m, b, 740 s, b, 693 s
XIII	3150 s, 3030 s, sh, 1495 m, 1420 s, 1310 w, 1265 s, 1120 s, 935 vs, b, 890 s, 855 s, 820 m, sh, 694 vs, b,

1 and 2. A full list of experimental procedures is shown in Table III.

Discussion

The above data show that chloramine reacts with several arsine derivatives to form chloramine adducts which, like the corresponding phosphine–chloramine adducts, condense to form arsenic–nitrogen chains, open and closed. A surprising feature of the chloramination reaction is the fact that arsenic–phenyl bonds are labile under the conditions of the reaction, resulting in the loss of chlorobenzene and leading to products other than simple adducts. Generally, this

TABLE II

No. on reaction diagram	Formula	Mp, °C		C	H	N	As	Cl
I	[(C₆H₅)₃AsNH₂]Cl	170 dec	Calcd	60.45	4.74	3.92	20.98	9.93
			Found	59.95	4.77	3.72	21.10	9.72
II	[(C₆H₅)₃As═N═As(C₆H₅)₃]Cl·DMF	255–260	Calcd	63.75	5.05	3.81	20.42	4.83
			Found	63.30	5.20	3.83	22.03	5.48
III	[(C₆H₅)₃As═N═As(C₆H₅)₃]Cl	255–260	Calcd	65.30	4.53	2.12	22.66	5.36
			Found	65.08	4.77	1.63	21.07	5.24
IV	[(C₆H₅)₃AsNH₂]Cl + [(C₆H₅)₂As(NH₂)₂]Cl	⎰Complete at 195	Calcd	55.10	4.74	6.42	...	10.85
			Found	55.80	4.76	6.34	...	9.18
V	C₃₀H₂₇N₂As₂Cl[a]	195	Calcd	60.00	4.54	4.64	24.94	5.90
			Found	60.29	4.64	4.55	24.70	6.10
VII	[(C₆H₅)₂As(NH₂)Cl]Cl	⎰Complete at 180	Calcd	45.55	3.80	4.43	23.72	22.40
			Found	45.70	4.07	4.63	23.88	22.29
VIII	[(C₆H₅)₂As═N═As(C₆H₅)₂]Cl with Cl, Cl	180	Calcd	...	...	2.42	...	18.40
			Found	...	...	2.41	...	17.90
IX	C₁₈H₁₈N₂Cl₄As₂[b]	120	Calcd	39.00	3.28	5.05	27.08	25.60
			Found	37.53	4.84	5.15	26.81	26.13
XI	[(C₆H₅)₂AsN]₃	155–157	Calcd	59.22	4.15	5.76	30.85	0.00
			Found	59.41	4.29	5.45	30.61	0.00
X	[(C₆H₅)₂As═N═As(C₆H₅)₂]Cl·nCHCl₃ (n = ²/₃) with NH₂, NH₂	⎰Complete at 160	Calcd	47.75	3.80	6.76	...	17.20
			Found	45.88	4.60	6.76	...	17.00
XIII	[(CH₃)₃AsNH₂]Cl	136–138	Calcd	21.00	6.41	8.16	43.70	20.71
			Found	20.99	6.31	8.36	43.78	20.34

[a] Probably [(C₆H₅)₃As═N—As(C₆H₅)₂]Cl with NH₂.   [b] Probably [(C₆H₅)₂As═N═As(C₆H₅)]Cl with Cl, Cl, Cl, NH₃.
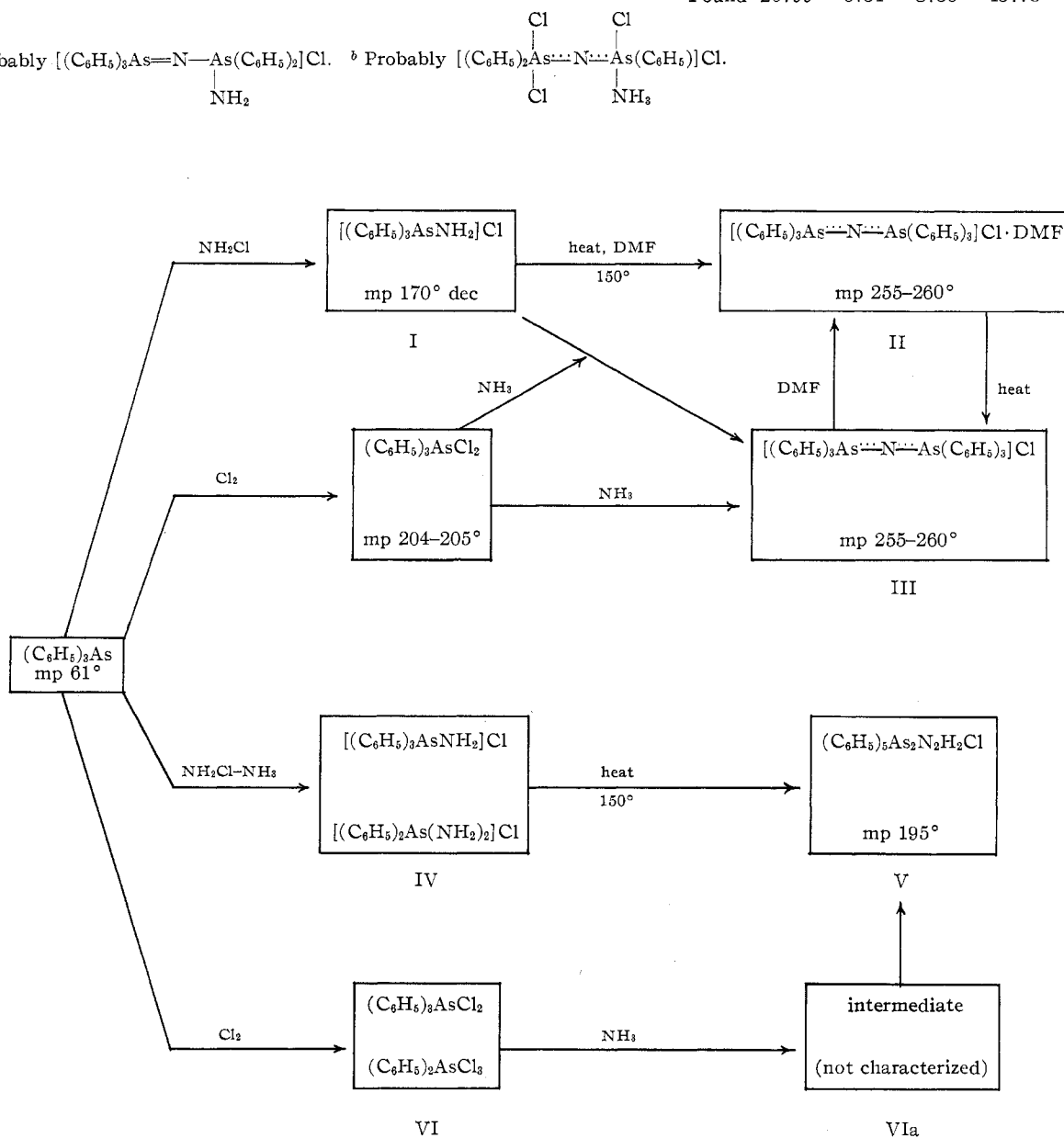
Figure 1.—Reaction scheme for triphenylarsine and chloramine products.

Figure reaction scheme:

- **VII** — [(C₆H₅)₂AsNH₂Cl]Cl, mp 150–180° dec
  $[(C_6H_5)_2AsNH_2Cl]Cl$
- **VIII** — $[(C_6H_5)_2As-N-As(C_6H_5)_2]Cl$ (with Cl, Cl substituents), mp 178–180°
- $(C_6H_5)_2AsCl_3$, mp 172°
- **IX** — $(C_6H_5)_3As_2N_2H_3Cl_4$, mp 120°
- $(C_6H_5)_2AsCl$, mp 39°
- intermediate (not characterized)
- intermediate (not characterized)
- **XI** — $[(C_6H_5)_2AsN]_3$, mp 155–157°
- **X** — $[(C_6H_5)_2As-N-As(C_6H_5)_2]Cl\cdot CHCl_3$ (with NH₂, NH₂ substituents), mp 130–160°
- **XII** — $[(C_6H_5)_2AsN]_3\cdot DMF$, mp 155–157°

Arrow labels: NH₂Cl; heat, DMF; Cl₂; NH₃; NH₂Cl–NH₃ Recrystallized from CHCl₃; standing; HCl; NH₃; heat, DMF
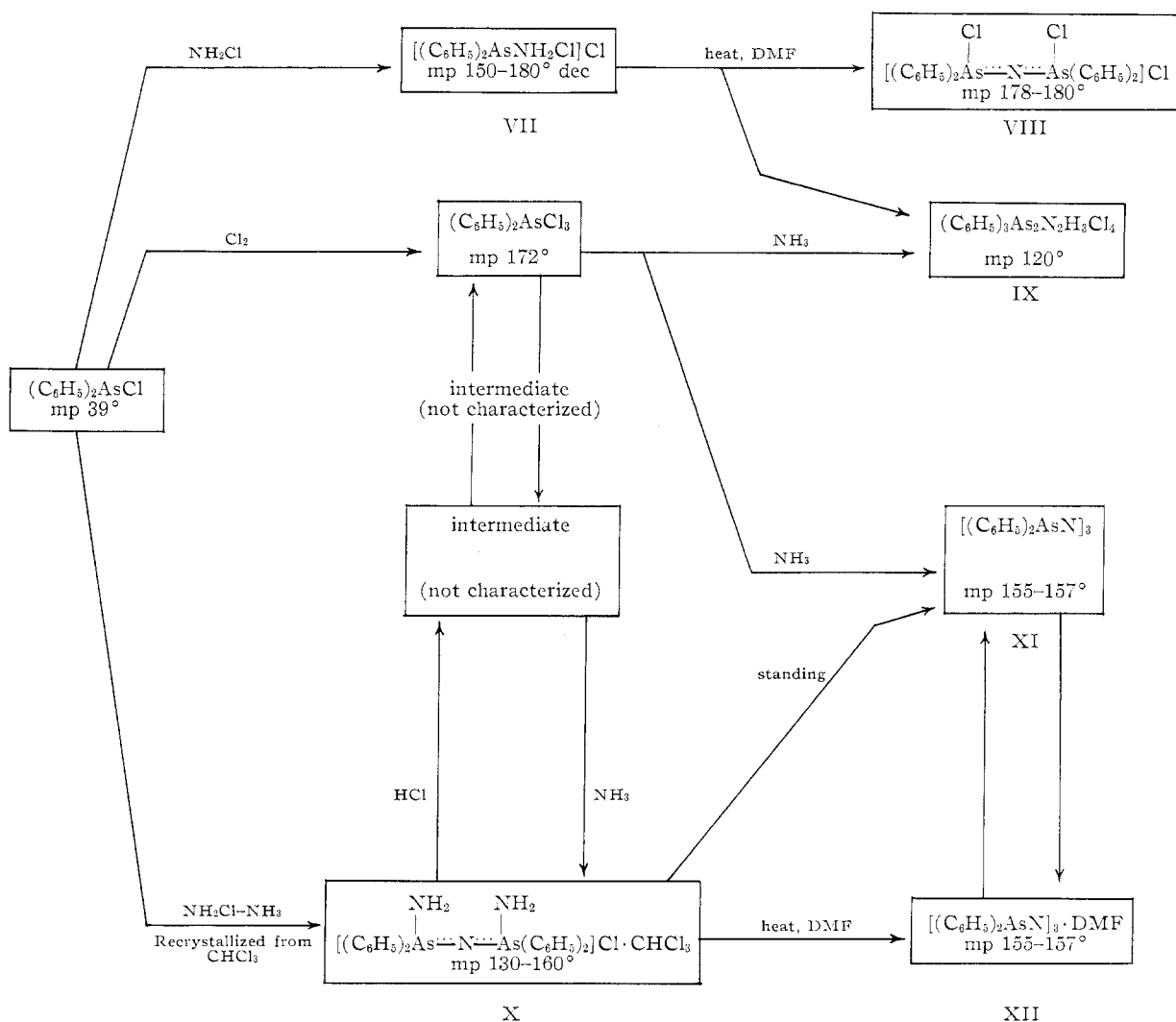
Figure 2.—Reaction scheme for diphenylchloroarsine and chloramine products

Table III

Starting material	Reagent or driving force	Method	Solvent	Temp, °C	Products	No. on diagram
$(C_6H_5)_3As$	NH_2Cl	A	$(C_2H_5)_2O$	−78 to −10	$[(C_6H_5)_3AsNH_2]Cl$	I
$(C_6H_5)_3As$	NH_2Cl-NH_3	C	C_6H_6	20	Mixture	IV
$(C_6H_5)_3As$	Cl_2	B(i)	C_6H_6	20	Mixture VI and $(C_6H_5)_3AsCl_2$	VI
$(C_6H_5)_3As$	Cl_2	B(i)	$(C_2H_5)_2O$	−78	$(C_6H_5)_3AsCl_2$	. . .
$(C_6H_5)_3AsCl_2$	NH_3	B(ii)	$CHCl_3$	20	$[(C_6H_5)_3As-N-As(C_6H_5)_3]Cl$	III
$(C_6H_5)_3AsCl_2$	NH_3	B(ii)	$CHCl_3$	−78	$[(C_6H_5)_3As-N-As(C_6H_5)_3]Cl$ and $[(C_6H_5)_3AsNH_2]Cl$	I and III
$[(C_6H_5)_3AsNH_2]Cl$	Heat	D	$(CH_3)_2NCHO$	150	$[(C_6H_5)_3As-N-As(C_6H_5)_3]Cl\cdot DMF$	II
Compound II	Heat	Vacuum	. . .	160	$[(C_6H_5)_3As-N-As(C_6H_5)_3]Cl$	III
Mixture IV	NH_3	B(ii)	C_6H_6	20	Mixture VIa	VIa
Mixture IV	Heat	D	$(CH_3)_2NCHO$	150	Compound V	V
Mixture VIa	Heat	D	$(CH_3)_2NCHO$	150	Compound V	V
$(C_6H_5)_2AsCl$	NH_2Cl	A	$(C_2H_5)_2O$	−78	"$[(C_6H_5)_2As(NH_2)Cl]Cl$"	VII
Compound VII	Heat	D	$(CH_3)_2NCHO$	150	$[(C_6H_5)_2As-N-As(C_6H_5)_2]Cl$ (with Cl, Cl)	VIII
$(C_6H_5)_2AsCl$	NH_2Cl-NH_3	C	$(C_2H_5)_2O$	−50	Mixture plus compound X	X
$(C_6H_5)_2AsCl$	Cl_2	B(i)	$(C_2H_5)_2O$	−78	$(C_6H_5)_2AsCl_3$	. . .
$(C_6H_5)_2AsCl_3$	NH_3	B(ii)	$CHCl_3$	−78	$[(C_6H_5)_2AsN]_3$	XI
Compound VII	HCl	B(i)	$(C_2H_5)_2O$	20	$(C_6H_5)_2AsCl_3$	. . .
Compound VII	Heat	D	$(CH_3)_2NCHO$	150	Compound IX	IX
Compound X	Heat	D	$(CH_3)_2NCHO$	150	$[(C_6H_5)_2AsN]_3\cdot DMF$	XII
Compound X	Time	. . .	$CHCl_3$	20	$[(C_6H_5)_2AsN]_3$	XI
$(CH_3)_3As$	NH_2Cl	A	$(C_2H_5)_2O$	−78	$[(CH_3)_3AsNH_2]Cl$	XIII
$[(CH_3)_3AsNH_2]Cl$	Heat	D	$(CH_3)_2NCHO$	150	No reaction	. . .

complication may be partially avoided by carrying out the reactions at $-78°$. Chloramination of trimethylarsine proceeds instantaneously in diethyl ether even at low temperatures. Diphenylchloroarsine undergoes chloramination at a visibly slower rate than trimethylarsine under these conditions. Triphenylarsine in ether solution does not react with chloramine at a measurable rate at $-78°$. At temperatures above $-10°$, however, it reacts readily and the reaction goes to completion. This variation in reaction rates may be correlated with the higher electron density on the arsenic atom in the methyl derivative than in the phenyl derivative. At room temperature, in the presence of an excess of ammonia, chloramination of triphenylarsine and diphenylchloroarsine takes place instantaneously and exothermally. Heating the resulting chloramination products to temperatures as high as $150°$ results in the formation of condensed products in which the C_6H_5:As ratio is lower than in the starting materials (compounds V and IX, Table II).

With respect to chlorination, triphenylarsine and diphenylchloroarsine react at $-78°$ to give the pure adducts $(C_6H_5)_3AsCl_2$ and $(C_6H_5)_2AsCl_3$, respectively. Chlorination at room temperature, however, yields mixtures of oily products having a wide melting range and consisting of species in which the C_6H_5:As ratio is lower than in the starting materials. Thus, it is apparent that As–C_6H_5 bonds are broken in the reaction.
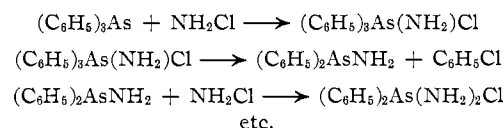
The ammonolysis of triphenyldichloroarsane yields mixtures of monomeric and condensed ammonolysis products. In the reaction at $-78°$, analytical and infrared data show that compound I predominates in the product. At room temperature, however, the reaction product consists principally of condensed products. When any mixture of these products was recrystallized from dimethylformamide at above $150°$, pure compound II was obtained in good yields. Likewise, ammonolysis of pure diphenyltrichloroarsane leads to a condensed compound with the elimination of ammonium chloride, producing a material having a cyclic structure and another which is probably analogous to $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$ which has been shown[6] to be a precursor to $[(C_6H_5)_2PN]_3$. On the other hand, ammonolysis of the mixture $(C_6H_5)_2AsCl_3 + (C_6H_5)_3AsCl_2$ produced by the room-temperature chlorination of triphenylarsine leads to an uncharacterized intermediate (VIa) which upon thermal condensation yields the "phenyl-deficient" compound V, with a C_6H_5:As ratio of 5:2. As indicated below, the probable formula for V is $[(C_6H_5)_3AsNAs(NH_2)(C_6H_5)_2]Cl$. On the basis of these results we may state the following generalizations: (1) Chlorination and chloramination of phenylarsines at room temperature alike result in the migration of phenyl groups. (2) Phenyl migration is inhibited by operating at lower temperatures. (3) Ammonolysis does not in itself result in phenyl group migration even at room temperature. (4) Ammonolysis does, however, promote condensa-

tion since the ammonia acts as a hydrogen chloride acceptor. Applying these facts to the chlorination of triphenylarsine, we can postulate the series of reactions

$$(C_6H_5)_3As + Cl_2 \longrightarrow (C_6H_5)_3AsCl_2$$
$$(C_6H_5)_3AsCl_2 \longrightarrow (C_6H_5)_2AsCl + C_6H_5Cl$$
$$(C_6H_5)_2AsCl + Cl_2 \longrightarrow (C_6H_5)_2AsCl_3$$
$$(C_6H_5)_2AsCl_3 \longrightarrow C_6H_5AsCl_2 + C_6H_5Cl$$
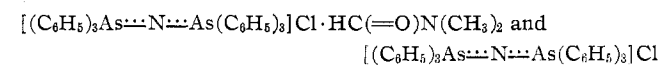$$\text{etc.}$$
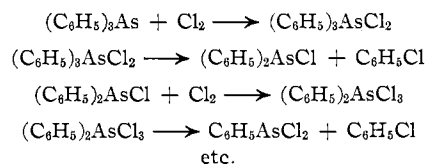
Thus, a mixture of various phenylchloroarsines may be obtained even when starting with a pure compound. In connection with this postulated series of reactions, it is noteworthy that, when melting the room-temperature chlorination product of triphenylarsine, there is always observed some decomposition and melting at $200°$, the decomposition temperature of $(C_6H_5)_2AsCl_3$.[7] Similarly, the melting of the chlorination product of $(C_6H_5)_2AsCl$ always shows some decomposition and evolution of chlorobenzene at $150°$, the temperature at which $C_6H_5AsCl_4$ decomposes.

A similar reaction sequence may be postulated for the chloramination process

$$(C_6H_5)_3As + NH_2Cl \longrightarrow (C_6H_5)_3As(NH_2)Cl$$
$$(C_6H_5)_3As(NH_2)Cl \longrightarrow (C_6H_5)_2AsNH_2 + C_6H_5Cl$$
$$(C_6H_5)_2AsNH_2 + NH_2Cl \longrightarrow (C_6H_5)_2As(NH_2)_2Cl$$
$$\text{etc.}$$

The presence of amino groups permits condensation to give molecules containing more than one arsenic atom per molecule. This postulated reaction sequence is supported by the isolation of compounds V and IX. Further support was obtained by examining the filtrate after carrying out a room-temperature chloramination. Chlorobenzene was found by vapor phase chromatography, whereas aniline was not, even though it was specifically sought.

Structures.—Based on the elemental analysis and on the fact that hydrolysis yields triphenylarsine oxide quantitatively, it is concluded that compound I is $(C_6H_5)_3As(NH_2)Cl$. If quaternary arsenic is assumed, the availability of an unshared pair of electrons in the nitrogen atom for π bonding with the arsenic atom would make $[(C_6H_5)_3AsNH_2]Cl$ a more probable structure than $[(C_6H_5)_3AsCl]NH_2$. Compounds II and III are readily interconverted by addition or removal of dimethylformamide. Compound II is obtained from I by condensation of dimethylformamide solution, and III from I by condensation in the absence of formamide. Recrystallization of III from dimethylformamide yields II, and heating II yields III. These facts and elemental analysis, combined with the presence in the infrared spectra of II and III of a band at 950 cm^{-1}, previously assigned to the N—As—N group in $[(C_6H_5)_2AsN]_4$,[8] support the following formulations of II and III, respectively

$$[(C_6H_5)_3As\text{---}N\text{---}As(C_6H_5)_3]Cl\cdot HC(\text{==}O)N(CH_3)_2 \text{ and}$$
$$[(C_6H_5)_3As\text{---}N\text{---}As(C_6H_5)_3]Cl$$

(6) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, 1, 84 (1962).

(7) W. LaCoste and A. Michaelis, *Ann.*, **201**, 198 (1880).

(8) W. T. Reichle, *Tetrahedron Letters*, **2**, 51 (1962).

This assignment of the 950-cm^{-1} band is reasonable in terms of the probable strength of the As–N bond.

The material labeled IV is not a pure compound for its properties vary from experiment to experiment. Generally, the ratio C$_6$H$_5$:As in IV is about 5:2. The peaks in the infrared spectra of various preparations of IV occur at the same frequencies but the intensities of the various absorptions show strong relative variation from sample to sample prepared under slightly varying conditions. However, when IV is recrystallized from dimethylformamide, ammonium chloride is eliminated and the substance V with the composition (C$_6$H$_5$)$_5$As$_2$N$_2$H$_2$Cl forms. Compound V is also obtainable by the ammonolysis of a mixture of (C$_6$H$_5$)$_3$AsCl$_2$ and (C$_6$H$_5$)$_2$AsCl$_3$. The physical properties, including infrared spectrum and melting point, of V are highly reproducible. It is tempting to write the formula [(C$_6$H$_5$)$_3$AsNAs(NH$_2$)-(C$_6$H$_5$)$_2$]Cl since the nmr H^1 spectrum shows two types of phenyl hydrogen atoms in a ratio of 3:2. However, there is no strong 950-cm^{-1} band in the infrared spectrum as would be expected from the As$\doteq$N$\doteq$As group. If this structure is correct, the different electronegativities of phenyl and of amino groups may have produced sufficient asymmetry in the molecule to modify the N$\doteq$As$\doteq$N band in the spectrum.

The analysis of product VII agrees with the formulation [(C$_6$H$_5$)$_2$As(NH$_2$)Cl]Cl. However, a prominent peak at 950 cm^{-1} is found in the infrared spectrum of VII, as well as the characteristic peaks for NH$_4$Cl. It is, therefore, suggested that VII consists at least in part of an equimolar mixture of NH$_4$Cl and [(C$_5$H$_5$)$_2$-As(Cl)NAs(Cl)(C$_5$H$_5$)$_2$]Cl. It will be noted that this mixture has the same elemental analysis as [(C$_6$H$_5$)$_2$-As(NH$_2$)Cl]Cl. This interpretation is supported by the fact that VII undergoes condensation to yield compound VIII whose composition and spectrum indicate that it is [(C$_6$H$_5$)$_2$As(Cl)NAs(Cl)(C$_6$H$_5$)$_2$]Cl. The infrared spectrum of VIII is very similar to that of VII except that the infrared peaks due to ammonium chloride are missing in the spectrum of VIII and the 950-cm^{-1} band is enhanced in the spectrum of VIII as compared with that of VII.

Also obtained in the recrystallization of VII is a small amount of compound IX. IX is obtained in higher yield by the ammonolysis of (C$_6$H$_5$)$_2$AsCl$_3$ and by the chloramination of diphenylchloroarsine in the presence of ammonia at room temperature. The infrared spectrum, melting point, and elementary analysis of IX are all highly reproducible. A large band at 3000 cm^{-1} suggests the presence of quaternary nitrogen. The nmr H spectral data show the pres-

ence of two types of phenyl groups in the ratio 2:1. There is no 950-cm^{-1} band in the infrared spectrum. The structure [(C$_6$H$_5$)$_2$As(Cl)$_2$NAs(Cl)(NH$_3$)(C$_6$H$_5$)]Cl is suggested as a possibility for IX, but this structure must be considered to be speculative.

The elemental analysis and infrared spectrum of X indicate that the formula [(C$_6$H$_5$)$_2$As(NH$_2$)NAs-(NH$_2$)(C$_6$H$_5$)$_2$]Cl·^{2}/$_3$CHCl$_3$ would be appropriate. In view of the demonstrated tendency for this solvate to effloresce, X probably consists of a mixture of [(C$_6$H$_5$)$_2$As(NH$_2$)NAs(NH$_2$)(C$_6$H$_5$)$_2$Cl·CHCl$_3$ and [(C$_6$-H$_5$)$_2$As(NH$_2$)NAs(NH$_2$)(C$_6$H$_5$)$_2$Cl. Sisler, et al.,[6] have shown that [(C$_6$H$_5$)$_2$P(NH$_2$)NP(NH$_2$)(C$_5$H$_5$)$_2$]Cl forms a similar solvate with chloroform which behaves similarly to X.

Recrystallization of X from dimethylformamide yields XII, a compound whose analysis, infrared spectrum, and molecular weight indicate that is consists of a dimethylformamide solvate of the cyclic trimer [(C$_6$H$_5$)$_2$AsN]$_3$, i.e., [(C$_6$H$_5$)$_2$AsN]$_3$·HC(=O)N-(CH$_3$)$_2$. Recrystallization of X or XII from chloroform yields XI, the unsolvated cyclic trimer [(C$_6$H$_5$)$_2$-AsN]$_3$. The formation of XI from X is exactly analogous to the formation of the diphenylphosphonitrilic trimer from [(C$_6$H$_5$)$_2$P(NH$_2$)NP(NH$_2$)(C$_6$H$_5$)$_2$]Cl.[6]

Compound XIII has an elemental analysis which agrees with the formula [(CH$_3$)$_3$AsNH$_2$]Cl.

Infrared Spectra.—The infrared spectra of all of the compounds I through XII have the peaks commonly associated with phenyl groups, e.g., C—H stretch in the 3000-cm^{-1} region, C—H in-plane vibration at 1465–1520 cm^{-1}, the C=C in-plane vibration at 1480 cm^{-1}, and the C—H out-of-plane vibration at 750 cm^{-1}. There are, of course, minor variations, to be expected from the different groups present in the molecule. For the compounds containing NH$_2$ groups, there are two peaks in the 3100-cm^{-1} region, usually incompletely resolved, which correspond to N—H stretch frequencies. Compounds II, III, VII, VIII, X, XI, and XII all exhibit a strong band in the region near 950 cm^{-1}. As stated above this band has been attributed to As$\doteq$N$\doteq$As resonance vibrations, which presumes electron delocalization similar to that found in the phosphazenes.[9,10] The presence of this peak in the spectrum of compound X argues in favor of the proposed structure shown in Figure 2. The majority of the remaining peaks coincide closely with reported values[11,12] and assignments for triphenylarsine and triphenylarsine oxide.

(9) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

(10) M. J. S. Dewar, E. A. C. Luken, and M. A. Whitehead, *ibid.*, 2423 (1960).

(11) J. Bernstein, M. Halmann, S. Pinchas, and D. Samuel, *ibid.*, 821 (1964).

(12) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **17**, 1875 (1963).