

Electrophilic Chemistry of the Cubic Arsaalkyne Tetramer (AsCtBu_4): Arsonium Ions of Ethylation (EtOTf), Benzylation (PhCH_2OTf), and Mono- and Diprotonation ($\text{FSO}_3\text{H}/\text{SO}_2$)

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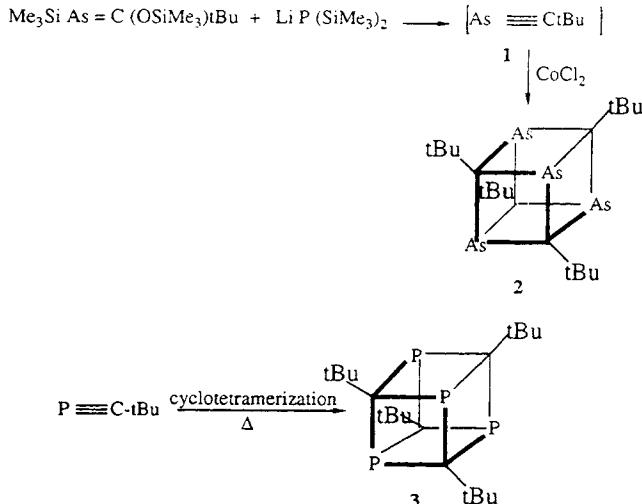
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ABSTRACT

The cubic arsaalkyne tetramer **2** reacts at room temperature with ethyl triflate to give the As-ethylated arsonium salt **4**. A similar reaction of **2** with benzyl triflate (generated *in situ* via $\text{PhCH}_2\text{Cl}/\text{AgOTf}$) gives the As-benzylated salt **5**. Low-temperature protonation of **2** with $\text{FSO}_3\text{H}/\text{SO}_2$ produces a mixture of arsonium ions **6** and **7** resulting from mono- and diprotonation. The NMR characteristics of the resulting arsonium ions are discussed and compared with those of the corresponding phosphonium ions derived from the tetraphosphacubane **3**. The FAB mass spectrum of **4** and its decomposition products (FAB-CAD-MS/MS) are also discussed.



SCHEME 1 Syntheses of $(\text{AsCtBu})_4$ **2** and $(\text{PCtBu})_4$ **3**.

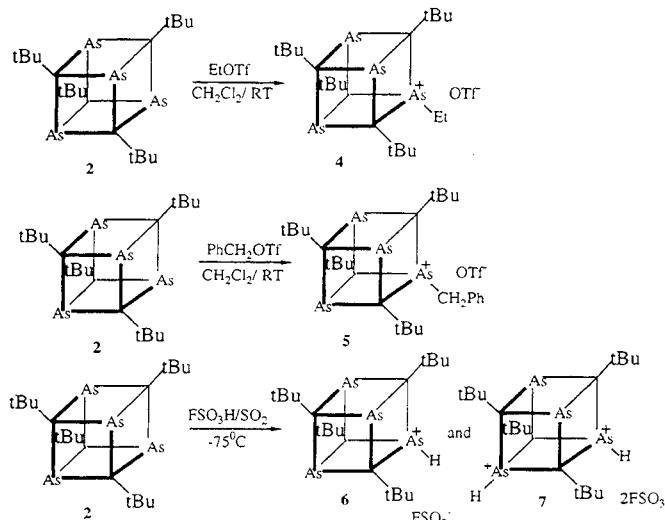
INTRODUCTION

The synthesis of the arsaalkyne tetramer **2** was recently reported by Nixon et al. [1] via a CoCl_2 -mediated cyclotetramerization of an *in situ* formed arsaalkyne¹, according to Scheme 1.

Compound **2** is the arsenic analogue of Regitz's tetraphosphacubane **3** [2,3], whose electrophilic chemistry we have been investigating [4,5].

The highly shielded nature of the cage-C carbons in **2** (observed at $\delta = -46.5$) in the ^{13}C NMR spectrum [1] suggests a polarized C-As bond, indicating that its bonding state could be analogous

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SCHEME 2 Arsonium ions of ethylation, benzylation, and protonation of **2**.

to that of **3**, where the $np \rightarrow \sigma$ PC delocalization is responsible for the observed cage carbon shielding ($\delta = -29.1$) and phosphorus deshielding ($\delta + 257.4$) [2,4]. Because the quadrupolar properties of the arsenic nucleus [6] usually prevent the observation of tervalent arsananes by ^{75}As NMR spectroscopy, corroboratory evidence to support a highly deshielded arsenic environment in **2** has not been obtained. Tetraalkyl (aryl) arsionium salts, on the other hand, were shown by Balimann and Pregosin [7] to be amenable to ^{75}As NMR studies, and we had hoped that the arsionium centers in the derived cations of **2** might be detectable (see the Discussion Section).

The cubic arsaalkyne tetramer **2** has recently been studied by photoelectron spectroscopy and theory by Nixon and associates [8a], and more recently [8b], Nixon and associates have fully structurally characterized the arsaalkyne $\text{As} \equiv \text{CC}_6\text{H}_2(\text{tBu})_3$ and its zerovalent platinum complex $[\text{Pt}(\text{PPh}_3)_2(\eta^2-\text{As} \equiv \text{CC}_6\text{H}_2-(\text{tBu})_3)]$.

RESULTS AND DISCUSSION

Compound **2** reacts smoothly with EtOTf at room temperature to give the ethylated arsionium salt **4** in ca. 60% yield after 6 hours stirring of the solution at room temperature (Scheme 2). Characteristic ^{13}C and ^1H NMR spectral data for **4** are gathered in Chart 1 and compared with those of the P-ethylated tetra-*tert*-butyltetraphosphacubane **8**.

The $\text{tBu}(\text{Me})$ groups give rise to two resonances in a 3:1 ratio at δ 24.8 and 21.0, and the $\text{tBu}(\text{C})$ resonances are seen at 33.3 and 27.0 (also 3:1). The three equivalent cage carbons (C_1) give rise to a slightly broad singlet at δ 10.1, corresponding to 36.4 ppm deshielding relative to the

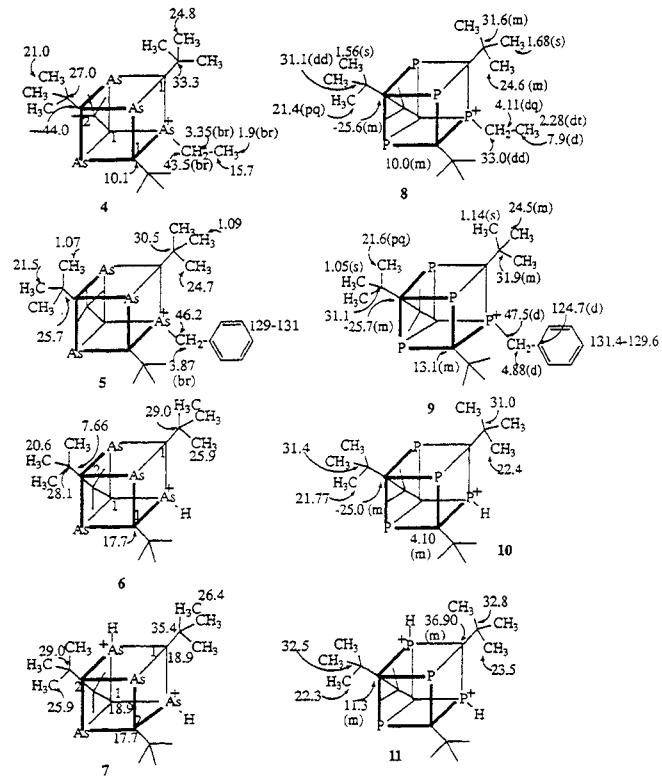
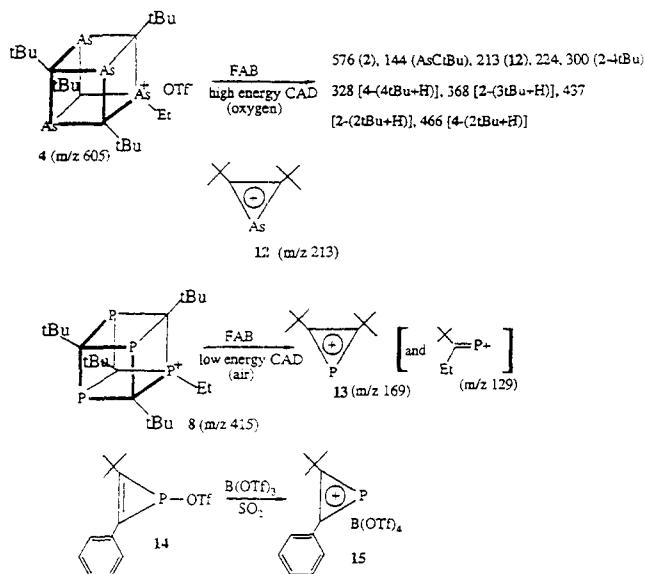


CHART 1 ^{13}C and ^1H NMR data for the arsionium ions derived from **2** and comparison with the corresponding phosphonium cations derived from **3**. The NMR data for the phosphonium ions are taken from Refs. [4] and [5].

cage carbon in precursor **2**. The ethyl group shows no resolved coupling to arsenic, the resonances being just slightly broadened. We note that both of the ethyl carbons in the arsionium ion are more deshielded and the ethyl protons more shielded as compared to those of the phosphonium analogue (see Chart 1). The ethyl protons deshielding order observed for **4** and **8** is opposite to those found for $\text{Et}_4\text{As}^+ \text{I}^-$ and $\text{Et}_4\text{P}^+ \text{I}^-$ in CHCl_3 [9].

In an attempt to directly observe the cation center, the ^{75}As NMR spectrum of **5** was examined. Under the instrument conditions, where $\text{Ph}_4\text{As}^+ \text{Cl}^-$ (solvent: $\text{HCl}/\text{H}_2\text{O}/\text{D}_2\text{O}$) and $\text{AsF}_6^- \text{K}^+$ (As-NMR standard; D_2O solvent) could be detected, no resonances could be seen for **4**.

Corroboratory evidence for the formation of **4** was obtained by a FAB mass spectrum using sulfolane as matrix, the compound exhibiting an intense m/z 605 peak for the arsionium cation. In a CAD MS/MS experiment, the decomposition of the m/z 605 ion was examined. Apart from a peak at m/z 576 (**2** $^+$), the major fragment ions formed were m/z 144 (tBuCAs), 213, 224, 300 (loss of 4tBu from **2**), 144 and 300, 328, 368, and 437 and 436 (Scheme 3). The ions having m/z 144 and 300 were previously found in the normal EI mass spectrum of **2** [1]. Ions at m/z 224, 368, and 437 represent an ad-



SCHEME 3 Fragmentation of cation **4** (m/z 605) by FAB-CAD-MS/MS and comparison with the decomposition of **8** (m/z 415); direct generation of **15** in solution.

ditional proton loss from 225, 369, and 438 fragments observed in the EI-MS of **2**. For the m/z 213 ion, we suggest structure **12**, the arsenic analogue of the phosphirenium cation **13** (m/z 169), previously observed as a predominant decomposition product of various phosphonium ions of **3** (like **8**) [10]. The phosphirenium cation **15** has been generated in solution from **14** according to Scheme 3 [11], and very recently, it has been structurally characterized as the nickel complex $[\text{Ni}(\eta^3\text{-PC}_2\text{tBu}_2)(\eta^5\text{-P}_3\text{C}_2\text{tBu}_2)\text{W}(\text{CO})_5]$ [13]. Collisional decomposition of m/z 213 ion gave tBu^+ and several major products via loss of C_3H_6 , C_4H_8 , and MeAsH .

Compound **2** reacts quickly with benzyl triflate (generated *in situ* from benzyl chloride and AgOTf) to give **5** (Scheme 2). Rapid precipitation of AgCl is accompanied by development of a red color. The ^{13}C NMR spectrum of **5** (Chart 1) shows two tBu groups in a 3:1 ratio and a benzylic methylene resonance at δ 46.2 showing no visible coupling to arsenic. Surprisingly, the cage carbons could not be detected in this case. In the ^1H NMR spectrum, the benzylic CH_2 resonance appears at δ 3.87 and is somewhat broad. The methylene protons in **5** are noticeably shielded compared to those in **9**.

Addition of a cold solution of $\text{FSO}_3\text{H}/\text{SO}_2$ to **2** in SO_2 (Dry Ice/acetone temperature) initially gave a light green solution, which rapidly changed to a persistent yellow. The ^{13}C NMR spectrum shows that a mixture of mono- and diprotonated arsonium cations **10** and **11** are formed (Scheme 2), for which the cage- C_1 resonance in **10** and the cage- C_2 resonance in **11** must be coincident (Chart 1). The observed dramatic downfield shifts of the cage carbons relative to those for **2** is noteworthy, and this

behavior is analogous to that observed for phosphonium ions formed from **3** [4]. The ^1H NMR spectrum exhibited four singlets between δ 0.83–0.97. As in *P*-protonated **3**, the $\text{As}-\text{H}^+$ resonance was not detectable as an independent signal. Prolonged cold storage of the sample did not lead to noticeable decomposition; slight changes that occurred in the relative signal intensities corroborated the assignments made.

In an attempt to effect exclusive diprotonation, protonation of **2** with $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (1:1) “magic acid^R”/ SO_2 was tried. A dark sample was obtained, whose ^{13}C NMR spectrum exhibited very broad poorly resolved tBu resonances, suggesting oxidation and formation of a paramagnetic arsenic radical cation.

In summary, we have produced the first examples of arsonium ions formed by alkylation, benzylation, and/or protonation of the arsenic cubic tetramer **2**. Although the arsenic cation center itself has not proved to be amenable to NMR study, the ^{13}C chemical shift trends for the cage carbons upon formation of the arsonium cation show dramatic downfield changes analogous to those observed in the phosphonium ions derived from **3**. It appears that the $\text{As}-\text{C}$ and $\text{P}-\text{C}$ bonding states in **2** and **3** are quite similar, and so are the changes that occur when these $\lambda^3\sigma^3$ molecules are transformed into $\lambda^4\sigma^4$ cations. The notion that the arsenic analogue of the phosphirenium cation **13**, which is formed in the gas phase by collisional decomposition of arsonium ions derived from **2**, could exist independently and issues pertaining to charge delocalization and aromatically in that species will be addressed in a future study.

EXPERIMENTAL

Compound **2** was synthesized as previously described [1]. EtOTf (Aldrich, Milwaukee, WI) was distilled under argon prior to use. AgOTf and benzyl chloride (both from Aldrich) were used as received. FSO_3H (Allied) and SbF_5 (Fluorochem) were distilled. SO_2 (anhydrous; Linde) was used without further purification. “Magic acid” was prepared as described previously [4,12]. NMR spectra were recorded on a GE GN-300 instrument. Detailed procedures for low-temperature NMR work have been published elsewhere [12]. Mass spectra were recorded on a VG Autospec trisector EBE instrument at the University of Akron.

The ambient temperature reactions were carried out on a ca. 35 mg scale in a Schlenk tube. For the ethylation reaction, CDCl_3 or CD_2Cl_2 was used as solvent for direct NMR studies. The reaction mixture, after 6 hours of stirring at room temperature, consisted of a yellow solution and a white solid. The white solid (in liquid SO_2 solvent) showed no NMR resonances and was not further investi-

gated. The reported NMR data are for the yellow liquid supernatant.

In the benzylation reaction, anhydrous CH_2Cl_2 was used as solvent. To a solution of the substrate was added AgOTf (1 equiv) in the dark under argon with stirring, followed by benzyl chloride (ca. 1.1 equiv). The Schlenk tube was sealed and the reaction was allowed to continue in the dark. Rapid precipitation of AgCl was noted and the color of the solution turned red. After 48 hours, the liquid phase was carefully removed with a pipet and the solvent evaporated under vacuum. The residue was redissolved in CDCl_3 to give a red-brown solution. NMR studies indicated that, apart from the desired **4**, some unreacted **2** and benzyl chloride had remained. These were removed by precipitating salt **4** from hexane.

Low-temperature protonation studies were carried out on a ca. 25 mg scale using our previously described methods [5,12].

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