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Tertiary Arsines: A New Synthesis Route and an NMR Study

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A series of highly pure tertiary arsines (R_3As, where R = Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^{sec}, Bu^t, vinyl, allyl, Me_3SiCH_2, Ph, Bzl, *p*-tolyl, and mesityl) are conveniently prepared in high yield from the reactions of organo-Al, -Mg, -Li, or -Zn reagents with the chlorodioxarsolane $\overline{OCH_2CH_2O}AsCl$. We have found that $\overline{OCH_2CH_2O}AsCl$ is a very versatile compound for the synthesis of a wide variety of tertiary arsines. Although similar reactions were carried out using $\overline{OCMe_2CMe_2O}AsCl$, the yields were poor. This synthetic procedure has been extended to the synthesis of tertiary phosphines. The synthesized arsines were characterized by their IR, NMR, and mass spectra. A complete analysis of the ^1H and ^{13}C NMR spectra of each of the arsines was carried out, and the results are discussed in terms of substituent effects and the arsine conformation(s) in solution.

Introduction

Recently, there has been considerable interest in the synthesis of organoarsines, since alkylarsines and designer III-V adduct precursors are being evaluated in the MOCVD production of GaAs for microelectronic technologies.[1-12] Such evaluations require electronically pure arsines. Over the past 100 years, tertiary aryl- and alkylarsines have been synthesized by using a variety of alkylating agents. The reaction of Grignard reagents with arsenic trihalides is probably the most extensively utilized preparative method, even though the yields are not large and finely divided metallic arsenic is often obtained as a byproduct.[13-22] Grignard reagents also react with As_2O_3,[23] primary[24] and secondary[25] haloarsines, and As_2S_3[26] to give the tertiary arsines contaminated with other arsenicals. Kamai and co-workers have reported 33-85% yields of tertiary arsines from the Grignard reaction with arsenic thioacid esters[27] and trialkyl arsenites.[28]

Lithium alkyls have also been utilized as alkylating agents, especially when difficulties are encountered with the Grignard reactions or the Grignard reagent is difficult to obtain.[29-31] For example, Schumann et al.[32] obtained Bu^t_3As by treating Bu^tLi with Bu^t_2AsCl. Lithium alkyls can also be used to alkylate arsonium salts.[33] Unfortunately, undesirable side reactions produce yields that are lower than those from the Grignard route and the side-products contaminate the trialkylarsines.

The reactions of aluminum alkyls with arsenic trihalides[34] and As_2O_3[35] produce trialkylarsines in variable, but moderate, yields that depend upon the alkyl group. Also the reaction periods are usually quite long. Although organozinc reagents[36,37] typically give low yields, very pure tertiary arsines can be obtained. Organomercurials, which are less reactive than RMgBr, RLi, and R_2Zn, react with the arsenic trihalides[38,39] to give tertiary arsines mixed with dialkylahlo- and alkyldihaloarsines. Organotin compounds can also serve as useful alkylating agents.[40] The Wurtz-Fittig reaction[41] when applied to arsenic chemistry does not give satisfactory results.

In summary, the high-yield synthetic routes produce impure tertiary arsines that require additional purification steps. Highly pure arsines are generally obtained in low yield.

Only fragmentary ^1H and ^{13}C NMR data have been published previously on tertiary arsines. We have found that as complete an NMR data analysis as possible under identical experimental conditions for each member in a homologous series of compounds is often very beneficial. Such NMR data are very useful in the studies of the reactivities of the tertiary arsines with, for example, Lewis acids such as the group 13 trialkyls R_3Al and R_3Ga. In many cases, both electronic and structural changes that result from functional group substitution can be noted by comparison of the NMR parameters with those for other members of a series.[42]

As part of our attempt to develop useful synthetic pathways to mixed alkyldihaloarsines, we investigated the alkylation of 2-chloro-1,3,2-tetrahydrodioxarsolane. Instead of obtaining the desired 2-alkyl-1,3,2-tetrahydrodioxarsolanes, we found a versatile,

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high yield, novel synthetic route to highly pure tertiary arsines. The R_3As series, where R = Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^{sec}, Bu^t, vinyl, allyl, Me_3SiCH_2, Ph, Bzl, *p*-tolyl, and mesityl, was synthesized by the facile reactions of $\overline{OCH_2CH_2OAs}Cl$ with Grignard reagents and aluminum, lithium and zinc alkyls. In this paper, we report the preparation; comparative yield information; and IR, multinuclear NMR, and mass spectral data for these homoleptic tertiary arsines.

Results and Discussion

Synthesis. The 14 tertiary arsines were synthesized in good yields (65–95%) by treating an excess of RMgX, RLi, or R_2Zn in diethyl ether or of R_3Al in *n*-hexane with $\overline{OCH_2CH_2OAs}Cl$ under a nitrogen atmosphere. The choice of alkylating agents was limited to those that are easily purchased, except for $Pr^n{}_2Zn$ and $Bu^n{}_2Zn$. These reagents were used to show the applicability of the synthesis to zinc alkyls. All the arsines were easily isolated from the other reaction products by distillation of the organic solvent layer after decomposing the excess alkylating agent with an aqueous solution of ammonium chloride. No attempt was made to isolate or characterize the non-arsenic-containing product(s). The liquid arsines were purified on a spinning-band column. The solid arsines, initially isolated by evaporation of the solvent, were recrystallized from boiling ethanol. A satisfactory elemental analysis was obtained for the previously unreported $Bu^{sec}{}_3As$. The method of preparation, yield, and melting or boiling point data are given in Table I.

Both the Grignard and alkylzinc reagents gave comparable yields of the tertiary arsines. In the few cases where alkyllithium compounds were used, the resulting arsine yields were the lowest. On the other hand, $Bu^t{}_3As$ was best prepared using Bu^tLi, since the reaction with Bu^tMgCl gave a reaction mixture that was very difficult to separate. The aluminum alkyls gave the lowest arsine yields, which is probably due to the formation of trialkylaluminum adducts of the product arsines. No matter which alkylating agent was used, the tertiary arsine yield increased in the order Et < Pr^n < Bu^n < Ph. This is consistent with the trend observed previously for the reactions of RMgX with $AsCl_3$.[43] The increasing bulkiness of the R group in going from Bu^n to Bu^{sec} to Bu^t appears to have very little effect on the arsine yield.

Alkylation of the chloroarsolane, $\overline{OCMe_2CMe_2OAs}Cl$, also gave the tertiary arsines, but the reaction mixture consisted of a solid mass from which product isolation was very difficult. This procedure resulted in significantly lower yields (Et_3As, 63%; $Pr^n{}_3As$, 76% from Grignard reactions). Thus, alkylation of $\overline{OCH_2CH_2OAs}Cl$ was the preferred route to the tertiary arsines.

All attempts to synthesize Me_3As from methylation of $\overline{OCH_2CH_2OAs}Cl$ resulted in less than a 20% yield. This is typical of other reported Me_3As syntheses in which the low yields are attributed to the difficulty of separating the Me_3As from the reaction mixture.[44] We have reported recently a better, higher yield (84%) synthesis of Me_3As from the reaction of $(Me_3Al)_2$ with $As(NMe_2)_3$.[45]

This new synthetic strategy to tertiary arsines has several distinct advantages over prior literature procedures. The chloroarsolane can be easily prepared in bulk and stored for later use, since it is a crystalline solid and the inherent safety problems associated with $AsCl_3$ and the alkylhaloarsines are not present. Although a variety of alkylating agents can be used to give high product yields, our work suggests that the less expensive, more widely available Grignard reagents can best be used with $\overline{OCH_2CH_2OAs}Cl$ to obtain a high arsine yield. This is advantageous, since a wide variety of Grignard reagents are commercially available. Also, the resulting tertiary arsines are isolated free of undesirable side-product contaminants.

This general synthetic procedure has also been extended to the synthesis of tertiary phosphines. In the reactions of EtMgBr and Pr^nMgBr with $\overline{OCH_2CH_2OP}Cl$, we obtain Et_3P and $Pr^n{}_3P$, each in 82% yield.

NMR Study. Both simple first-order and more complex non-first-order ^1H NMR spectra were obtained for compounds I–XIV. The experimentally measured values of the ^1H NMR chemical shifts (δ_H, ppm; TMS) and spin–spin coupling constants ($^nJ(H,H)$) are reported in Tables II and III for those compounds exhibiting first-order spectra (III, VI, VII, X, and XIII). Standard iterative computer analysis methods were conducted on the spectra of the remaining compounds. Calculated values of δ_H and $^nJ(H,H)$ are given in Tables II and III for compounds I, II, VIII, IX, XII, and XIV. Severe overlap and/or degeneracy of spectral transitions precluded successful non-first-order analysis of the ^1H NMR data for IV, V, and XI, and only approximate values are reported.

The ^1H NMR data suggest that, for a given compound, the three R groups are individually undergoing rapid conformational averaging about the arsenic atom and are equivalent on the NMR time scale, except for R = Bu^{sec} (V). In this case, the ^1H and ^{13}C NMR data indicate that at least four isomers/conformers are present in solution.

Both $\{^1H\}$-decoupled and coupled ^{13}C NMR spectra were obtained for all the compounds in this study in order to verify the ^{13}C NMR chemical shift assignments. Additional experiments, as noted in the Experimental Section, were conducted where necessary. The ^{13}C NMR chemical shift (δ_C, ppm; TMS) and $^1J(C,H)$ data are listed in Table IV. δ_C values for I,[42,46,47] II,[42,46] III,[46] IV,[46,47] VIII,[48] and XI[42] are in agreement with previously reported values. An extensive discussion of the factors influencing δ_C in tertiary alkyl arsines and phosphines has been reported.[42,46,47,49]

Examination and analysis of the coupled ^{13}C NMR spectra of the compounds led to the determination of $^nJ(C,H)$ for III, VI, VII, VIII, X, and XIII from first-order considerations and for IX and XII from non-first-order iterative computer techniques. Only partial analyses were successful for I, II, XI, and XIV. The $^1J(C,H)$ data for I, II, III, and VI are reflective of those for simple aliphatic compounds[50] with the exception of the carbon adjacent to the arsenic atom. Since the Pauling electronegativity values for As and H are the same, these data would suggest that some other factor or factors such as bond angle distortion must be contributory[46,50] to the larger observed $^1J(C,H)$ value. Similarly, this effect is noted in VIII [$^1J(C,H)$ for ethylene is 156.4 Hz[50]] and in IX (cf. propene[51]). The $^2J(C,H)$, $^3J(C,H)$, and $^4J(C,H)$ values obtained for the analyzed compounds are in agreement with standard reference values[50,52–54] for the given organic functional groups.

Experimental Section

All experimental manipulations were carried out in a dry nitrogen atmosphere and in a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train. The NMR data were obtained by using a GE (Nicolet) 300 MHz multinuclear Fourier-transform NMR spectrometer operating at 300.1 MHz for ^1H, 75.5 MHz for ^{13}C, and 59.6 MHz for ^{29}Si. Spectral data were obtained for 0.20 M chloroform-*d* solutions of the compounds at 24 °C. Me_4Si was used as an

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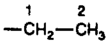
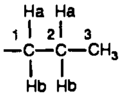
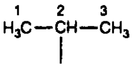
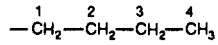
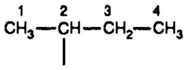
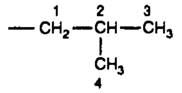
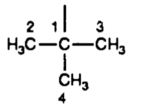
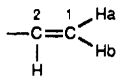
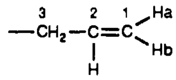
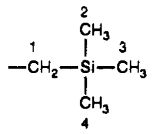
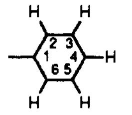
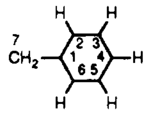
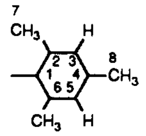
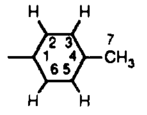
Table I. Synthesized Tertiary Arsines

compd	formula	alkyl/aryl numbering system	synthetic route[a]	yield, %	bp, °C/*P*, Torr or mp, °C
I	Et_3As	 $-CH_2-CH_3$	A C D	82 84 71	140/76
II	Pr^n_3As		A C D	83 87 78	73/8
III	Pr^i_3As		A	78	96/38
IV	Bu^n_3As	 $-CH_2-CH_2-CH_2-CH_3$	A B C D	88 70 92 90	102/8
V	Bu^{sec}_3As		A B D	86 68 90	95/8
VI	Bu^i_3As		D	76	119/31
VII	Bu^t_3As		A B	60 82	50–52/0.2
VIII	$(vinyl)_3As$		A	70	124/760
IX	$(allyl)_3As$		A	70	111/50
I	$(Me_3SiCH_2)_3As$		A	95	67–68
XI	Ph_3As		A B	88 80	60–61
XII	Bzl_3As		A	80	105–107
XIII	$(mesityl)_3As$		A	89	170
XIV	$(p\text{-tolyl})_3As$		A	71	146

[a] Key: A = organomagnesium, B = organolithium, C = organozinc, and D = organoaluminum.

internal reference. Both ^{13}C coupled and $\{^1H\}$-decoupled spectra were obtained for each of the compounds. The ^1H and ^{13}C NMR data are reported in Tables II–IV. Previously reported NMR data are referenced in the tables. Where necessary, single frequency $\{^1H\}$-decoupled and APT[55] ^{13}C NMR spectra were also obtained. The ^{13}C NMR assignments for Bu^n_3As were confirmed by spin–lattice relaxation (T_1) measurements.[47] The ^{29}Si NMR spectra of $(Me_3SiCH_2)_3As$ consisted of a single resonance at 0.48 ppm relative to 0.00 ppm for Me_4Si.

Low-resolution EI-MS data were recorded on a HP 5985A GC/MS/MS mass spectrometer operated at 70 eV, with a 2400-V electron multiplier. Samples were introduced either by the batch technique or by using a direct-insert probe. The source temperature was maintained at 200 °C, and the probe temperature was 25 °C. These data on compounds not previously reported, which are filed as supplementary data, indicate ions associated with the fragmentation of the R_3As moiety. The data are consisted with those reported previously for Et_3As,[56,57] Pr^n_3As,[57] Bu^n_3As,[57] and Ph_3As.[58]

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Table II. ^1H Chemical Shifts (ppm, TMS) of Tertiary Arsines

		chem shift										
compd	R	H-1	H-1a	H-1b	H-2	H-2a	H-2b	H-3	H-4	spectral type	rms error	ref
I	Et	1.40			1.12					A_2B_3	0.039	42
II	Pr^n		1.40	1.40		1.49	1.49	0.98		$AA'BB'X_3$	0.098	42
III	Pr^i	1.18			1.86			1.18		*a*		
IV	Bu^n	1.41			1.41			1.38	0.90	*b*		
V	Bu^{sec}	1.0–1.5			1.9–2.5			1.5–1.8	0.8–1.0	*b*		
VI	Bu^i	1.35			1.75			0.98	0.98	*a*		
VII	Bu^t				1.30			1.30	1.30	*a*		32
VIII	vinyl		5.68	5.93	6.51					AMX	0.009	48
IX	allyl		4.99	4.98	5.83			2.28		$ABMX_2$	0.023	
X	Me_3SiCH_2	0.67			0.053			0.053	0.053	*a*		63

		chem shift							
compd	R	H-2,6	H-3,5	H-4	H-7,9	H-8	spectral type	rms error	ref
XI	Ph	7.32	7.32	7.32			*c*		42
XII	Bzl	7.06	7.24	7.13	2.77		$AA'BB'CX_2$	0.052	
XIII	mesityl		6.77		2.13	2.23	*a*		64
XIV	*p*-tolyl	7.22	7.12		2.32		$AA'BB'X_3$	0.028	65[b]

[a] First order. [b] Approximate values only. [c] Degenerate.

Table III. $^nJ_{HH}$ (Hz) of Several Tertiary Arsines

compd	R	$^2J_{HH}$	$^3J_{HH}$	$^{4,5}J_{HH}$
I	Et		*J*(1,2) = 7.81	
II	Pr^n	*J*(1a,1b) = −13.46 *J*(2a,2b) = −12.48	*J*(1a,2a), *J*(1b,2b) = 5.87 *J*(1b,2a), *J*(1a,2b) = 10.15 *J*(2a,3), *J*(2b,3) = 7.26	
III	Pr^i		*J*(1,2), *J*(2,3) = 7.20	
VI	Bu^i		*J*(1,2) = 7.14 *J*(2,3), *J*(2,4) = 6.65	
VIII	vinyl	*J*(1a,1b) = 1.55	*J*(1a,2) = 18.62 *J*(1b,2) = 11.37	
IX	allyl	*J*(1a,1b) = 1.95	*J*(1a,2) = 16.95 *J*(1b,2) = 10.09 *J*(2,3) = 8.07	*J*(1a,3) = −1.29 *J*(1b,3) = −0.79
XII	Bzl		*J*(2,3), *J*(5,6) = 7.72 *J*(3,4), *J*(4,5) = 7.48	*J*(2,4), *J*(4,6) = 1.26 *J*(2,5), *J*(3,6) = 0.58 *J*(2,6) = 1.76 *J*(3,5) = 1.57
XIV	*p*-tolyl		*J*(2,3), *J*(5,6) = 7.72	*J*(2,5), *J*(3,6) = 0.51 *J*(2,6) = 1.85 *J*(3,5) = 1.78

Table IV. ^{13}C Chemical Shifts (ppm, TMS) of Several Tertiary Arsines[a]

		chem shift				
compd	R	C-1	C-2	C-3	C-4	ref
I	Et	16.34 (128.7)	10.69 (126.1)			42, 46,[d] 47[d]
II	Pr^n	27.78 (130.9)	20.39 (126.1)	16.61 (124.9)		42, 46[d]
III	Pr^i	21.38 (125.5)	22.44 (131.3)	21.38 (125.5)		46[d]
IV	Bu^n	24.90	29.16	25.03	13.82 (124.5)	46,[d] 47[d]
V	Bu^{sec}	16.77, 17.05 17.25, 17.52	28.70, 29.06 29.10, 29.71	27.79, 28.34 28.65, 28.98	12.82, 12.82 12.90, 12.97	
VI	Bu^i	38.31 (129.2)	27.21 (125.8)	24.66 (124.6)	24.66 (124.6)	
VII	Bu^t	35.92	31.83 (125.4)	31.83 (125.4)	31.83 (125.4)	
VIII	vinyl	127.83 (157.6)	138.58 (159.0)			48[d]
IX	allyl	115.29 (158.3)[d] (154.1)[c]	134.47 (153.1)	27.96 (133.9)		
X	Me_3SiCH_2	17.71 (121.5)	0.27 (118.5)	0.27 (118.5)	0.27 (118.5)	

		chem shift				
compd	R	C-1	C-2,6	C-3,5	C-4	C-7,9	C-8
XI	Ph[e]	139.57	133.66 (160.5)	128.60 (160.0)	128.39 (160.1)		
XII	Bzl	139.14	128.62 (157.5)	128.41 (159.5)	125.35 (160.6)	32.22 (133.9)	
XIII	mesityl	135.86	142.83	129.51 (155.0)	137.38	23.13 (126.5)	20.85 (126.1)
XIV	*p*-tolyl	136.46	133.60 (160.0)	129.38 (158.3)	138.10	21.27 (126.4)	

[a] ^1J(C,H) in parentheses. [b] $^1J(\text{C-1,H}_b)$. [c] $^1J(\text{C-1,H}_a)$. [d] Chemical shift data only. [e] See ref 42 for reported δ_c values.

IR spectra were recorded on a Perkin-Elmer IR 283 spectrometer. The spectra were obtained on the solids as Nujol mulls and on the neat liquids by using CsI plates in the 4000–250-cm^{-1} range. Previously unreported data are filed as supplementary data.

Pinacol, ethylene glycol, PCl_3, EtMgBr, Pr^{n}MgBr, Bu^{n}MgCl, Bu^{sec}MgCl, Bu^{t}MgCl, (allyl)MgBr, BzlMgBr, (*p*-Tolyl)MgBr, (Mesityl)MgBr, Me_3SiCH_2MgCl, Bu^{n}Li, Bu^{sec}Li, Bu^{t}Li, PhLi, and Et_2Zn were purchased from Aldrich and were used as obtained. Triethylamine was obtained from Aldrich, treated with KOH, distilled, and stored over molecular sieves. Diethyl ether was dried over Na/Benzophenone. Petroleum ether (40–60 °C) and *n*-hexane were distilled over calcium

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hydride and stored over molecular sieves. Ethanol was dried over P_4O_{10} and stored over molecular sieves. $CDCl_3$ and Me_4Si were purchased from MSD and Aldrich, respectively, and stored over molecular sieves. $AsCl_3$, Pr^iMgCl, (vinyl)MgCl, and PhMgCl were obtained from Strem Chemical Co. Et_3Al, Pr^n_3Al, Bu^n_3Al, and Bu^i_3Al, and Bu^i_3Al were purchased from Ethyl Corp. and used as obtained.

Pr^n_2Zn and Bu^n_2Zn were synthesized by the slow, room-temperature addition of the stoichiometric amount of the appropriate trialkylalane to a suspension of anhydrous $Zn(C_2H_3O_2)_2$ (obtained from the commercial dihydrate with boiling acetic anhydride) in *n*-hexane. After the addition was complete, the reaction mixture was refluxed for 7 h, the solvent was distilled, and the dialkylzinc compound was purified by distillation on a spinning-band column: Pr^n_2Zn (77 °C (56 Torr), 86% yield) and Bu^n_2Zn (61 °C (4 Torr), 92% yield). The ^1H (Pr^n_2Zn[59] and Bu^n_2Zn[60]) and ^{13}C NMR (Bu^n_2Zn[60]) spectral data agreed with those previously reported. The ^{13}C spectral data (δ_C, ppm) for Pr^n_2Zn are as follows: 19.27, ($\underline{C}H_3CH_2CH_2As$); 19.78, ($CH_3\underline{C}H_2CH_2As$); 21.12, ($CH_3CH_2\underline{C}H_2As$).

$\overline{OCH_2CH_2OAs}Cl$ and $\overline{OCMe_2CMe_2OAs}Cl$ were synthesized by using a slight modification of the previously described procedure.[61] The use of Et_3N, in place of pyridine, provided a better yield (62%). $\overline{OCH_2CH_2OP}Cl$ was synthesized from the reaction of PCl_3 with ethylene glycol.[62]

General Synthesis of R_3As by the Reactions of RMgX (X = Cl, Br) and RLi with $\overline{OCH_2CH_2OAs}Cl$. In a typical synthesis, 0.06 mol of $\overline{OCH_2CH_2OAs}Cl$ was added to 400 mL of Et_2O (*n*-hexane for the RLi reactions) in a 1-L three-necked, round-bottom flask fitted with a reflux condenser, a mechanical stirrer, and a pressure-equalizing addition funnel. A solution of 0.18 mol of the appropriate alkylating reagent was added slowly over a period of 2 h to the vigorously stirred chloroarsolane solution that was maintained at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. [In the case of $(mesityl)_3As$, the mixture was refluxed for 12 h. The RLi reactions were refluxed for 24 h.] Unreacted alkylating agent was then hydrolyzed with a degassed, saturated NH_4Cl solution. After the organic solvent layer, which contained the arsine, was isolated, the aqueous layer was extracted three times with 75 mL of Et_2O or *n*-hexane and the extracts were added to the initial solvent layer. The arsine-containing solution was dried over anhydrous Na_2SO_4. Following distillation of the solvent, the liquid tertiary arsines were purified by distillation on a spinning-band column. In the case of the solid tertiary arsines, the pure compounds were obtained from the residue by recrystallization from hot ethanol. Yield data are given in Table I.

General Synthesis of R_3As from the Reactions of R_2Zn and R_3Al with $\overline{OCH_2CH_2OAs}Cl$. In a 1-L, three-necked, round-bottom flask equipped with a reflux condenser, mechanical stirrer, and pressure-equalizing addition funnel, 0.06 mol of $\overline{OCH_2CH_2OAs}Cl$ was added to 400 mL of *n*-hexane. Then, 0.12 mol of the appropriate alkylating agent in 100 mL of hexane was added slowly with vigorous stirring at room temperature. The reaction mixture was then refluxed for 24 h. After the reaction was cooled to room temperature, any unreacted metal alkyl was hydrolyzed by using 200 mL of a degassed, saturated NH_4Cl solution. The mixture was filtered to remove the solid hydrolysis products. The hexane layer of the filtrate was separated, the three 50-mL hexane extracts of the aqueous layer were combined with the initial hexane layer, and the hexane solution of the arsine was dried over anhydrous Na_2SO_4. After distillation of the hexane, the arsine was distilled on a spinning-band column. Yield data are given in Table I.

The purity of all synthesized arsines was checked by melting point; boiling point; IR spectroscopy; ^1H, ^{13}C, and/or ^{29}Si NMR spectroscopy; and EI mass spectrometry. A satisfactory elemental analysis for Bu^{sec}_3As was obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY. Anal. Calcd: C, 58.52; H, 11.05. Found: C, 58.36; H, 11.02.

Supplementary Material Available: Tables of mass spectral data and IR data (2 pages). Ordering information is given on any current masthead page.

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The Hexafluorochlorate(V) Anion, ClF_6^-

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The low-temperature reactions of either $N(CH_3)_4F$ or CsF with ClF_5 in CH_3CN solutions produce white solids, which on the basis of material balances and low-temperature Raman spectra, contain the ClF_6^- anion. The similarity of the Raman spectrum of ClF_6^- to that of the octahedral BrF_6^- ion indicates that ClF_6^- is also octahedral and that the free valence electron pair on chlorine is sterically inactive. The existence of the ClF_6^- anion was further supported by an ^{18}F exchange experiment between ClF_5 and ^{18}F-labeled FNO that showed complete randomization of the ^{18}F isotope among the two molecules. A high-field ^{19}F NMR study of neat ClF_5 and ClF_5 in anhydrous HF solution in the presence and absence of excess CsF has provided accurate measurements of the ClF_5 NMR parameters including, for the first time, both $^{37/35}Cl$ secondary isotopic ^{19}F NMR shifts. Moreover, the NMR study also supports the existence of ClF_6^-, showing that ClF_5 undergoes slow chemical exchange with excess CsF in anhydrous HF at room temperature.

Introduction

The hexafluorohalate(V) anions belong to the interesting class of AX_6E compounds,[2] which possess six X ligands and a free valence electron pair E. Depending on the size of the central atom A, the free valence electron pair E can be either sterically active or inactive. Thus, a recent study has shown that in IF_6^- the free valence electron pair is sterically active, while in BrF_6^- it is not.[3] Whereas the ClF_5 molecule was discovered 27 years ago,[4] and the BrF_6^- and IF_6^- anions have been known for about as long,[5,6]

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