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Application of Specific Deuterium Labeling and Nuclear Magnetic Resonance Spectroscopy to the Study of the Mechanism of Pyrolysis of *tert*-Butylarsine and *tert*-Butylarsine-d_2

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The synthesis of *tert*-butylarsine-d_2 from *tert*-butylarsenic dichloride and $LiAlD_4$ is described. No resonances at 2.65 ppm (from AsH_2) are observed in the ^{1}H NMR spectrum, indicating the isotopic purity is greater than 95%. The pyrolyses of *tert*-butylarsine and *tert*-butylarsine-d_2 were studied by using a flow reactor operated between 425 and 550 °C at total pressures of 0.001, 5, and 700 Torr. At 5 and 700 Torr, nitrogen was used as the carrier gas. The volatile products of the reaction were trapped in a liquid nitrogen cooled trap, transferred under vacuum into an NMR tube, and quantitatively analyzed by using ^{1}H NMR spectroscopy. Three important results from the study are (1) the isobutane produced during the pyrolysis of *tert*-butylarsine-d_2 was Me_3CD, (2) C_2Me_6 was proven not to be a product of the reaction, (3) isobutane was found to be the major product at atmospheric pressure, while isobutene was predominant at low pressures in agreement with previous studies. These data allow us to evaluate the possible mechanisms for the pyrolysis and discard a mechanism involving radical non-chain reactions.

Introduction

There has been much interest in developing an alternative source of As for the organometallic vapor-phase epitaxy of GaAs.[1-13] The high toxicity and low boiling point of AsH_3 combine to make it difficult to handle. Most of the alternative precursors incorporate one or more alkyl group(s) bound to the arsenic, rendering the compound less volatile. Unfortunately, this modification often leads to poorer quality GaAs due to the incorporation of carbon into the film.[1,4,5,11]

Among the most attractive alternatives described recently is *tert*-butylarsine (TBAs).[3,4,7,10-12] Several papers have already appeared that describe many of the possible mechanisms for cleavage of the As–C bond.[7,10] These thorough studies conducted under somewhat different conditions reach different conclusions about the pyrolysis mechanism. Because cleavage of the As–C bond is critical for its use in growing GaAs, we report here on further studies designed to differentiate (and hopefully choose) among the different mechanisms for cleavage of the As–C bond. The methodology adopted here relies on nuclear magnetic resonance (NMR) spectroscopy as the analytical tool. When combined with the use of specifically isotopically labeled compounds, a precise picture of the location of isotopes in the products is determined.

Experimental Section

General Techniques. Di-*n*-butyl ether (99%) and tetrahydrofuran (THF) were distilled from sodium and sodium benzophenone ketyl, respectively. Potassium was cleaned under hexanes before transfer to the drybox with final cleaning just prior to use. Anhydrous magnesium chloride (98%), 2-chloro-2-methylpropane (99%), and arsenic trichloride (99+%, Alfa, lot no. L%OG) were used as received. Lithium aluminum hydride (95%) and lithium aluminum deuteride (98 atom % D, Aldrich) were stored in the glovebox and used as received.

Benzene-d_6 (99.5 atom % D) and toluene-d_8 (99+ atom % D) were obtained from Aldrich and transferred into vacuum storage bulbs under a nitrogen atmosphere. Lecture bottles of isobutane, Matheson, and isobutene (Union Carbide) were used without further purification. Azoisobutane (Alfa) was used as received.

Infrared spectra were obtained on a Mattson Cygnus 25 FTIR spectrometer with a HgCdTe detector, using a 15-cm gas cell with sodium chloride windows. ^{1}H and ^{13}C NMR spectra were obtained on an IBM NR-200 AF NMR spectrometer. Deuterium spectra were run on a Nicolet NFT 300 MHz spectrometer. Manipulations in inert atmosphere were carried out in a recirculating glovebox manufactured by the Vacuum Atmospheres Co.

Caution: Arsine and *tert*-butylarsine are highly toxic. All preparations and pyrolysis were conducted in a fume hood. All residual starting materials and products were destroyed by using bromine water, which was subsequently treated with Na_2S to precipitate arsenic sulfide. This was disposed of as solid hazardous waste.

tert-Butylmagnesium chloride was prepared by the Rieke method[14] and reacted immediately with $AsCl_3$ to give *tert*-butylarsenic dichloride.[15] The product was stored in a refrigerator under a nitrogen atmosphere; ^{1}H NMR (C_6D_6) δ 0.90 (s, Me).

***tert*-Butylarsine.** This method is essentially the same as the literature procedure[16] except for the use of a different solvent and

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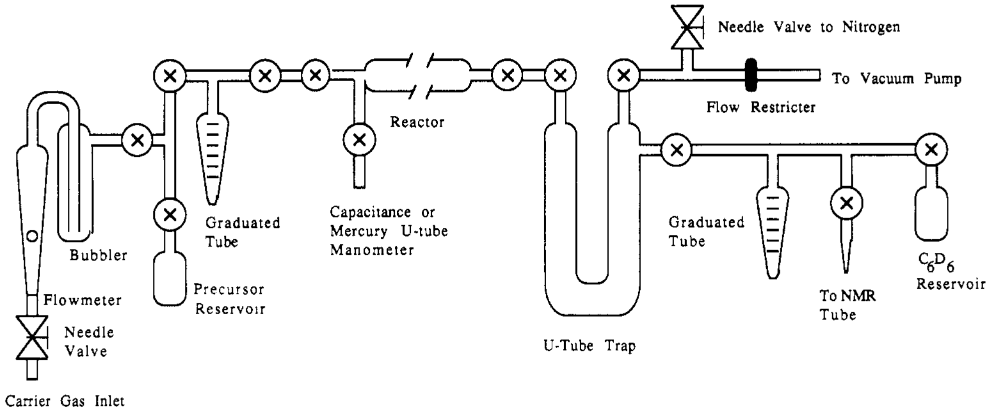

Figure 1. Pyrolysis apparatus.

a variation on the purification procedure. Lithium aluminum hydride (1.29 g, 0.034 mol) was placed in a 100-mL three-necked flask in the glovebox. It was suspended in freshly distilled di-*n*-butyl ether. The *t*-$BuAsCl_2$ (13.65 g, .067 mol) was dissolved in di-*n*-butyl ether in a Schlenk tube and transferred to a dropping funnel by cannula. This solution was added dropwise to the $LiAlH_4$ solution over 30 min. The *tert*-butylarsine was distilled from the mixture of product, solvent, and salts through a vigreux column and short-path condenser. Collection of product ceased as the distillation temperature approached 100 °C. A 10-mL two-necked pear-shaped flask was used as a collection flask, and this was subsequently used as the distillation flask for the final purification. The flask was fitted with an Ace spinning band microdistillation column. A Schlenk tube was used for the collection vessel to permit handling the product under a flow of nitrogen; ^1H NMR (C_6D_6) δ 1.19 (s, Me), 2.65 (s, AsH_2), ^{13}C NMR (C_6D_6) δ 28.58 (s, C), 33.76 (s, CH_3); IR ν_{As-H} (gas phase) 2088 cm^{-1}.

***tert*-Butylarsine-*d*$_2$.** The preparation of *tert*-butylarsine-d_2 duplicated the preparation of *tert*-butylarsine with the exception of the use of lithium aluminum deuteide as the reducing agent; ^1H NMR (C_6D_6) δ 1.19 (s, Me); ^{13}C NMR (C_6D_6) δ 28.58 (s, C), 33.76 (s, CH_3); ^2H NMR (C_6D_6) δ 2.65 (s, AsD_2); IR ν_{As-D} (gas phase) 1512 cm^{-1}; mp -2 °C.

AsH_3 and AsD_3. The vacuum transfer of a stoichiometric amount of $AsCl_3$ to a frozen solution of lithium aluminum hydride in di-*n*-butyl ether results in the generation of arsine on warming of the solution.[17] The arsine and other volatiles were transferred to a trap at liquid nitrogen temperatures. After transfer, the liquid nitrogen was replaced by a CS_2/CO_2 slush bath, and the arsine was transferred to a gas storage bulb for further use; ^1H NMR (C_6D_6) δ 1.25 (s, AsH_3).

Arsine-d_3 was generated by the same method used for arsine; ^2H NMR (C_6D_6) δ 1.25 (s, AsD_3).

Pyrolysis Apparatus. Figure 1 illustrates the reactor used for the pyrolyses. The quartz tube that served as the reactor for all experiments was 28-mm o.d. × 30 cm. The tube was terminated on each end with 29/42 quartz ground-glass joints with the remainder of the apparatus constructed of Pyrex tubing, vacuum stopcocks, and ground-glass joints. A single-stage tube furnace was used to heat the reactor, and temperatures were measured at the top of quartz tube at the midpoint of the furnace. Reactor pressures were measured either with a mercury manometer for pressures near atmospheric or with an Inficon IG3 capacitance manometer for pressures from 10^{-3} to 10 Torr. Use of carrier gases required addition of 3-mm glass beads to the U-tube for efficient product trapping. The outlet of the U-tube trap leads to the vacuum pump past a nitrogen inlet and through a flow restrictor, which were used to reduce the reactor throughput to 40–50 sccm at pressures of 700 Torr.

Pyrolysis Conditions: Millitorr Regime. Pyrolysis of *tert*-butylarsine was done in the absence of a carrier gas at a pressure of $\sim$1 mTorr (maintained with adjustments to stopcocks at both the inlet and outlet side of the reactor). The precursor volatilized on warming of the precursor bath to approximately -80 °C.

Low-Pressure Pyrolysis. Initial runs with carrier gas at pressures of 5 Torr demonstrated that some of the products were swept through the U-trap to the pump trap. Quantitative experiments indicated trapping efficiency had dropped to 50–60%. Addition of 3-mm glass beads to the outlet arm of the U-trap allowed quantitative trapping of all condensible gaseous products, yet avoided plugging the trap with condensible liquids. Initial experiments were carried out prior to obtaining the flow meter, and residence times were estimated to be a few milliseconds from subsequent experiments. In a single run when the reactor temperature was reduced from 550 to 450 °C, low conversion (<10%) was observed.

Pyrolysis with Toluene-*d*$_8$. The carrier gas was bubbled through toluene-d_8 and was directed over the *tert*-butylarsine contained in the graduated centrifuge tube. When both were maintained at the same temperature, the volume of toluene introduced to the reactor was 3–10 times that of the *tert*-butylarsine. At 5 Torr the residence time in the heated portion of the reactor is 0.14 s. Residence times at 690 Torr are 72 s. If less than 1 mL of toluene was introduced, the NMR sample was diluted to 1 mL with C_6D_6 prior to sealing. To prevent plugging the U-tube during the experiment, the glass beads on the inlet side of the U-tube must be well below the liquid nitrogen level.

Pyrolyses near Ambient Pressure. Operation of the reactor near ambient pressures required the use of a flow restrictor at the pump inlet and a N_2 inlet between the pump trap and flow restrictor. Prior to each run, the flow rate of the carrier gas was adjusted to the desired value while the toluene and *tert*-butylarsine remained frozen in liquid nitrogen.

Addition of Glass Beads. A single run was carried out in which the reactor was filled with 240 g of 3-mm glass beads. From the mass and size of the beads it is estimated that the surface area in the active region reactor increased by a factor of 12–13. The reactor tube is constructed of quartz, while the beads were borosilicate glass. Packing the reactor with beads reduced the residence time to 40% of the previous value.

Pyrolysis of Azoisobutane. A known quantity of azoisobutane was distilled into the graduated test tube. The procedures for the pyrolysis at high and low pressures as well as in the presence or absence of toluene-d_8 were identical with those followed for *tert*-butylarsine.

Quantitative Analysis. Analysis of the various products of the pyrolysis were accomplished by measurement of the integrated intensities of the various resonances. Known quantities of the internal standard, triphenylmethane, were placed in NMR tubes sealed to 14/35 ground-glass joints. Following a pyrolysis, the products were transferred under vacuum to the NMR tubes, where they were diluted with 1.0 mL of benzene-d_6. The relative signal responses of the products (methyl group hydrogens) and standard were plotted vs the relative molalities of the products and standard. The calibration curves, prepared by passing known volumes of isobutane and isobutene through the entire system to duplicate closely an actual pyrolysis, obtained for isobutane were assumed to hold for *tert*-butylarsine and *tert*-butylarsine-d_2.

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Table I. Results of *tert*-Butylarsine and *tert*-Butylarsine-d_2 Pyrolyses

expt[a]	P_{total}[b]	temp[c]	prec temp[c]	$P_{t\text{-BuAsH}_2}$[b]	% conv	mass bal	C_4H_8/C_4H_{10}	% C_4H_9D
4-H[d]	0.001	550	−79	0.001	77 (4)	87 (15)	1.7 (0.2)	
1-H	5	555	−79	0.005	87	71	1.7	
2-H	5	555	−47	0.006	90	71	5.4	
2-H	5	555	−25	0.04	88	80	2.9	
2-D	5	555	−47	0.005	75	83	5.6	89
2-D	5	555	−25	0.04	79	82	5.9	*e*
4-H + T	5	550	−25	0.04	91 (4)	95 (29)	4.1 (1.9)	0[f]
2-H + T	700	425	+45	5.4	75	77	0.63	0[f]
2-D	700	425	+45	5.4	89	77	0.53	90
1-D + B	700	425	+45	5.4	75	93	0.74	87

[a] (Number of experiments) − (*tert*-butylarsine (H) or *tert*-butylarsine-d_2 (D)) + (toluene-d_8 (T)) or (glass beads (B)), i.e., 4-H + T means that four independent pyrolyses of *tert*-butylarsine were run in the presence of toluene-d_8. [b] Torr. [c] °C. [d] For those conditions for which four runs were made, the numbers in parentheses are the standard deviations of the means. For those conditions for which two runs were made, the average value is reported. [e] The resonances due to C_4H_{10} and C_4H_9D were not sufficiently resolved in this spectrum for meaningful integrations. [f] Deuterium incorporation was below detection limits of the method.

Control Reactions. Toluene, isobutane, and isobutene were individually subjected to the pyrolysis conditions (ca. 550 °C, 5 Torr) without change. Mixtures of AsD_3 and isobutene were also subjected to the same pyrolysis conditions without reaction or deuterium exchange with the hydrocarbon.

Results

Characterization of *tert*-Butylarsine-d_2. The preparation of *tert*-butylarsine-d_2 was accomplished by the reaction of $LiAlD_4$ with *tert*-butylarsine dichloride. It was convenient to use a high-boiling solvent, in this case di-*n*-butyl ether, to minimize the amount of solvent found as an impurity in the final product. Figure 2a is a ^1H NMR spectrum of *tert*-butylarsine-d_2 dissolved in C_6D_6. Only trace amounts of di-*n*-butyl ether remain, and the absence of any resonance at 2.65 ppm indicates a very high degree (>95%) of isotopic enrichment. Figure 2b shows the ^2H NMR spectrum of the same compound. As expected the only significant resonance observed (2.65 ppm) is due to the deuteriums bound to the arsenic. The gas-phase infrared spectrum of the deuterated material contained a ν_{As-D} band at 1512 cm^{-1}, which is shifted from 2088 cm^{-1} for the protio species.

Pyrolysis of *tert*-Butylarsine at 1 mTorr. The pyrolyses of *tert*-butylarsine and the *tert*-butylarsine-d_2 were studied under several different conditions, and these results will be separately described in the following sections. First, we will describe in detail the procedure adopted for collecting and analyzing the data using the low-pressure pyrolysis as an example. The *tert*-butylarsine was stored in a glass vessel equipped with a Teflon stopcock. Immediately before each experiment *tert*-butylarsine was freshly transferred under vacuum into a graduated test tube permanently attached to the line. The volume of liquid *tert*-butylarsine was adjusted to 0.1 mL by removal of any excess under vacuum. The liquid nitrogen bath was replaced by the slush bath after pressure, temperature, and flow conditions reached the values chosen for the experiment. The pressure in these pyrolysis experiments was measured with the capacitance manometer and was controlled by the vapor pressure of the *tert*-butylarsine and the inlet stopcocks. The time required for complete passage of all the precursor through the reactor was 120 min when the precursor temperature was maintained at −47 °C. The products of the pyrolysis were trapped quantitatively in a U-tube immersed in liquid nitrogen. After completion of the pyrolysis, this trap was sealed from the line and warmed to room temperature, which allowed the volatile products to be transferred under vacuum into the graduated test tube. The volume observed was similar to the volume of the starting material. These products were finally transferred under vacuum into a NMR tube that contained a known quantity of triphenylmethane, the internal standard. After distillation of a known quantity of C_6D_6 into the NMR tube, it was sealed and cut from the line with a torch.

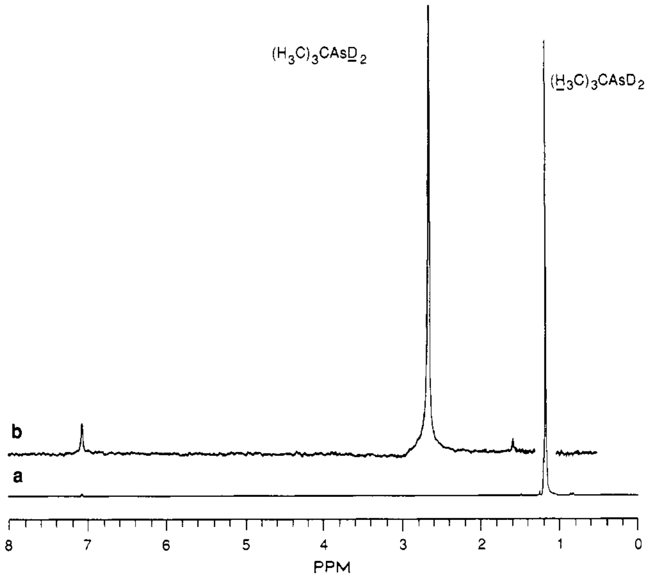

Figure 2. (a) ^1H NMR spectrum (in C_6D_6) of *tert*-butylarsine-d_2. (b) ^2H NMR spectrum (in C_6D_6) of *tert*-butylarsine-d_2. The peak at 1.57 ppm is due to Me_3CD formed during the sealing of the NMR tube, and the peak at 7.15 ppm is due to natural abundance deuterium in benzene.

Figure 3 shows the ^1H NMR spectrum that results from a typical pyrolysis at 1 mTorr. Every peak in the spectrum has been identified, and the assignment is shown in the figure. Independent calibration curves were prepared from known quantities of isobutane and isobutene, and the quantities reported in Table I obtain from these curves. The quantities reported for the remaining compounds were derived assuming a similar sensitivity for each hydrogen as found for those in isobutane and isobutene. The results show that the following compounds are present in pyrolysis mixture in order of decreasing abundance: isobutene, isobutane, *tert*-butylarsine, a small amount of arsine (AsH_3).[18] Also indicated in Figure 3 are the resonances due to di-*n*-butyl ether and traces of water. The intensity of the water resonance is consistent with a contamination level of the carrier gas of approximately 1 ppm. On the basis of the literature procedures[15,16] used to synthesize *tert*-butylarsine, which include an aqueous wash step,

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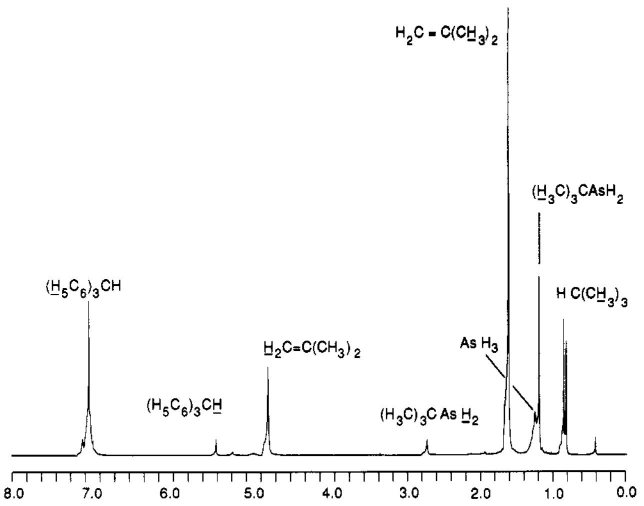

Figure 3. ^1H NMR spectrum (in C_6D_6) of the products of a pyrolysis conducted at 1 mTorr. The assignment of all the resonances are given. The peaks located at 0.45 and 4.95 ppm are due to H_2O. The barely observable triplet at 3.28 ppm is due to traces of di-*n*-butyl ether present in the precursor. The lower scale is offset by 0.1 ppm to the right.

tert-butylarsine does not react with water at room temperature. The mass balances listed in Table I are based on the total of the hydrocarbon resonances.

Effect of Total Pressure on the Pyrolysis. The pyrolysis of *tert*-butylarsine was also studied at 5 and 700 Torr (total pressure) by using N_2 as the carrier gas. Each experiment was conducted by passing a stream of nitrogen gas through the rotameter and over the tube containing the precursor. The partial pressure of the precursor was not independently measured but could be estimated on the basis of the time required to evaporate the known quantity of the precursor. The temperature of the precursor vessel was maintained such that the time required to volatilize 0.1 mL or precursor was approximately 20 min at 5 Torr and 50 min at 700 Torr. The flow rate of nitrogen was 150 sccm for the experiments conducted at 5 Torr, making the residence time in the reactor 0.14 s. For the experiments run at 700 Torr, the conductance of the pump had to be restricted. With the flow rate of 45–50 sccm, the residence time was 72 s. As indicated in Table I, isobutene was the predominant product for all reactions conducted at 5 Torr. At 700 Torr, however, the product distribution changed so that isobutane was favored by a factor of 2. To run the reactions at 700 Torr to similar percent conversion, the temperature of the reactor was lowered to 425–430 °C.

Effect of Increasing Surface Area. In an attempt to examine the effect of surface area on the product distribution, the glass reactor, which itself had a surface area within the furnace of 160 cm^2, was filled with 240 g of glass beads (3-mm diameter). This increased the surface area within the hot zone to nearly 2000 cm^2. In an experiment conducted at 700 Torr, there was no change in the observed product distribution (Table I).

Effect of Toluene-d_8 Addition. The nitrogen carrier gas could be spiked with toluene-d_8 by filling the bubbler shown in Figure 1 with toluene-d_8. The vapor pressure of the toluene was controlled by varying its temperature. The temperature of the toluene was chosen such that its rate of evaporation was 3–10 times greater than that of the *tert*-butylarsine. This assured that excess toluene was present throughout the entire pyrolysis. For the reactions conducted at 700 Torr the toluene was maintained at 45°C, while the toluene was cooled to −10 °C for the 5 Torr reactions. Using both ^1H and ^2H NMR spectroscopy, no evidence of deuterium abstraction from toluene-d_8 was observed.

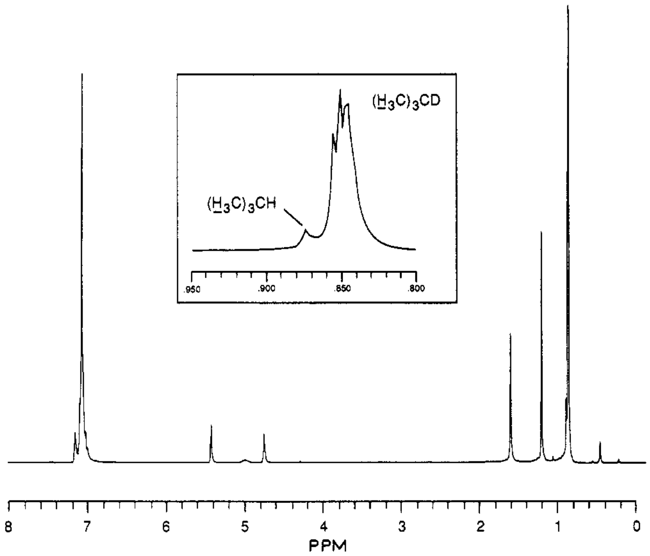

Figure 4. ^1H NMR spectrum (in C_6D_6) of products of the pyrolysis of *tert*-butylarsine-d_2 at 700 Torr. The inset illustrates the expanded methyl region of Me_3CD and Me_3CH.

Pyrolysis of *tert*-Butylarsine-d_2. Figure 4 shows the ^1H NMR spectrum of the products resulting from the pyrolysis of *tert*-butylarsine-d_2. Several points are important. First, the doublet (J_{H-H} = 6.58 Hz) due to the methyl groups of isobutane has collapsed to a triplet with a much smaller hydrogen–deuterium coupling constant (J_{H-D}) of 0.9 Hz. Because of the small but observable effect of deuterium on the chemical shift of the hydrogens, this triplet is now centered at 0.847 ppm (upfield by 0.008 ppm from the doublet in isobutane). An enlargement of this region of the spectrum (inset in Figure 4) shows a resonance at 0.87 ppm due to small amounts of Me_3CH. The integrated intensities show this amount to be due to 11% of the protio product.

The second noticeable feature is the absence of the peak due to AsH_3 normally located at 1.25 ppm. The third important observation is the presence of a small resonance located at 2.65 ppm, which is assigned to hydrogens of *tert*-butylarsine. This indicates that a small amount of H/D exchange involving the arsine deuteriums and, presumably, surface hydroxyl groups occurs during the reaction. The percent of H/D exchange (6%) could account for the small amount of Me_3CH observed in the reaction. That this number is less than the fraction of Me_3CH observed may be attributable to a kinetic isotope effect (i.e., for a k_H/k_D of only 2, Me_3CH would be twice as abundant as Me_3CD in the early stages of pyrolysis of Me_3CAsHD). On many of the samples, ^2H NMR spectra were also obtained, and, as shown in Figure 5, the predominant peak is due to Me_3CD. Smaller amounts of *tert*-butylarsine-d_2 and $AsD_{3-x}H_x$ are clearly observed. The resonance at 0.45 ppm is due to trace amounts of $H_{2-x}D_xO$. This results from surface H/D exchange of water that is initially adsorbed on the surface or is present in the carrier gas. Table I shows that the replacement of the hydrogens with deuteriums has no measurable effect on the extent or course of the reaction.

Discussion

The results obtained during the course of this research (1) show that Me_3CD is produced from the pyrolysis of *tert*-butylarsine-d_2, (2) prove that C_2Me_6 is not a product

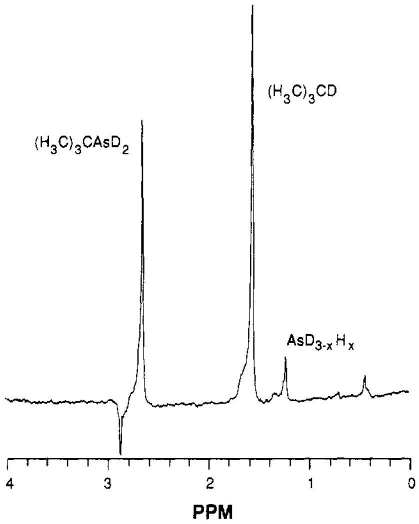

Figure 5. ^2H NMR spectrum (in C_6H_6) of products of the pyrolysis of *tert*-butylarsine-d_2 at 700 Torr. The negative peak at 2.87 ppm results from the foldover of the resonance due to C_6D_6.

of the reaction, and (3) verify the product distributions found in the earlier mass spectral studies both at low and high total pressures. To discuss the relevance of these observations to the reaction mechanism, we will begin by outlining the possible paths for the pyrolysis and summarize the results from earlier studies of the reaction. We will then discuss how our results allow us to rule out some of the possible routes to the products.

Summary of Possible Reaction Mechanisms. Schemes I–III highlight the most likely gas-phase mechanisms (i.e., not involving surface reactions) occurring in the pyrolysis of *tert*-butylarsine.

Scheme I. Nonradical Reactions

$$Me_3CAsH_2 \rightarrow Me_3CH + AsH \qquad (1)$$

$$Me_3CAsH_2 \rightarrow Me_2C{=}CH_2 + AsH_3 \qquad (2)$$

Scheme II. Radical (Nonchain) Reactions

$$Me_3CAsH_3 \rightleftharpoons Me_3C^\bullet + {}^\bullet AsH_2 \qquad (3)$$

$$2Me_3C^\bullet \rightarrow Me_2C{=}CH_2 + Me_3CH \qquad (4)$$

$$2Me_3C^\bullet \rightarrow Me_3CCMe_3 \qquad (5)$$

$$Me_3C^\bullet + {}^\bullet AsH_2 \rightarrow Me_3CH + AsH \qquad (6)$$

$$Me_3C^\bullet + {}^\bullet AsH_2 \rightarrow Me_2C{=}CH_2 + AsH_3 \qquad (7)$$

Scheme III. Radical Chain Reactions

Initiation

$$Me_3CAsH_2 \rightleftharpoons Me_3C^\bullet + {}^\bullet AsH_2 \qquad (8)$$

Propagation

$$Me_3C^\bullet + Me_3CAsH_2 \rightarrow Me_3CAsH^\bullet + Me_3CH \qquad (9)$$

$${}^\bullet AsH_2 + Me_3CAsH_2 \rightarrow Me_3CAsH^\bullet + AsH_3 \qquad (10)$$

$$Me_3CAsH^\bullet \rightarrow Me_3C^\bullet + AsH \qquad (11)$$

$$Me_3C^\bullet + Me_3CAsH_2 \rightarrow Me_2({}^\bullet CH_2)AsH_2 + Me_3CH \qquad (12)$$

$$Me_2({}^\bullet CH_2)AsH_2 \rightarrow Me_2C{=}CH_2 + {}^\bullet AsH_2 \qquad (13)$$

$${}^\bullet AsH_2 + Me_3CAsH_2 \rightarrow Me_2({}^\bullet CH_2)AsH_2 + AsH_3 \qquad (14)$$

Termination

see eqs 4–7 in Scheme II

Table II. Comparison of Conditions and Results with Previous Studies

pressure, Torr	temp, °C	C_4H_8/C_4H_{10}	ref
700	425	0.12	10
700	425	0.5	this work
20	502	3	7
5	555	4	this work

There have been two significant studies on the pyrolysis mechanism of *tert*-butylarsine. Both studies used mass spectrometry as the analytical probe. The results reported by Stringfellow and co-workers[10] were conducted in an atmospheric pressure flow tube reactor using D_2 as the carrier gas. Although both isobutene and isobutane were observed, *isobutane* was found to be the predominant organic product at all temperatures studied. No effect of the surface area of glass was found, and the data were fit to a model involving reactions 1 and 2 (Scheme I) occurring in the gas phase. Contrary to these results, Jensen and co-workers observed[7] that *isobutene* was the prominent organic product at temperatures greater than 300 °C. These experiments were studied in a reactor equipped with a molecular beam sampling procedure and run at low pressures (20–50 Torr) of H_2, D_2, or He as the carrier gas. Jensen and co-workers proposed that the pyrolysis of *tert*-butylarsine involved a free-radical process.

One of the important results of our studies is the verification using a single reactor that the total pressure of the pyrolysis affects the product distribution. As shown in Table II, the product distribution obtained at different pressures is in reasonable agreement with that found in both of the earlier studies. The explanation for this difference remains obscure, and quantitative kinetic studies at low pressures will be required before this issue can be effectively addressed.

Of some concern in the report by Jensen and co-workers was the lack of observation of the *tert*-butyl radical dimerization product, 2,2,3,3-tetramethylbutane. Because of the known fragmentation of $Me_3C{-}CMe_3$ in the mass spectrometer, it was impossible to determine whether or not any formed in the reaction. Under no conditions in any of our experiments was a singlet observed at 0.84 ppm, the location of the ^1H resonance of 2,2,3,3-tetramethylbutane in benzene. As described below, it would be stable and readily detected if it formed under the reaction conditions. We conclude, therefore, that $Me_3C{-}CMe_3$ is not a product of the pyrolysis of *tert*-butylarsine.

Pyrolysis of *tert*-Butylarsine-d_2. The goal of studying the pyrolysis of *tert*-butylarsine-d_2 was to differentiate among the different reactions for forming isobutane. If reaction 4 were operative, there would be no effect of changing the H to D on the arsenic. Reaction 1, however, would require that the methine position be substituted with deuterium, forming Me_3CD. Reaction 12, in analogy to reaction 4, would put only hydrogen in the methine position. The results show that 89% of the methine position is substituted with deuterium. The remaining 11% of the isobutane is substituted with hydrogen, some of which may be formed by pyrolysis of *tert*-butylarsine-d_1 and *tert*-butylarsine-d_0. These latter species are formed presumably by H/D exchange between *tert*-butylarsine-d_2 and the walls of the reactor. It is also possible that some portion of the hydrogen content in the methine position could be accounted for by a small amount of a different reaction mechanism than is proposed for the Me_3CD formation. The isotopic selectivity observed in these experiments unambiguously rules out any reaction (4 and 12) in which the *tert*-butyl radical abstracts a hydrogen from another *tert*-butyl group as being anything but a small

Table III. Results of Pyrolysis of Azoisobutane

expt[a]	pressure[b]	temp[c]	% C_4H_8	% C_4H_{10}	% C_8H_{18}	C_4H_8/C_4H_{10}	% C_4H_9D
1	50	550	52	26	22	2.0	
2 + T	50	550	43	35	23	1.3	0
1 + T	700	425	50	36	14	1.4	0
1	700	425	53	37	10	1.4	

[a] (Number of experiments) + (toluene-d_8 (T)) or (glass beads (B)), i.e., 2 + T means that two independent pyrolyses of azoisobutane were run in the presence of toluene-d_8. [b] Torr. [c] °C.

contributor to the overall reaction.

The fact that reactions 4 and 5, both of which are well-established reactions of *tert*-butyl radicals, contribute very little to the reaction rate greatly reduces the likelihood that the radical nonchain mechanism is a candidate for the reaction mechanism.

Attempted Radical Trapping with Toluene-d_8. In the radical chain mechanism shown in Scheme III, the only products that will be detected will result from the propagation stage (reactions 9–14) provided that the length of the chain reaction is long compared to the termination events. Reactions 9 and 10 involve the abstraction of one of the arsenic hydrogen atoms, whereas the radical attacks a C–H in reactions 12 and 14. The strength of the As–- bond (determined for AsH_3[19]) of 71 kcal/mol compared to the C–H bond of the methyl groups (98 kcal/mol[20]) make reaction 14 seem less probable than reaction 12. Recall that the deuterium labeling unambiguously ruled out reaction 12 as a part of the mechanism. Reactions 9–11 remain as viable routes to the products, but alone they cannot explain the formation of isobutene.

Because the hydrogen atom abstraction by the *tert*-butyl or AsH_2 radical did not involve another radical (reactions 9 and 10), we felt that it might be possible to intercept the *tert*-butyl radical with toluene. The benzylic C–H bond of toluene is weaker (85 kcal/mol[20]) and readily abstracted by the *tert*-butyl radical[21] (the methine C–H bond strength in isobutane is 92 kcal/mol[20]). For instance, in studies of the photolysis of toluene solutions of azoisobutane (an excellent source of *tert*-butyl radicals) the abstraction of the benzylic hydrogen led to products such as neopentylbenzene and bibenzyl as well as the primary products (isobutane, isobutene, and 2,2,3,3-tetramethylbutane) produced in the absence of toluene.[21] Price and Richards used this method in their studies of the gas phase pyrolysis of $AsMe_3$.[22] The experiment used to test this in the current studies involved pyrolysis of *tert*-butylarsine in the presence of a 3–10-fold mole excess of toluene-d_8. The production of only Me_3CD would be easily detected and would rule out the intramolecular route (reaction 1) to isobutane. The results clearly showed that no deuterium incorporation into isobutane (or anything else) was observed in this experiment.

Because of this negative result, it was necessary to conduct a control experiment to determine whether or not our conditions would allow detection of deuterium abstraction from toluene-d_8. Azoisobutane itself was pyrolyzed[23] under identical conditions in place of *tert*-butylarsine but in the presence of toluene-d_8. The results (Table III) were unambiguous and showed that no incorporation of deuterium into the isobutane was found. The conclusion is that under the conditions of our experiments the efficiency of toluene trapping is too low to detect. This is probably due to an insufficiently large ratio of toluene to *tert*-butylarsine in the reactor. In the studies on the pyrolysis of Me_3As, Price and Richards used[22] a 17–112-fold excess of toluene. This means that we cannot rule out reactions 9 and 10, and therefore the radical chain mechanism in Scheme III (modified by the elimination of reactions 12 and 13) remains a viable candidate for the reaction mechanism.

An important result of the pyrolysis of azoisobutane was the isolation of a large amount of 2,2,3,3-tetramethylbutane. This confirms that this product is indeed stable under the pyrolysis conditions and rules out reaction 5 of the radical nonchain mechanism (Scheme II).

Comparison to Known Reactions of Organoarsenic and Related Compounds. Are there any known reactions that can serve as models for the three remaining primary events (reactions 1, 2, and 8)? First, the pyrolysis of $AsMe_3$ at 491–585 °C proceeds by rate-determining homolysis of the Me_2As–Me bond to give $Me_2As^\bullet$ and $Me^\bullet$.[22] This is direct precedent for the first step in Scheme III (reaction 8).

Both reactions 1 and 2 are at least partially thermally forbidden events based on orbital symmetry arguments.[24,25] The high values of the activation energies observed[10] by Stringfellow and co-workers for the isobutane production (41.5 kcal/mol) and isobutene production (48.5 kcal/mol) would be consistent with the "allowedness" of these reactions.[10] For reaction 1, which is referred to as a reductive elimination, the arsenic is undergoing a reduction of oxidation state from +3 to +1. Reaction 15 is one example[26]

$$n(\mathrm{MeAsHI}) \rightarrow (\mathrm{MeAs})_n + n\mathrm{HI} \qquad (15)$$

of such a conversion. Arsenic(I) is an uncommon (but not unknown) oxidation state while arsenic(III) is the most common, a fact consistent with the lack of precedent for the reductive elimination reaction from the +3 oxidation state. Because very few of the previous studies in the organoarsenic literature were conducted in the temperature regime used in these pyrolyses,[27,28] the lack of precedent for this reductive elimination cannot be used as an insurmountable argument against reaction 1.

There is much more in the way of precedent for reaction 2, which yields isobutene and arsine. First, a clarification is in order. While the movement of atoms in this reaction involves a β-hydrogen elimination process, there is no reason to expect this to be facile (as it is with most metal alkyls). For such eliminations to be facile, as, for example, with triisobutylaluminum, an empty, energetically, low-lying orbital must be available on the metal to stabilize the transition state. The empty d-orbitals on arsenic are higher in energy, and while nothing prohibits their interaction, they would be relatively less effective at stabilizing

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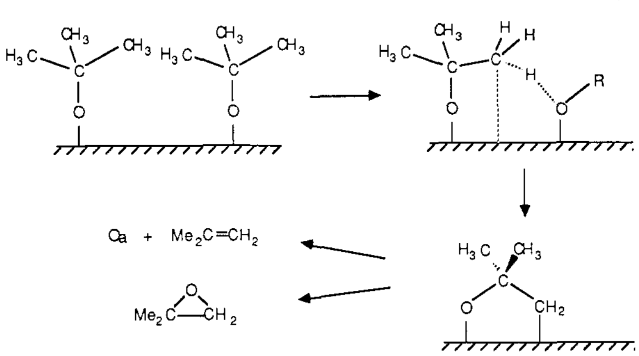
Scheme IV

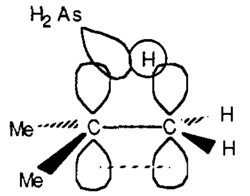


the transition state. As described below, it is still possible for such a reaction to occur, but it will have a much higher activation energy.

The gas-phase pyrolyses of several *tert*-butyl halides and pseudohalides have been studies (reaction 16).[24,29]

$$\mathrm{Me_2CX} \rightarrow \mathrm{Me_2{=}CH_2} + \mathrm{HX}\ (\mathrm{X} = \mathrm{Cl, Br, OH, SH}) \qquad (16)$$

Quantitative kinetic studies were completed using shock-tube methods in the temperature range 427–677 °C. For X = Cl and Br, the reactions occurred by a unimolecular process and had activation energies of 46.2 and 41.5 kcal/mol, respectively.[29] In the study by Stringfellow and co-workers, the value obtained for the isobutene-producing reaction was 48.5 kcal/mol, which is appropriately close to the values found for the halides to suspect it involves a similar mechanism. The diagram below illustrates the orbitals involved in the four-centered transition state proposed for these reactions:



One explanation for the observed pressure dependence involves producing isobutene in a surface-catalyzed reaction as well as by the homogeneous reaction. Although increasing the surface area did not alter the product distribution at 700 Torr, surface effects may still play a role at reduced pressures. Brainard and Madix recently described[30] a study of the mechanism of reaction of *tert*-butyl alcohol (Me_3COH) with a Ag(110) surface both with and without exposure to oxygen. The two main products of the reaction are isobutene and its corresponding epoxide, and the mechanism of their formation is shown in Scheme IV. While differences clearly exist between this system and *tert*-butylarsine, it does provide some precedent for the type of events that could take place. *tert*-Butylarsine could react at a Lewis acid site on the SiO_2. This could be followed by deprotonation of a β-hydrogen by an adjacent hydroxyl or oxo group. Because the arsenic analogue of isobutene oxide would be unstable, isobutene would be the only major product. The interaction of the arsenic atom with the surface would facilitate H/D exchange of the arsine hydrogens; a feature of the reactions that is observed.

In summary, we find some precedent for all of the primary events described in Schemes I–III as well as some less directly related precedent for a surface catalyzed reaction. While this gives the least amount of support for the reductive elimination reaction (reaction 1), none of possible mechanisms can be dismissed based on the literature precedent alone.

Nature of Arsenic Products. Last, some mention of the nature of the arsenic products is appropriate. Arsine (AsH_3), which was isolated as a product in the NMR experiments described here and observed in the earlier mass spectral studies, is the only hydride of arsenic stable at room temperature. Diarsine (As_2H_4) is a much more reactive species, which is reported to be somewhat stable in the gas phase but decomposes at temperatures above −100 °C when condensed.[31] It has been synthesized by passing AsH_3 through a silent electric discharge[31] and by the reaction of H atoms with AsH_3.[32] Arsinidene (AsH) is only known in the gas phase, where it can be formed by photolysis of AsH_3[33] or by the reaction of H atoms (from a microwave discharge) with AsH_3[32] or arsenic metal.[34] Upon condensation AsH would be expected to polymerize. Although discrete $(AsH)_n$ molecules have not be identified, several related organoarsinidene molecules such as cyclo-$(MeAs)_5$ are known, volatile, and fully structurally characterized compounds.[35] If the related oligomers of AsH formed, we would expect them to be unstable but perhaps volatile enough for transfer under vacuum. As the temperature of the $(AsH)_n$ is raised toward room temperature, hydrogen migration could lead to some AsH_3 and/or H_2.

In our reactor, the effluent of the furnace is directed into a liquid nitrogen cooled trap. The amount of arsenic metal that is deposited on the glass at the end of the hot zone depends on the conditions of the pyrolysis. In experiments conducted at 1 mTorr, inception of pyrolysis is noted by the deposition of a black solid (presumably elemental arsenic) at the outlet of the furnace. A white deposit in the portion of the U-tube trap cooled by liquid nitrogen left a nonvolatile residue when the volatile products were vacuum transferred into the measuring tube. Allowing the U-tube to reach room temperature prior to the transfer process caused this residue first to turn yellow, then brown, and ultimately black. If the vacuum transfer of the volatiles was begun prior to allowing the U-tube to warm to room temperature, these unstable materials could also be transferred to the measuring tube and ultimately to the NMR tube before decomposing. These samples precipitated a reddish solid before it was possible to obtain an NMR spectrum. This behavior is similar to the observations of Jolly and co-workers,[31] who characterized the solid formed from the decomposition of As_2H_4 as a subhydride of arsenic with an experimentally determined formula of $AsH_{0.52}$. It is noteworthy that in the reaction conducted at 700 Torr and in the presence of the glass beads, all of the unstable arsenic compounds were apparently converted to elemental arsenic, which deposited in a narrow region at the end of the furnace.

In summary, the pyrolysis of *tert*-butylarsine produces AsH_3 and at least one unstable lower hydride of arsenic.

Conclusions

The results of this research allow us to rule out the radical non-chain process (Scheme II) as the primary reaction mechanism for the pyrolysis of *tert*-butylarsine. Also eliminated from consideration are certain parts of a

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radical chain process that produce isobutene. This means that the mechanism for pyrolysis of *tert*-butylarsine must involve at least two independent reactions. The isobutane producing reaction could occur either by a reductive elimination step (reaction 1) or by a radical chain process. The reaction to form isobutene in the gas phase results from a concerted, four-centered β-hydrogen elimination. The total reactor pressure influences the pyrolysis route, but the reason for this is unknown. It is possible that isobutene could be formed in both homogeneous and heterogeneous steps, the latter of which would become increasingly important at lower pressures. Quantitative rates studies in the low-pressure regime are needed to clarify this point.

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Synthesis and Characterization of Alkaline-Earth Indium Sulfides

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In the course of studies of the AIn_2S_4 (A = Ca, Sr, Ba) system, a number of sulfides with metal stoichiometries near, but not necessarily equal to, 1:2 were encountered, including the new phases $Ca_{1.2}In_{1.9}S_4$ and $Sr_{0.9}In_{2.1}S_4$. Indexed X-ray powder diffraction patterns of $Ca_{3.3}In_{6.5}S_{13}$ ("$Ca_{1.0}In_{2.0}S_{4.0}$"), $Sr_{0.9}In_{2.1}S_4$, $SrIn_2S_4$, and $BaIn_2S_4$ are reported. All compounds have been grown as crystals from ACl_2–KCl (A = Ca, Sr, Ba) fluxes. $Ca_{3.3}In_{6.5}S_{13}$ ("$Ca_{1.0}In_{2.0}S_{4.0}$") forms in the monoclinic space group $C2/m$ with unit cell parameters $a = 37.628$ (4), $b = 3.8360$ (8), $c = 13.722$ (1) Å, and $\beta = 91.66$ (1)°. X-ray powder diffraction data indicate that this compound is isostructural with the previously reported phases $Ca_{3.1}In_{6.6}S_{13}$ ("$Ca_{1.0}In_{2.0}S_{4.0}$"), $Sn_{2.5}In_7S_{13}$ ("$Sn_{0.8}In_{2.2}S_{4.0}$"), and $Pb_3In_{6.67}S_{13}$ ("$Pb_{0.9}In_{2.1}S_{4.0}$"). These compounds, along with the known phases $Sn_{5.5}In_{11}S_{22}$ ("$Sn_{1.0}In_{2.0}S_{4.0}$"), $Sn_{3.5}In_9S_{17}$ ("$Sn_{0.8}In_{2.1}S_{4.0}$"), and $Pb_4In_9S_{17}$ ("$Pb_{0.9}In_{2.1}S_{4.0}$"), share structural features that consist of stepped "layers" of edge-sharing InS_6 octahedra interconnected by vertex-sharing with columns comprised of other InS_6 octahedra to form a three-dimensional structure. The divalent cations reside in bicapped trigonal prismatic sites in the channels formed by the In–S framework. Observed X-ray powder diffraction data for crystals of a new compound, $Ca_{1.2}In_{1.9}S_4$, are reported. Another newly prepared phase, $Sr_{0.9}In_{2.1}S_4$, forms with a C-centered monoclinic unit cell, $a = 27.66$ (1), $b = 3.943$ (2), $c = 12.683$ (7) Å, and $\beta = 94.25$ (4)°. The poor crystallinity of these phases has precluded single-crystal X-ray structure determinations. Indexed powder diffraction data are also given for the previously reported orthorhombic forms of $SrIn_2S_4$ and $BaIn_2S_4$. Although the empirical formulas are similar, the structures of these two latter compounds are unrelated to those of the other ternary indium sulfides mentioned above and feature tetrahedrally coordinated indium.

Introduction

Ceramic compounds that transmit in the long-wavelength infrared region are currently of interest. The variety of structures found in the literature for AIn_2S_4-related (A = Ca, Sr, Ba) compounds suggests that these systems may comprise a fruitful area to search for new compounds. Our investigation of these ternary indium sulfide systems was undertaken to identify new compounds for possible applications as optical ceramics and to confirm reported structures and structural interrelationships.

Previously reported ternary alkaline-earth indium sulfides are $CaIn_2S_4$ (two forms), $Ca_{3.1}In_{6.6}S_{13}$, $SrIn_2S_4$, and $BaIn_2S_4$. Our interest in these systems was piqued by the report that $CaIn_2S_4$, synthesized from CaS and In_2S_3 in an evacuated silica ampule, has the normal spinel structure ($a = 10.77$ Å).[1] This report is surprising, since the large Ca^{2+} ion would occupy a tetrahedral site in a normal spinel. It is possible that the reported X-ray powder diffraction data correspond to β-In_2S_3, which has a spinellike structure.[2] Another report of a compound with the stoichiometry $CaIn_2S_4$, synthesized from the corresponding ternary oxide under H_2S, gives a cubic unit cell ($a = 10.63$ Å) and an X-ray powder diffraction pattern different from that of spinel.[3] A compound with a similar formula, $Ca_{3.1}In_{6.6}S_{13}$,[4] has been synthesized as yellow whiskers by iodine transport of a mixture of CaS and In_2S_3. An X-ray single-crystal structure determination[5] found the indium octahedrally coordinated and the calcium in bicapped trigonal prismatic coordination in a monoclinic unit cell (space group $C2/m$: $a = 37.63$ (1), $b = 3.8358$ (9), $c = 13.713$ (3) Å, $\beta = 91.65$ (1)°; $Z = 4$).

$SrIn_2S_4$ and $BaIn_2S_4$ were first reported in 1974.[6] These compounds were prepared from the elements by iodine transport and found to be isostructural to each other by X-ray powder diffraction. The powder patterns were in-

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