Synthesis and Characterization of some Aminoarsonium Chlorides

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Abstract

R_3As reacts with NR′R″Cl to give good yields of a new homologous series of aminoarsonium chlorides, $[R_3AsNR'R'']Cl$, in which R = Me, Et, n-Pr, and Ph; R′ and/or R″ = H, Me. IR, NMR, mass, and X-ray spectral data suggest that the arsenic is tetracoordinate. Electrical conductivity and temperature and concentration dependent NMR studies suggest that hydrogen-bonding interactions are important in solution. Quaternization of the arsenic produces a downfield ^1H NMR chemical shift for the protons in the alkyl chains and a change from non-equivalence to equivalence of the C-1 protons. The NMR data are compared with those for the analogous phosphorus compounds. The electron impact, chemical ionization, and negative ion mass spectral data and fragment ion identities are given for the compounds. Ions corresponding to a variety of AsCl containing species, in addition to those associated with fragmentation of the R_3As moieties, are observed in the EI mass spectra. As–N, As–N–As, and As–N–As–N containing fragments are observed in the CI mass spectra and As–Cl bonding species in the NI mass spectra. A preliminary X-ray diffraction study of $[n\text{-}Pr_3AsNH_2]Cl$ indicates near tetrahedral geometry about the arsenic atom.

Introduction

Previous studies have established that chloramine [1, 2] and dimethylchloramine [2] react with trialkylarsines and triphenylarsine to give aminoarsonium chlorides. The reactivity of monomethylchloramine towards tertiary arsines has not been investigated previously. Chloramine [3–6], monomethylchloramine [5, 6], and dimethylchloramine [4, 6] react with trialkylphosphines and triphenyl phosphine to give aminophosphonium chlorides. In this paper, we report the preparation; properties; and IR, ^1H NMR, mass spectral, conductivity, and X-ray data of an homologous series of aminoarsonium chlorides, $[R_3AsNR'R'']Cl$, in which R, R′, and R″ are varied in a systematic manner, *i.e.* R = Me, Et, n-Pr, and Ph; R′ and/or R″ = H, Me (Table I). Whereas the literature contains several reports dealing with the ^{13}C and/or ^{31}P NMR studies of phosphonium and aminophosphonium salts [1, 6–13], no reports deal with detailed NMR studies of aminoarsonium salts. We were interested in noting any structural and electronic effects on ^1H chemical shifts that are produced by varying R, R′, and R″; determining the character of the As–N bond; establishing the coordination number of the arsenic atom in these compounds; and comparing the properties and spectral data for these compounds with those of the analogous series of aminophosphonium salts [6].

Experimental

All storing and transferring of arsines 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-493 Dri-Train. All reactions were carried out in an atmosphere of prepurified nitrogen or *in vacuo*. Trimethylarsine, triethylarsine, and tri-n-propylarsine were prepared by the reaction of arsenic(III) oxide with the respective trialkylaluminum compound according to the procedure of Stamm and Breindel [14]. Triphenylarsine, methylamine hydrochloride, and dimethylamine hydrochloride were obtained from Eastman Chemical Company and used as obtained. Ammonia and methylamine were obtained from Matheson and used as obtained.

All synthesized compounds were characterized by elemental analysis*; melting point (m.p.); IR; ^1H, and ^{13}C NMR; electron impact (EI); chemical ionization (CI); and negative ion (NI) mass spectrometry; and electrical conductivity. Melting points were determined by using the Thomas–Hoover capillary melting point apparatus with an uncorrected thermometer (Table I). Infrared spectra were recorded on a Perkin-Elmer IR 283 spectrometer, interfaced to a PRIME 750 computer. The spectra

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*Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. (Table I).

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TABLE I. Elemental Analyses and Melting Point Data

Compound	Chemical formula	Melting point data	% Yield	Elemental analyses (%)[a]				
				C	H	N	As	Cl
I	$[Me_3AsNH_2]Cl$ [1]							
II	$[Me_3AsN(H)Me]Cl$	128 phase change; 165 glass; liquid by 172	23	26.03	7.54	7.41	40.23	18.90
				(25.88)	(7.06)	(7.55)	(40.39)	(19.11)
III	$[Me_3AsNMe_2]Cl$ [2]							
IV	$[Et_3AsNH_2]Cl$ [2]							
V	$[Et_3AsN(H)Me]Cl$	132–134	68	37.21	8.68	6.14	33.14	15.30
				(36.92)	(8.42)	(6.16)	(32.93)	(15.58)
VI	$[Et_3AsNMe_2]Cl$ [2]							
VII	$[n\text{-}Pr_3AsNH_2]Cl$ [2]							
VIII	$[n\text{-}Pr_3AsN(H)Me]Cl$	73–75	43	44.79	9.36	5.20	27.69	13.10
				(44.53)	(9.35)	(5.20)	(27.79)	(13.15)
IX	$[n\text{-}Pr_3AsNMe_2]Cl$ [2]							
X	$[Ph_3AsNH_2]Cl$ [1]							
XI	$[Ph_3AsN(H)Me]Cl$	206–209	36	61.39	5.35	3.92	20.20	9.31
				(61.37)	(5.15)	(3.77)	(20.17)	(9.54)

[a] Calculated values given in parentheses.

were obtained on the solids in the form of Kel-F mulls by using KBr plates for the 4000–1300 cm^{-1} range and as Nujol mulls by using CsI plates for the 1300–250 cm^{-1} range**.

All NMR studies were conducted using a Nicolet 300 MHz multinuclear Fourier-Transform NMR spectrometer. The ^1H NMR spectra for the synthesized compounds were recorded as a function of concentration (0.0125–0.2 M) and temperature (−50 to 25 °C) with chloroform-d ($CDCl_3$) as the solvent and TMS as the internal reference. All chemical shifts are reported using the convention that a positive δ-value corresponds to higher frequency chemical shifts. The NMR spectral data are listed in Table II.

Electrical conductivity data were collected using a YSI Model 32 conductance meter with YSI 3400 series conductivity cells (cell constant, 1.030 cm^{-1}). All measurements were made in nitromethane at 25 °C over the concentration range of 10^{-3} to 5×10^{-2} M.

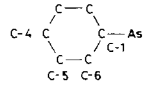
Low resolution EI and CI-MS data*** recorded on a HP 5985A GC/MS/DS mass spectrometer operated at 70 eV, 2400 volt electron multiplier and a direct insert probe (DIP). Isobutane was used as the ionizing gas. The source temperature was maintained at 200 °C and the probe temperature was 25 °C.

High resolution EI-MS data*** were recorded on an AEI MS-30 mass spectrometer operated at 70

TABLE II. ^1H NMR Chemical Shift Data for Aminoarsonium Chlorides[a]

Compound	Chemical shifts (ppm)				
	C-1	C-2	C-3	NMe	NH
Me_3As	0.98(s)				
I	1.59(s)				7.08(br)
II	2.26(s)			2.71(d)	5.06(q)
III	2.45(s)			2.76(s)	
Et_3As	1.26(m)	1.22(t)			
IV	2.62(q)	1.40(t)			4.46(s)
V	2.69(q)	1.42(t)		2.76(d)	5.29(q)
VI	2.98(q)	1.43(t)		2.86(s)	
$n\text{-}Pr_3As$	1.48(m)	1.39(m)	0.98(t)		
VII	2.36(m)	1.68(m)	1.01(t)		6.51(br)
VIII	2.59(m)	1.79(m)	1.12(t)	2.74(d)	5.41(q)
IX	2.90(m)	1.79(m)	1.14(t)	2.82(s)	
	Ortho (C-2)	Meta (C-3)	Para (C-4)	NMe	NH
Ph_3As	7.32(m)	7.32(m)	7.32(m)		
X	7.88(m)	7.75(m)	7.83(m)		6.01(br)
XI	7.86(m)	7.66(m)	7.74(m)	2.84(d)	7.69(q)

[a] Abbreviations: br, broad unresolved multiplet; d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet. All data collected in $CDCl_3$ at 25 °C at 0.2 M in TMS as an internal standard. Carbon atoms are numbered in the alkyl chains as follows: 3 2 1, C–C–C–As. Carbon atoms are numbered on the phenyl ring as follows:



**Previously unreported infrared absorption peaks of all compounds have been filed as a Table, see 'Supplementary Material'.

***All mass spectral data have been filed, see 'Supplementary Material'.

eV and equipped with a DS-30 data system. Samples were introduced using DIP. Perfluorokerosene was used for the high-resolution reference standard. The source temperature was maintained near 70 °C. The probe temperature was 25 °C. High resolution NI and CI-MS data were recorded with a Nicolet FTMS 1000. Self CI was carried at 30–50 °C chamber temperature and 25 °C probe. NI data were obtained by electron capture at a few tenths of an electron volt.

X-ray diffraction data were collected on single crystals of $[n\text{-}Pr_3AsNH_2]Cl$ that crystallized from benzene in the monoclinic space group $P2_1/c$ with $a = 8.746(3)$, $b = 12.903(3)$, $c = 12.841(3)$ Å, $\beta = 111.29(3)^\circ$, $\rho = 1.257$ g cm^{-3}, $V = 1451.7$ Å^3, and $Z = 4$. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. Nickel-filtered Cu Kα radiation was used. The final R index was 0.126 for 2211 reflections. Because of the sensitivity of the crystals to epoxy glues and mineral oil, the crystal was mounted on the tip of a capillary inside a sealed outer capillary.

Syntheses

Chloramine, NH_2Cl, was synthesized on a generator by the direct reaction of ammonia and chlorine with nitrogen as a diluting gas [15]. Monomethylchloramine and dimethylchloramine were synthesized by a procedure analogous to the Raschig synthesis of chloramine [6]. Monomethylchloramine was also synthesized by a procedure analogous to that used for NH_2Cl [6]. The rates of flow of monomethylamine, nitrogen, and chlorine through the generator were maintained at 1.2:0.3:0.1 mol/h, respectively.

The aminoarsonium chlorides were synthesized using two previously reported procedures [6], i.e., Method A: direct bubbling of the effluent gases from the generator [5] through a diethylether solution of the arsine, and Method B: distillation of a solution of the respective chloramine onto a diethylether solution of the arsine at −76 °C *in vacuo*. When the latter procedure utilized chloramine or monomethylchloramine, the excess ammonia or monomethylamine was removed by passing the ethereal solution through a column of anhydrous copper sulfate [17].

Results and Discussion

The products of the reactions of the substituted chloramines with the trialkylarsines and triphenylarsine were found, in each case, to be the aminoarsonium chlorides. The NH_2Cl reactions proceed instantaneously below 0 °C, MeNHCl reactions proceed slower and Me_2NCl reactions proceed the slowest. The latter occur slowly even at room temperature. In the case of triphenylarsine, no appreciable reaction occurred with Me_2NCl.

Our previous study of the reactions of the analogous tertiary phosphines with MeNHCl [6] indicated that Method A favored the formation of one isomeric form of $[R_3PN(H)Me]Cl$ while Method B gave a racemic mixture of products. All the experimental data for the products of the reaction of tertiary arsines with MeNHCl indicate that the same aminoarsonium products are obtained from Method A and Method B.

The reactions involving MeNHCl (Method B) also gave the respective R_3AsCl_2 compounds as side products (approximately a 10% conversion of R_3As). These compounds were identified from their m.p. and IR data [18–20]. The following are the δ_H chemical shift values for these compounds ($CDCl_3$ solvent, TMS internal standard): Me_3AsCl_2, 2.92 pm; $n\text{-}Pr_3AsCl_2$, 2.84(t) ppm $\mathit{CH_2}CH_2CH_3$, 1.85(m) ppm $CH_2\mathit{CH_2}CH_3$, and 0.78(t) ppm $CH_2CH_2\mathit{CH_3}$; and Ph_3AsCl_2, 8.05–7.40(m) ppm.

The electrical conductivity data for **IV**, **VIII**, and **IX** were analyzed. The molar conductances in nitromethane for these compounds are lower than expected for 1:1 electrolytes [21] such as tetraphenylphosphonium and tetraphenylarsonium compounds [22] where the value is about 80 Ω^{-1} cm^2 mol^{-1}. The Kohlrausch plots for these compounds are non-linear. In the concentration range of 1×10^{-3} to 5×10^{-2} M, the molar conductances are 32 to 15 Ω^{-1} cm^2 mol^{-1} with lower conductance values at higher concentrations. These data suggest that strong ion-pairing is present in solution [6].

^1H NMR Spectra

^{1}H NMR chemical shift data for compounds **I**–**XI** are given in Table II. Quaternization of the arsenic atom produces the expected downfield shift in δ_H for all protons on the alkyl groups attached to arsenic ($\Delta\delta_{H(C\text{-}1)} = 0.6$ to 1.7 ppm; $\Delta\delta_{H(C\text{-}2)} = 0.2$ to 0.4 ppm; $\Delta\delta_{H(C\text{-}3)} = 0.1$ ppm) (see footnote ^{a} in Table II for numbering notation). Quaternization results in a decrease in electron density on the arsenic, which has an electron withdrawing effect on all the alkyl group protons. The change in δ_H of the C-1 protons upon quaternization decreases in the order Me > Et > n-Pr. This ordering is consistent with the ordering of the analogous C–P–C bond angle changes that should occur upon quaternization [6], *i.e.* largest bond angle changes relate to largest δ_H changes. $\delta_{H(C\text{-}1)}$ are upfield of those in the corresponding phosphorus compounds [6]. This is consistent with the increased shielding of the C-1 protons that results from larger atom size, lesser electronegativity, and more diffuse orbitals of the Group 15 element when phosphorus is replaced with arsenic in these compounds. The δ_H values of the >NMe protons are independent of the nature of the Group 15 element.

The ^1H NMR spectra indicate that quaternization of the arsenic also causes a change from nonequivalence to equivalence of the C-1 protons. All the Me–As and Et–As arsonium chloride compounds exhibit typical first-order spectra for the C-1 and C-2 protons. Typically vicinal H,H-coupling constants of $^3J_{HCCH} = 7.80$ Hz are observed for the Et-As compounds. The n-Pr compounds exhibit $AA'MM'X_3$ spectra for the C-1, C-2, and C-3 protons. $AA'BB'C$ spectra are observed for the protons on the monosubstituted aromatic ring of the Ph derivatives. The analysis of these and the ^{13}C NMR spectral data will be given in a subsequent publication.

For a given -N(H)R′ series, δ_{NH} moves downfield as R changes from Me to Et to n-Pr to Ph, with the furthest downfield δ_{NH} occurring when R is Ph. This is a consequence of the electron withdrawing effect of the phenyl group which produces a deshielding of the NH proton. A comparison of these data with those for the analogous phosphorus compounds [6] shows an upfield shift of δ_{NH} upon replacing the phosphorus with the arsenic. This is expected, since the arsenic atom is less electronegative and larger than the phosphorus atom. The $^3J_{HNCH}$ vicinal coupling constants for all compounds containing the $-NHCH_3$ group are 5.85 ± 0.15 Hz.

The ^1H NMR chemical shifts are concentration dependent for the $-NH_2$ and –N(H)Me groups. Upon dilution, δ_{NH} shifts downfield for the –N(H)Me containing compounds, but the concentration dependence is much less than in the analogous phosphorus compounds [6]. For the $-NH_2$ series, a slight upfield shift is observed for the Et and a large upfield shift for the n-Pr derivative upon dilution. These data suggest that ion-pair formation is less effective in the –N(H)Me substituted As than the P compounds [6]. Data for the $-NH_2-$ substituted arsonium salts are consistent with solute/solvent and/or solute/solute H-bonding interactions. They further suggest that H-bonding interactions are more effective in the n-Pr than the Et or Me compounds.

IR Spectra

The infrared bands associated with N–H, C–H, and As–C stretching and $As-CH_3$, $As-CH_2$, and $AsNC_2$ structural units are observed in the appropriate regions of the spectra. The AsC_3 stretching and methyl and CH_2 rocking and deformation bands shift to higher wavenumbers when the tertiary arsine forms the respective arsonium salt. This suggests that the strength of the As–C bond increases upon quaternization of the arsenic atom. In the Me_2NCl derivatives, strong bands are observed around 1150 and 940 cm^{-1}, which are probably due to the NC_2 structural unit attached to arsenic, *i.e.* $\nu_{as}(AsNC_2)$ and $\nu_s(AsNC_2)$, respectively.

Compared with the infrared spectra of the parent tertiary arsines, the spectra of the respective products show new peaks in the 900–750 cm^{-1} and 700–600 cm^{-1} regions. These peaks, usually quite strong and broad, are assigned to the asymmetric and symmetric As–N stretching modes, respectively, in these aminoarsonium chlorides [2, 6]. In each case, the As–N stretching frequency is observed at a lower wavenumber than that observed for the P–N stretching frequency in the analogous aminophosphonium chloride [6]. Typically peaks associated with the symmetric $AsNC_2$ and AsN stretching modes are observed at 50 to 100 cm^{-1} lower wavenumbers than those of the PNC_2 and PN stretching modes in the analogous aminophosphonium compounds [6]. When the hydrogen is replaced with a methyl group on the nitrogen, there is a shift to lower wavenumber for ν_s(As–N). The As–N stretching mode is observed at successively lower wavenumbers as the group attached to arsenic changes from Me to n-Pr to Et to Ph in the $>NH_2$ compounds. The asymmetric and symmetric $AsNC_2$ stretching frequencies vary only about 10–15 cm^{-1} with the change in R in these compounds.

Mass Spectra

The EI mass spectra of the aminoarsonium chlorides give peaks with high relative abundance that correspond to $R_3As^{+\cdot}$ and the known fragmentation modes of these moieties [23]. In addition, chlorine containing species, *i.e.* R_3AsCl^+ and associated fragmentation products, are observed as major peaks. Only the ethyl derivatives exhibit ions assignable to an As–N bonded species, $Et_3AsNH_2{}^+$, and then only in a relatively low abundance. No As–N bond containing fragments were observed for the other aminoarsonium chlorides. The spectra of the NMe_2 derivatives contain fragments associated with fragmentation of the NMe_2 moiety [23]. The relative intensities of the HCl fragments decrease in going from the NH_2 to the NMe_2 derivatives and in increasing the length of the alkyl chain. A comparison of the EI-MS data with those of the analogous aminophosphonium chlorides [6] suggests that the As–N bond in these aminoarsonium chlorides is much more labile than the P–N bond in the analogous aminophosphonium chlorides.

The CI mass spectra of the alkyl derivatives of these compounds exhibit major peaks for chlorine containing species and those associated with the fragmentation of $R_3As^{+\cdot}$. Peaks of lesser intensity are observed for As–N bond containing ions. Only in the case of $[n\text{-}Pr_3AsNMe_2]Cl$ are peaks assignable to the As–N–As species $[Pr_3As(H)NH_2As(NH_2)Pr_3]^+$, $[Pr_2AsNMe_2AsPr_2]^{+\cdot}$, and $Pr_3AsNH_2]^+$ observed in high abundance. When the retention time is increased, chemical self-ionization ensues and associated species containing As–N–As bonds appear and become the peaks of highest abundance. The phenyl derivatives give peaks assignable to Ph_3AsH^+ and $PhAs^{+\cdot}$.

The NI mass spectra of these compounds indicate major peaks assignable to As–Cl bonded compounds, *i.e.* $[R_2AsCl_2]^-$ where R = Me and n-Pr, $[Me_3As(Cl)(NMe_2)_2]^-$, and $[Et_3AsCl_2]^-$. Some peaks of lower abundance that are associated with As–N bonded species, *i.e.* $[AsNHCl]^-$, $[AsN]^-$, and $[MeN(H)AsCl_2]^-$ are also observed.

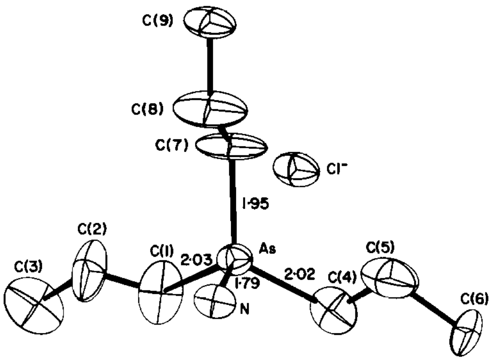


Fig. 1. ORTEP drawing (18% probability ellipsoids) of $[n\text{-}Pr_3AsNH_2]Cl$ showing the atom labelling scheme.

X-ray Spectra

The X-ray diffraction study of $[n\text{-}Pr_3AsNH_2]Cl$ indicates a near tetrahedral geometry about the As atom (Fig. 1) [24]. The following bond angles were observed: NAs–C(1) 114°, NAs–C(4) 105°, NAs–C(7) 108°, and C(1)–As–C(7) 109°. There is also a tetrahedral orientation of atoms about the nitrogen, *i.e.* As–N···Cl, 111°; and Cl···N···Cl, 110°. The As–N bond distance of 1.79 Å suggests only single bond character in the As–N bond [25, 26].

Supplementary Material

IR and mass spectral data are available from the Editor-in-Chief on request.

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