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(HALOMETHYL)ARSENIC COMPOUNDS

I. SYNTHESIS AND CHARACTERIZATION OF (CHLOROMETHYL)-ARSINE

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Summary

(Chloromethyl)arsine, $ClCH_2AsH_2$, can be prepared by the reduction of chloromethylarsonic acid. Bromomethyl and iodomethyl analogs could not be prepared. NMR, IR, and mass spectral data are included.

Introduction

Compounds containing halomethyl-substituted metals and metalloids have long interested organometallic chemists as potential carbene precursors and as intermediates in the preparation of methylene-bridged bimetallics [1]. A recent investigation of potentially important non-bonded metal—halogen p_π—d_π interactions in (halomethyl)-silanes and -germanes has brought further attention to this group of compounds [2].

Information about primary halomethyl derivatives of metals possessing non-bonding electron pairs (Groups V and VI) is limited to a single substantiated example*: (chloromethyl)phosphine, $ClCH_2PH_2$ [4,5]. The presence of non-bonding electron pairs on the central atom presents additional possibilities (both attractive and repulsive) for "across-space" metal—halogen interactions. This paper reports the preparation and properties of (chloromethyl)arsine, $ClCH_2AsH_2$.

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* A claim has been made for the preparation of (chloromethyl)amine, $ClCH_2NH_2$, but only decomposition products were isolated [3].

Results and discussion

Preparation and characterization of XCH_2AsH_2 compounds

$ClCH_2AsCl_2$, obtained from the diazomethane—$AsCl_3$ insertion reaction [6,7], could not be directly reduced to $ClCH_2AsH_2$ by any of the following reducing agents in yields greater than 1%: Zn/HCl, Zn/H_2SO_4, $NaBH_4$ or $LiAlH_4$; the $NaBH_4$ reactions were conducted in both H_2O and di-n-butyl ether, and $LiAlH_4$ in di-n-butyl ether. It was found necessary to first oxidize $ClCH_2AsCl_2$ with 15% H_2O_2 to the arsonic acid, $ClCH_2AsO(OH)_2$, and then reduce by the Zn/H_2SO_4 couple; a 65% yield of $ClCH_2AsH_2$ is obtained.

Likewise, $BrCH_2AsBr_2$ failed to yield $BrCH_2AsH_2$ on direct reduction and attempts to oxidize $BrCH_2AsBr_2$ to $BrCH_2AsO(OH)_2$ were accompanied by a strong evolution of bromine; no arsonic acid could be isolated from the reaction products. Also all attempts to prepare (bromomethyl)- and (iodomethyl)arsine by metathetical halogen exchange on $ClCH_2AsH_2$ led to decomposition products only.

Proton magnetic resonance spectra

(Chloromethyl)arsine: The 60 MHz PMR spectrum of (chloromethyl)arsine is shown in Fig. 1. Spectral parameters tabulated in Table 1 were obtained from a LAOCOON III computer-generated "best-fit" spectra, with the assumption that free rotation about the C—As bond would allow assignment of the molecule to the spin system, *AA'BB'* [8]. These data derive from iteratively converged, observed and calculated, line positions with a satisfactory resultant RMS error of 0.033 Hz. While normal *AA'BB'* spectra exist in two mirror-image halves which can lead to difficulties in assigning the *A* and *B* proton sets, the up-field half of the spectrum in Fig. 1 clearly shows the effects of quadrupolar broadening from ^{75}As ($I = 3/2$, 100% abundant). The up-field half is therefore assigned to protons directly bonded to arsenic.

The possibility of restricted rotation was tested by examining spectra of $ClCH_2AsH_2$ in t-butylbenzene through the temperature range —100 to 110°C. While temperature-dependent changes in $\Delta\nu(AB)$ (5 Hz at —100°C; 45 Hz at 110°C) and the effects of quadrupolar broadening (almost no broadening at —100°C) were found, there was no indication of restricted rotation. Any line intensity discrepancies may be the simple result of unequal (but small) quadrupolar broadening of the individual lines of the methylene half of the spectrum [9]. An inherent ambiguity arises in the assignment of the two geminal coupling constants, *J*(HAsH) and *J*(HCH). Consequently, assignment must be made by comparison to known values.

TABLE 1

COMPARATIVE NMR DATA[a]

Compound	τ(CH)	τ(EH)	*J*(HCH), *J*(HEH)	*J*(HCEH)
$ClCH_2PH_2$[b]	6.38	6.65	9.8, 10.4[d]	10.2, 4.9
$ClCH_2AsH_2$[c]	6.829	7.174	—6.78, —10.23	6.28, 5.57

[a] τ10.00 = TMS, *J* values in Hz, E = P or As. [b] Neat (ref. 5). [c] 10% solution in benzene. [d] Both values probably negative.

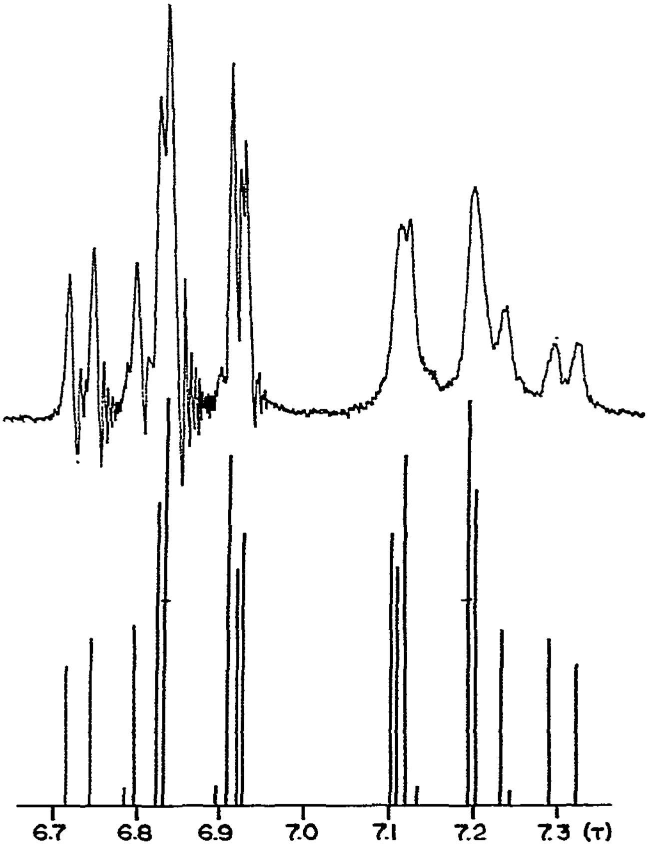

Fig. 1. 60 MHz PMR spectrum of ClCH$_2$AsH$_2$ (upper) as a 10% solution in benzene with the "best fit" computer simulation (lower). The up-field half of the observed spectrum is broadened by residual quadrupolar coupling to ^{75}As. Chemical shifts are measured from TMS = τ10.

Although no J(HAsH) values have been previously reported, values (Hz) for J(HNH) range from −10.35 to −13.23 [10-12] and for J(HPH) from −12.46 to −13.43 [12-14]. On this basis, a tentative assignment of the −10.23 Hz geminal value to J(HAsH) can be made. A value of −6.78 Hz for J(HCH) is reasonable for sp^3 hybridized carbon, but does demonstrate some opening up of the H—C—H bond angle [15] in comparison to ClCH$_2$PH$_2$. The two vicinal coupling constants, by analogy to results from 1,2-disubstituted ethanes, represent the *trans* and *gauche* conformers (for rotation about the C—As bond). The much smaller difference in the vicinal constants for ClCH$_2$AsH$_2$ than for ClCH$_2$PH$_2$ result from a closer similarity for the energies of the *trans* and *gauche* conformers [8b] for ClCH$_2$AsH$_2$; the trend toward equalization of conformational energies can be attributed to the longer bond length in ClCH$_2$AsH$_2$.

Mass spectrum of ClCH$_2$AsH$_2$

The mass spectrum of ClCH$_2$AsH$_2$, shown in Table 2, was obtained at an ionizing voltage of 70 eV and an ionizing chamber pressure of 2×10^{-6} mmHg. Some features of the spectra require special comment. The base peak, *m/e* 90,

TABLE 2

MASS SPECTRUM OF $ClCH_2AsH_2$

m/e	Rel. abund.	Assignment[a]
150	4.4	As_2^+
128	7.4	$^{37}ClCH_2AsH_2^+$
127	1.0	$^{37}ClCH_2AsH^+$
126	27.6	$^{35}ClCH_2AsH_2^+$ (23.3), $^{37}ClCH_2As^+$ (4.3)
125	4.0	$^{35}ClCH_2AsH^+$ (2.5), $^{37}ClCHAs^+$(1.5)
124	13.3	$^{35}ClCH_2As^+$ (13.0), $^{37}ClCAs^+$ (0.3)
123	4.4	$^{35}ClCHAs^+$
122	1.1	$^{35}ClCAs^+$
113	5.7	$^{37}ClAsH^{+}$(R)
112	5.0	$^{37}ClAs^{+}$(R)
111	19.8	$^{35}ClAsH^{+}$(R)
110	16.2	$^{35}ClAs^{+}$(R)
92	27.5	$CH_3AsH_2^+$
91	8.7	$CH_2AsH_2^+$
90	100.0	CH_2AsH^+
89	62.8	CH_2As^+
88	55.9	$CHAs^+$ (53.4), $CH_2{}^{37,37}Cl_2^+$ (2.5)
87	5.0	CAs^+
86	12.2	$CH_2{}^{35,37}Cl_2^+$
84	28.9	$CH_2{}^{35,35}Cl_2^+$
78	39.8	AsH_3^+
77	16.2	AsH_2^+
76	69.4	AsH^+
75	33.1	As^+
51	12.8	$^{37}ClCH_2^+$
50	2.6	$^{37}ClCH^+$
49	43.9	$^{35}ClCH_2^+$ (38.3), $^{37}ClC^+$ (5.6)
48	7.8	$^{35}ClCH^+$
47	16.8	$^{35}ClC^+$
37	2.3	$^{37}Cl^+$
35	7.1	$^{35}Cl^+$

[a] Parenthetical numbers are the relative abundances of species of same unit *m/e* value; R represents obvious rearrangement peaks, other fragments may also be the result of rearrangement, e.g., $ClCH_2As$; metastable transition data were not available.

suggests a process involving loss of the elements of HCl to yield CH_2AsH^+. Since it is frequently possible to show good agreement between thermal and electron-impact decompositions, it is noteworthy that the structural isomer, CH_3AsHCl, decomposes thermally with the loss of HCl [16]. The base peak in the spectrum of CH_3AsH_2 is also at *m/e* 90, but the spectrum of CD_3AsH_2 demonstrates that both arsenic-bonded hydrogens are lost preferentially [17].

The peaks at *m/e* 110-113 represent rearrangements involving formation of As—Cl bonds. Identical rearrangements have been found in α-halosilanes and -germanes [2b]. Dobbie and Cavell have found similar and extensive rearrangement in the spectra of CF_3-substituted phosphines and arsines [18]. They attribute the rearrangement process to an initial interaction between the fluorine *p* orbitals and the unoccupied *d* orbitals of the metalloid, and they strengthen their argument by citing earlier work which indicated that CF_3-substituted amines did not show these rearrangement peaks [19].

Infrared spectra

(Chloromethyl)arsine is expected to possess C_s symmetry, the symmetry plane being described by the heavy atoms. It proved useful in assigning observed absorptional frequencies to the fundamental modes to examine the rotation—vibration band contours of vapor-phase spectra [20].

In the spectra for $ClCH_2AsH_2$ (see Table 3), the complex band at 2900-3000 cm^{-1} must include both a symmetric and an antisymmetric C—H stretching band. While the resolution in the infrared spectra is not sufficient to assign the bands on the basis of contour characteristics alone, analogy can be made to Raman depolarization data from related compounds [21]. Thus, in methylarsine the antisymmetric mode is found at higher frequency.

Two bands are expected for the As—H stretching vibrations: one symmetric, giving rise to an *A*—*B* hybrid band contour; the other antisymmetric, giving rise to a *C* band. The complex band at 2050-2150 cm^{-1} surely contains both modes, but again unambiguous assignment of the observed frequencies to expected modes does not seem possible without Raman corroboration. The weak band centered at 1410 cm^{-1} is characteristic of the methylene group and is attributed to the CH_2 scissors vibration. No rotational character is observed. Other bands characteristic of the methylene group are observed in the region above 1000 cm^{-1}. The wagging mode, an A' vibration centered at 1188 cm^{-1}, has the expected *A*—*B* hybrid envelope. The CH_2 twist occurs at 1108 cm^{-1} and is weak, but exhibits the type *C* envelope expected of an A'' vibration.

The band centered at 963 cm^{-1} bears a strong type *C* resemblance (perhaps evidence for the molecule being a nearly symmetric rotor), but must be the *A*—*B* hybrid expected for the As—H scissor vibration. This mode is observed at 973 cm^{-1} in methylarsine [21]. In a number of methylarsine derivatives, the AsH_2

TABLE 3

IR SPECTRUM OF $ClCH_2AsH_2$

Vib. no.	Assignment	Frequency (cm^{-1})	Intensity[a]
A' Species			
$\nu 1$	C—H stretching	2950-2970	m
$\nu 2$	As—H stretching	2085-2130	vs
$\nu 3$	CH_2 scissors	1410	vw
$\nu 4$	CH_2 wagging	1188	s
$\nu 5$	AsH_2 scissors	963	m
$\nu 6$	AsH_2 wagging	760-800	m
$\nu 7$	C—Cl stretching	727	m
$\nu 8$	C—As stretching	528	w
$\nu 9$	Cl—As—C deformation (not observed)	250 (est.)	—
A'' Species			
$\nu 10$	C—H stretching	2950-2970	m
$\nu 11$	As—H stretching	2085-2130	vs
$\nu 12$	CH_2 twisting	1108	m
$\nu 13$	AsH_2 rocking	862	m
$\nu 14$	AsH_2 twisting	760-800	m
$\nu 15$	CH_2 rocking	700	w(sh)

[a] v = very strong, s = strong, m = medium, w = weak, sh = shoulder.

twisting and wagging vibrations show strong interactions and usually appear within 20 cm^{-1} of each other [21]. The wagging vibration will produce an *A—B* hybrid envelope, while the antisymmetric twisting mode is expected to produce a band of type *C*. The complex envelope at 760-800 cm^{-1} is thought to contain both modes, the absence of adequate resolution again prevents an unambiguous assignment.

The band centered at 862 cm^{-1} is of type *C* and is attributed to the antisymmetric AsH_2 rocking mode. The C—Cl stretching vibration displays essentially a *B* type envelope and is centered at 727 cm^{-1}. The antisymmetric CH_2 rocking vibration is located at the shoulder centered at 700 cm^{-1}. This assignment is tentative. The assignments are summarized in Table 3. The C—As stretching vibration must be incorporated in the group of absorptions in the region from 500-550 cm^{-1}, but the absence of an obvious contour type prevents the designation of a specific band origin. The skeletal deformation mode is likely in the region near 200 cm^{-1}, but could not be observed.

Experimental

Volatile, air-sensitive materials were handled in an all-glass vacuum system of standard design. NMR spectra were recorded on either a Varian A60A or a Perkin—Elmer R20B in sealed tubes; chemical shifts and coupling constants were obtained from minimum sweep-width spectra and represent the average of normally no fewer than five spectra. Mass spectra were recorded on a Varian M-66 and a duPont 21-492; air-sensitive samples and all gases were introduced through an unheated inlet system fitted through the liquid-sample port. The IR spectrum was recorded on a Perkin—Elmer 225 using a 10-cm pathlength gas cell fitted with CsBr windows. $AsCl_3$ (Fisher Scientific) was distilled before use; $AsBr_3$ and $ClCH_2POCl_2$ (both Alfa Inorganics) were used as obtained.

Chloromethylarsonic acid

According to the procedure described by Yakubovich and Braz [6], $ClCH_2AsCl_2$ [7] was oxidized to $ClCH_2AsO(OH)_2$ by 15% H_2O_2. In vacuo drying of the white crystalline product at 75°C was required to obtain consistently correct H analyses (due, presumably, to loss of weakly-held water of hydration). (Found: C, 6.96; H, 2.33; As, 42.84; Cl, 20.46. CH_4AsClO_3 calcd.: C, 6.88; H, 2.29; As, 42.97; Cl, 20.33%.) M.p. 135.5-136.5°C (lit. [6], 133-135°C.)

(Chloromethyl)arsine

A standard preparation of primary arsines (Zn/HCl reduction of an arsonic acid) [22] was modified by using H_2SO_4 instead of HCl and by minimizing the arsonic acid solution concentration by slow addition, a technique found important in maximizing arsine yields in related reductions of As_2O_3 [23]. These modifications are also noteworthy because of the complete absence of As-mirror or subhydride formation which often accompany Zn/HCl reductions of As^V acids.

A 250 ml, 3-neck flask equipped with a dropping funnel and attached to the vacuum system via a 16 mm o.d. connecting tube packed with 15 cm of Linde 3A molecular sieve was charged with 20 g of Cu-coated Zn dust (prepared by treatment with 2 g of $CuSO_4 \cdot 5H_2O$), 50 ml of H_2O, and 10 ml of methylcarbitol (to control foaming). The flask was sealed, partially evacuated and cooled to 0° C in an ice-brine bath. The funnel was charged with a solution of 15 g of $ClCH_2AsO(OH)_2$ in 50 ml of 3 *N* H_2SO_4. While maintaining the reaction temperature at 0° C, the solution was added dropwise over a 1 h period. During this hour and a subsequent period of 9 h the volatile contents of the flask were withdrawn through a series of cooled traps (—45°C, —78°C, —196°C) whenever the pressure in the flask exceeded 50 mmHg (measured by an auxiliary manometer filled with Unichlor 60L-60 chlorocarbon oil). The —196°C trap contained small quantities of AsH_3 and CO_2 as identified by their vapor-phase IR spectra. The —78°C trap contained 6.63 g of $ClCH_2AsH_2$ (61% yield based upon $ClCH_2AsO(OH)_2$). The —45°C trap contained small quantities of water and a dense liquid tentatively identified as $(ClCH_2)_2AsH$ due presumably to traces of $(ClCH_2)_2AsO(OH)$ in the arsonic acid. Final traces of H_2O were removed by repetitive condensation on P_4O_{10}. Ideal gas-law molecular weight of the product thrice passed through the same trap sequence was 125.5 (calcd. 126.4). The vapor pressure data for $ClCH_2$-AsH_2 in the temperature range, —47.5 to 13.2 is represented by log *P*(mm Hg) = $-1690 \times 31\ K^{-1} + 7.48407$, and yield an extrapolated normal b.p. of 94.0°C and heat of vaporization of —32.31 kJ mol^{-1}. The extrapolated b.p. compares reasonably with $ClCH_2PH_2$, 68°C [4]. Because of its tendency to dissolve in mercury, a separate sample was used for each vapor pressure measurement. (Chloromethyl)-arsine is a colorless liquid which showed no evidence of decomposition instability after storage at room temperature for one year. The NMR, MS and IR data are given in Tables 1-3.

(Chloromethyl)phosphine

$ClCH_2PH_2$ has been prepared by the thermal decomposition of chloromethylphosphinic acid [4], a not easily accessible starting material. Although we found that commercially available $ClCH_2POCl_2$ could be reduced with $LiAlH_4$ in di-n-butyl ether to $ClCH_2PH_2$ in 15% yield, we also found that the yield can be tripled if $ClCH_2POCl_2$ is first converted to $ClCH_2PO(OCH_3)_2$.

To 10.8 g (0.1 mol) of $NaOCH_3$ suspended in 50 ml di-n-butyl ether was slowly added 16.75 g of $ClCH_2POCl_2$ in 100 ml di-n-butyl ether at 0°C. After it had warmed to room temperature, the mixture was filtered and the filtrate was placed in a 1000 ml, 3-neck flask attached to the vacuum line. To this was added slowly 2 g of $LiAlH_4$ suspended in 150 ml of di-n-butyl ether at —20 to —30°C. Volatile products were removed periodically for 24 h. 2-Ethoxy-ethanol (10 ml) then was added to destroy excess $LiAlH_4$ and any $LiAl(PHCH_2Cl)_4$ [24] that had formed. Following fractional condensation purification of the crude product, 3.7 g of $ClCH_2PH_2$ (45% yield based on $ClCH_2POCl_2$), confirmed by its molecular weight and spectral properties [4], was obtained. Small quantities of PH_3 and CH_3Cl were removed during purification. The initial attempt at this reduction was conducted at room temperature; the yield was only 10% and a large quantity of CH_3Cl was obtained, presumably the result of C—P bond cleavage.

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