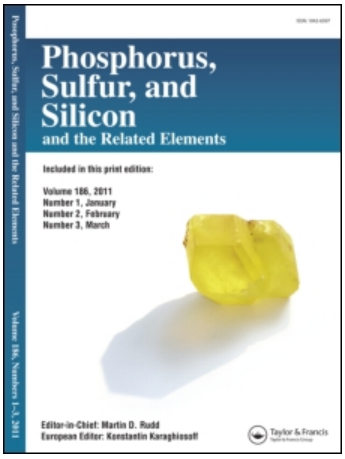

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TERT-BUTYL ARSOLANE AND ARSENANE: SYNTHESIS AND MASS SPECTROMETRY

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TERT-BUTYL ARSOLANE AND ARSENANE: SYNTHESIS AND MASS SPECTROMETRY

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The reaction of $^tBuAsCl_2$ with $BrMg(CH_2)_nMgBr$ ($n = 4, 5$) in ether at 0°C yields *cyclo*-$(CH_2)_nAs^tBu$, with *cyclo*-$(CH_2)_nAsBr$ and *cyclo*-$(CH_2)_nAsCl$ as minor constituents. Reaction of the *tert*-butyl substituted compounds with Cl_2 in CCl_4 gives the dichlorides, *cyclo*-$(CH_2)_nAs(Cl_2)(^tBu)$. Upon mild heating, the dichloride for $n = 5$ loses ^tBuCl to give the monochloride, while the dichloride for $n = 4$ is inert to thermolysis. Mass spectral data for the As(III) compounds is used to speculate on their suitability as GaAs MOCVD precursors.

Key words: Arsenic; arsenane; arsolane; organoarsenic.

INTRODUCTION

It has been commonly assumed that in order to limit the undesirable incorporation of carbon in semiconductor films grown by metal organic chemical vapor desposition (MOCVD), metal organic precursors should contain a minimum of organic substituents. Thus AsH_3 has been widely used as an arsenic source for the growth of gallium arsenide.[1] The high toxicity of AsH_3 makes storage and handling difficult.[2] There has been, therefore, much interest in finding an alternative, in particular an organoarsenic compound with controllable decomposition pathways.[3] With this objective in mind we have investigated the synthesis and mass spectra of *tert*-butyl arsolane and arsenane.

RESULTS AND DISCUSSION

The reaction of $BrMg(CH_2)_nMgBr$ ($n = 4, 5$) and $^tBuAsCl_2$ yields *cyclo*-$(CH_2)_nAs^tBu$ [$n = 4$ (**1**), $n = 5$ (**2**)] as the major products (Equation 1). The GC-MS of the crude reaction mixture shows, however, that the halides, *cyclo*-$(CH_2)_nAsX$ [$n = 4$; $x = Cl$ (**3**), Br (**4**); $n = 5$; $x = Cl$(**5**), Br (**6**)], exist as *ca.* 10% of the arsenic containing products.

$$^tBuAsCl_2 + BrMg(CH_2)_nMgBr \xrightarrow[0°C]{\text{ether}} \textit{cyclo}\text{-}(CH_2)_nAs^tBu + 2MgBrCl \quad (1)$$

Compounds **3** and **5** have been previously reported.[4] The direct reaction of the appropriate digrignard reagent with $AsCl_3$ produces **3** and **5** in low yields. Separation of the present mixtures can be effected by careful fractional vacuum

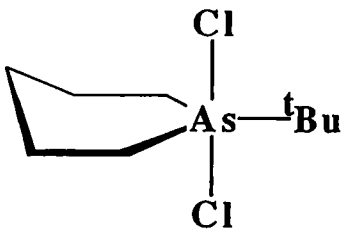
distillation through a 12" Vigreaux column, slight decomposition of the higher-boiling components does occur due to thermolysis.

Reaction of **1** and **2** with Cl_2 in CCl_4 at 0° results in the formation of the hydrocarbon-soluble dichlorides *cyclo*-$(CH_2)_nAs(Cl)_2(^tBu)$ [$n = 4$ (**7**), 5 (**8**)] (Equation 2). When **8** is subjected to mild heat (*ca.* 40°) under a dynamic vacuum, *tert*-butylchloride is eliminated with **5** as the arsenic-containing product (Equation 3). In contrast, **7** withstands thermolysis at 100°C, for 2 days with no decomposition observable by ^1H NMR.

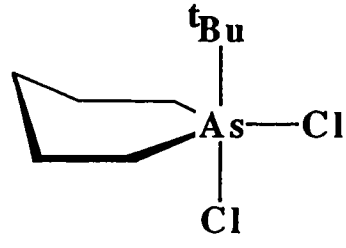
$$cyclo\text{-}(CH_2)_nAs^tBu + Cl_2 \rightarrow cyclo\text{-}(CH_2)_nAs(Cl)_2(^tBu) \quad (2)$$

$$cyclo\text{-}(CH_2)_5As(Cl)_2(^tBu) \rightarrow cyclo\text{-}(CH_2)_5AsCl + {}^tBuCl \quad (3)$$

Reductive elimination of an alkyl halide from As(V) chloroalkyls is well-known,[5] thus the difference in reactivity between **7** and **8** is rather extraordinary. The majority of alkyl halide reductive eliminations from group 15 elements occur at temperatures above 100°, it is an apparent anomaly that the decomposition of **8** occurs at *ca.* 40°.[5] The structures of the dihalo adducts of arsenanes have been proposed to exist in the flattened chair form, with the mutually *trans*-halides occupying the axial sites of the trigonal bipyramidal arsenic center (I).[5]



I



II

In this conformation, the steric bulk of the alkyl group would be expected to have minimal effect on the elimination of alkylhalide. If the chlorides are *cis*, considerable steric repulsion between the *tert*-butyl group and the γ-methylene of the ring, in the *syn* conformation (II), would provide a steric assist to *tert*-butylchloride reductive elimination. No such assistance would of course be present for the arsolane **1**. We have been unable to obtain any spectral data to support/oppose this postulate due to the instability of **8**.

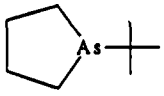
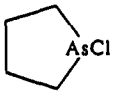
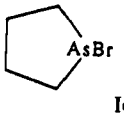
Mass Spectrometric Data

Electron impact (EI) mass spectrometry has previously been employed as a method of assessing the suitability of compounds as MOCVD precursors.[6] The mass spectra of **1–6** are given in Tables I and II.

The compounds **1–6** all display molecular ions in their EI mass spectra. In addition, both **1** and **2** show loss of isobutylene, as expected considering the presence of the *tert*-butyl groups in both of the parent compounds. Loss of ethylene and propylene is observed in **1–6**, these fragments undoubtedly arising from the organic portion of the heterocyclic rings, providing further evidence for

TABLE I

m/e fragments of arsolanes (**1**, **3**, **4**), obtained with EI-source at 70 eV energy

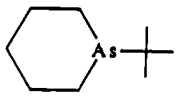
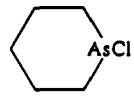
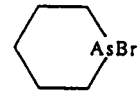
					
m/e	Ion	*m/e*	Ion	*m/e*	Ion
188	$C_4H_8As^tBu^+$	166	$C_4H_8AsCl^+$	210/212	$C_4H_8AsBr^+$
132	$C_4H_8AsH^+$	138	$C_2H_4AsCl^+$	182/184	$C_2H_4AsBr^+$
131	$C_4H_8As^+$	110	$AsCl^+$	154/156	$AsBr^+$
103	$C_2H_4As^+$	89	$AsCH2^+$	131	$C_4H_8As^+$
101	$C_2H_2As^+$	75	As^+	130	$C_4H_7As^+$
89	$AsCH_2^+$			103	$C_2H_4As^+$
57	$C_4H_9^+$			102	$C_2H_3As^+$
55	$C_4H_7^+$			101	$C_2H_2As^+$
				89	$AsCH_2^+$
				75	As

controlled decomposition. Surprisingly, **1** and **2** show negligible amounts of As^+ in their mass spectra. The presence of this fragment is desirable in view of the proposal that As, As_2 and As_4 are the major species present at the growth surface of GaAs by MOCVD.[7] The halides **3–6**, however, do give appreciable abundances of As^+ ions. This is not surprising since CVD of GaAs was originally carried out using the arsenic trihalides as arsenic sources.

An ion observed in the fragmentation patterns of **1–4** and **6** has the *m/e* ratio of 89, corresponding to $AsCH_2^+$. A common undesirable contaminant in GaAs thin films deposited by MOCVD using arsenic alkyls is carbon,[3] which acts as a residual electron acceptor and thus degrades the electronic properties of the material. Observation of this fragment ion may provide a clue as to the mechanism of carbon incorporation into growing thin films and consequently guide future systematic studies on this problem.

TABLE II

m/e fragments of arsenanes (**2**, **5**, **6**), obtained with EI-source at 70 eV energy

					
m/e	Ion	*m/e*	Ion	*m/e*	Ion
202	$C_5H_{10}As^tBu^+$	180	$C_5H_{10}AsCl^+$	224/226	$C_5H_{10}AsBr^+$
146	$C_5H_{10}AsH^+$	138	$C_2H_4AsCl^+$	196/198	$C_3H_6AsBr^+$
118	$C_3H_6AsH^+$	110	$AsCl^+$	182/184	$C_2H_4AsBr^+$
117	$C_3H_6As^+$	75	As^+	168/170	CH_2AsBr^+
101	$C_2H_2As^+$			155/170	$HAsBr^+$
89	$AsCH_2^+$			154/156	$AsBr^+$
69	$C_5H_9^+$			145	$C_5H_{10}As^+$
57	$C_4H_9^+$			117	$C_3H_6As^+$
55	$C_4H_7^+$			103	$C_2H_4As^+$
				101	$C_2H_2As^+$
				89	$AsCH_2^+$
				75	As^+

EXPERIMENTAL

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. Digrignard reagents[8] and $^tBuAsCl_2$[9] were synthesized by the literature methods. Solvents were distilled and degassed prior to use. Mass Spectrometry (EI, 70 eV) was carried out on a Kratos MS-50 Mass Spectrometer. GC-MS was performed on a Hewlett–Packard 5992A using an 8 mm × 6 ft stainless steel column packed with SE30 absorbed on Chromosorb P. Injection port temperatures were 298° for both mixtures, oven temperatures were 150° and 120° for the tetra- and pentamethylene mixtures respectively. Proton NMR spectra [δ in ppm relative to $SiMe_4$ (external)] were obtained on a Bruker AM-250 instrument. Infrared spectra (cm^{-1}) were obtained from neat films between CsI plates on a Perkin–Elmer 598 spectrometer.

$BrMg(CH_2)_4MgBr + {}^tBuAsCl_2$. A 500 ml round-bottom Schlenk flask equipped with a stirbar was charged with the di-grignard product and solvent resulting from the reaction of 7.0 ml (58.5 mmol) of 1,4-dibromobutane with excess magnesium in 100 ml ether. A dropping funnel was then placed on the flask, and charged with 19.9 ml of a 2.93 M solution of $^tBuAsCl_2$ in ether. The flask was wrapped in aluminum foil and cooled to 0°, and the funnel contents added dropwise over 1 hr with stirring. A copious white precipitate formed in the flask. The reaction mixture was allowed to stir overnight and warm to room temperature. Pentane (70 ml) was added to the flask, and the contents were stirred for 1 h, then filtered yielding a pale yellow liquid. The solvent was removed from the filtrate by atmospheric pressure distillation under N_2, then the resulting liquid residue was vacuum transferred through a short-path apparatus using an oil bath temperature of 100°, receiver temperature of −78°, and a static vacuum of *ca.* 10^{-2} torr. This yielded a mixture of **1**, **3** and **5** (determined by GC-MS), from which pure **1** was obtained as a colorless liquid by vacuum distillation (b.p. 57°C, 3 torr). Yield: 50–60%.

$BrMg(CH_2)_5MgBr + {}^tBuAsCl_2$. The reaction was carried out as above using the di-Grignard product resulting from the reaction of 7.4 ml (54.4 mmol) of 1,5-dibromopentane with excess magnesium and 18.56 ml of a 2.935 M solution of Bu^tAsCl_2 in ether. Yield: 65–70%.

Characterization Data

Cyclo-*$(CH_2)_4As^tBu$* (**1**). ^{1}H NMR: 1.36–1.64 (m, 8H, CH_2), 0.99 [s, 9H, $C(CH_3)_3$]. IR: 2950 vs sh, 2920 vs br, 2860 vs, 2820 s sh, 1460 vs br, 1917 s, 1360 vs, 1304 m, 1249 m, 1241 m sh, 1169 s, 1090 s, 1030 m, 1010 m, 950 m, 932 m sh, 860 w, 793 s, 740 m, 591 m, 566 s, 472 s, 354 m.

Cyclo-*$(CH_2)_5As^tBu$* (**2**). ^{1}H NMR: 1.18 (m, 2H, γ-CH_2), 1.66 (m, 4H, β-CH_2), 3.27 (t^1, $^1J_{H-H} = 6.8$ Hz, α-CH_2, 4H), 0.93 [s, 9H, $C(CH_3)_3$]. IR: 2980 m sh, 2910 vs, 2850 vs, 2280 m vbr, 1460 m sh, 1440 s, 1398 s, 1275 s, 1180 w, 1115 w, 1015 m, 920 s, 860 s sh, 745 vs br, 712 vs br, 640 s, 540 m, 475 w, 355 vs, 325 m sh, 230 m sh, 210 s.

Cyclo-*$(CH_2)_4As(Cl)(^tBu)$* (**7**). ^{1}H NMR: 2.69 (t, $J_{H-H} = 6.2$ Hz, 4H, CH_2), 1.53 (m, 4H, CH_2), 1.21 [s, 9H, $C(CH_3)_3$] IR: 2955 vs sh, 2930 vs, 2860 s, 1460 m sh, 1450 s br, 1431 s, 1402 m, 1330 m, 1269 s, 1220 s, 1051 m, 1018 m, 951 m, 778 m, 751 s, 723 s, 706 s, 699 s, 560 s, 385 vs sh, 363 vs, 266 s, 245 m.

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