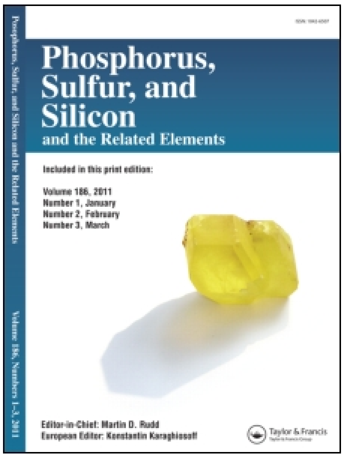

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ISOLATION AND CHARACTERIZATION OF THE ARSORANE $(Me_3SiCH_2)_3AsCl_2$

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Reaction of Me_3SiCH_2MgCl with $AsCl_3$ (1:1 mole ratio) afforded a brown solid and a liquid consisting of $(Me_3SiCH_2)_2AsCl$ and an unidentified substance. Reduction of the liquid with $LiAlH_4$ gave $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_3As$. Reaction of $(Me_3SiCH_2)_3As$ with $AsCl_3$ produced the crystalline arsorane $(Me_3SiCH_2)_3AsCl_2$ which was characterized by partial elemental analysis (C, H, and Cl), NMR spectroscopy (^1H and $^{13}C\{^1H\}$), and mass spectrometry (electron impact).

Key words: Organoarsenic; arsorane; synthesis; NMR; mass spectrometry; redox.

INTRODUCTION

Our research involving the preparation of gallium-arsenic compounds has required a variety of specific new organoarsenic starting materials, including primary and secondary arsines; thus, certain synthetic procedures have had to be developed in our laboratories to meet these needs.[1] Of course, all of the attempts to synthesize desired materials were not productive and, at times, side reactions were significant. For example, reduction of $(Me_3SiCH_2)_2AsCl$ with Zn amalgam in refluxing MeOH resulted in an extremely poor yield of $(Me_3SiCH_2)_2AsH$, but gave $(Me_3SiCH_2)_2AsAs(CH_2SiMe_3)_2$ in a 60% yield.[1a] On the other hand, reduction of the same chloride with a Zn/Cu amalgam in an $HCl_{(aq)}$/THF solution at room temperature afforded the secondary arsine in 86% yield.[1b]

In the case of $Me_3SiCH_2AsH_2$, our success in designing a satisfactory overall scheme for its preparation (in 47% yield)[1c] was not possible without trying other much less rewarding procedures. For example, reaction of Me_3SiCH_2MgCl with As_2O_3 (2:1 mole ratio) in ether, followed by reduction with Zn/Cu amalgam, produced $Me_3SiCH_2AsH_2$ in only 4% yield and $(Me_3SiCH_2)_2AsH$ in 60% yield.[2] Here we report a scheme which failed to give any of the primary arsine, but rather gave results which prompted a follow-up experiment; *viz.*, reaction of $(Me_3SiCH_2)_3As$ with $AsCl_3$, with one product being the new arsorane $(Me_3SiCH_2)_3AsCl_2$.

RESULTS AND DISCUSSION

Combining Me_3SiCH_2MgCl with $AsCl_3$ (1:1 mole ratio) in an ether/pentane mixture at −78°C, followed by warming to room temperature, afforded a brown solid (presumably elemental As) and a yellow liquid. Based on its ^1H NMR spectrum, the liquid appeared to consist only of $(Me_3SiCH_2)_2AsCl$ and an unidentified compound(X) (Equation 1); reduction with $LiAlH_4$ gave $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_3As$ (Equation 2).

$$Me_3SiCH_2MgCl + AsCl_3 \longrightarrow (Me_3SiCH_2)_2AsCl + X + \text{brown solid} \quad (1)$$

$$(Me_3SiCH_2)_2AsCl + X \xrightarrow{LiAlH_4} (Me_3SiCH_2)_2AsH + (Me_3SiCH_2)_3As \quad (2)$$

Others have observed elemental As during reactions between alkyl Grignard reagents and $AsCl_3$.[5,6] Its formation has been explained by the reduction of $AsCl_3$ by the trialkylarsine[6]; however, to the best of our knowledge the identity of the oxidation product has never been reported. Considering these observations and our results, it seemed plausible to assume that Me_3SiCH_2MgCl and $AsCl_3$ had reacted to yield some $(Me_3SiCH_2)_3As$ which then underwent a redox reaction with $AsCl_3$ to give elemental As and $(Me_3SiCH_2)_3AsCl_2$. On testing this assumption, we indeed found that reaction of $(Me_3SiCH_2)_3As$ with $AsCl_3$ produced a brown powder and the arsorane as a white crystalline substance (Equation 3); the latter being characterized by

$$3(Me_3SiCH_2)_3As + 2AsCl_3 \longrightarrow 3(Me_3SiCH_2)_3AsCl_2 + 2As \quad (3)$$

partial elemental analysis (C, H, and Cl), mass spectrometery (electron impact), and NMR spectroscopy (^1H and $^{13}C\{^1H\}$). The ^1H NMR spectrum of $(Me_3SiCH_2)_3AsCl_2$ [δ 0.25 (Me_3Si), 2.71 (CH_2)] resembled that of X (Equation 3) (δ 0.23, 2.64).

Finally, it should be noted that a more well known reaction of tertiary arsines with arsenic trihalides is the redistribution reaction which yields a mixture of R_3As, R_2AsX, $RAsX_2$, and AsX_3; the ratio of products is dependent on the mole ratio of the reactants, the reaction temperature and time, and the R group.[5,7] Thus, heating Ph_3As with $AsCl_3$ gives redistribution products almost exclusively and the kinetics of this reaction have been investigated.[8] On the other hand, although redistributions between $(CH_2CH)_3As$ and $AsCl_3$ or $AsBr_3$, and between Et_3As and $AsBr_3$ have been used as a synthetic method for the respective primary and secondary arsenic halides, the formation of unidentified black solid indicates that a redox process occurs as well in these particular reactions.[9]

EXPERIMENTAL

General Information. All manipulations and reactions were carried out either in Schlenk or standard apparatus, I^2R glove bags, or a Vacuum/Atmospheres HE-43 Dri Lab under an inert atmosphere (argon or nitrogen), or on a vacuum line. Deionized water was degassed prior to use. Organic solvents were distilled from sodium benzophenone ketyl, CaH_2, or P_2O_5 under nitrogen. $AsCl_3$ and $LiAlH_4$ were purchased from Alfa Products, Inc., and Me_3SiCH_2Cl from Petrarch Systems, Inc. All commercially available reagents were not further purified. Me_3SiCH_2MgCl and $(Me_3SiCH_2)_3As$ were prepared by the respective literature methods.[3,4] ^1H NMR spectra were recorded on an IBM NR-80 spectrometer and ^{13}C NMR spectra were obtained on a Joel FX-90Q. All spectra were referenced to TMS using the residual protons or the carbons of the deuterated solvents as the chemical shift reference; for ^1H, C_6D_5H δ 7.15, for $^{13}C\{^1H\}$, C_6D_6 δ 128.0. All NMR tubes were flame-sealed under vacuum. The electron impact mass spectrum was recorded on an HP 5988 A mass spectrometer. The melting point measurement was made by using a Buchi 510 apparatus and a flame-sealed capillary. Elemental analyses were carried out by E + R Microanalytical Laboratory, Inc., Corona, NY.

Reaction of Me_3SiCH_2MgCl with $AsCl_3$ and Subsequent Reduction with $LiAlH_4$. Freshly prepared Me_3SiCH_2MgCl [Me_3SiCH_2Cl (5.55 g, 45.2 mmol) and Mg (1.25 g, 51.4 mmol)] was transferred to a dropping funnel attached to a 3-necked flask containing $AsCl_3$ (8.2 g, 45.2 mmol) dissolved in an ether/pentane mixture, and equipped with a stir-bar and an argon inlet. The Grignard was added dropwise to the stirred solution at −78° and, on warming, the resultant mixture steadily turned browner. After filtration and washing with pentane, distillation of solvents from the filtrate left a liquid and a brown precipitate. Subsequent filtration with benzene washing, followed by removal of the benzene from the filtrate, afforded a clear yellow liquid and a very small amount of a colorless crystalline solid. ^1H NMR of liquid (C_6D_6): δ 0.08, 1.25 [$(Me_3SiCH_2)_2AsCl$][1b]; δ 0.23, 2.64 (X). ^1H NMR of solid (C_6D_6): δ 0.23, 2.64 (X).

Slow addition of $LiAlH_4$ (1.0 g, 26 mmol) to a THF solution of the yellow liquid resulted in a *very* exothermic reaction and the formation of a brown mixture, filtration of which yielded a yellow filtrate and solid (7 g). Hydrolysis of the solid (performed in a glove bag) gave an orange-brown slush which was mixed with *conc* HCl and extracted with ether; after drying the extract with $MgSO_4$ and removal of the solvents and a small quantity of butanol by distillation at atmospheric pressure, there remained $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_3As$ (identified from ^1H and $^{13}C\{^1H\}$ NMR spectra of the mixture which were comparable to those of authentic samples). *In vacuo* evaporation of volatiles from the yellow filtrate gave a yellow solid [IR (nujol, KBr plates): cm^{-1} 2050 (m, AsH), 1300 (w), 1250 (s), 1050 (s, br), 840 (vs, br), 780 (s), 770 (s), 700 (s), 680 (s)]. After addition of methanol to the solid, all volatiles were removed under vacuum; only methanol, THF and $(Me_3SiCH_2)_2AsH$ were evident in the ^1H NMR spectrum of the combined evaporates.

Reaction of $(Me_3SiCH_2)_3As$ with $AsCl_3$: Isolation of $(Me_3SiCH_2)_3AsCl_2$. A small quantity of ether and $AsCl_3$ (0.76 g, 4.2 mmol) were combined with a hexane/benzene solution of $(Me_3SiCH_2)_3As$ (2.0 g, 5.9 mmol) in a reaction tube which was heated to dissolve all of the latter reactant (total volume *ca.* 10 mL). A brown solid began to precipitate as soon as the $AsCl_3$ was added; and after 24 h, 0.033 g of brown solid was isolated by filtration. The filtrate was allowed to stand 39 days in a stoppered flask before re-filtration; 0.175 g of brown solid (presumably elemental As) was separated. Volatiles were removed from the filtrate leaving a wet solid [^1H NMR (C_6D_6, 80 MHz): δ major peaks 0.25 (s, Me_3Si), 2.71 (s, CH_2); δ minor peaks 0.04, 0.12, 0.14 (Me_3Si), 0.66, 0.72, 0.76, 1.94, 2.39 (CH_2)] which was recrystallized from ligroin to yield crystals containing fine brown powder. Dissolution of the latter in C_6H_6, followed by filtration through a fine frit covered with dry alumina powder, *in vacuo* evaporation of solvent from the filtrate, and two subsequent recrystallizations from ligroin afforded white crystalline $(Me_3SiCH_2)_3AsCl_2$ (0.43 g, 17% yield, mp 112–114.5°C). Anal. Calcd. (Found) for $C_{12}H_{33}Si_3AsCl_2$: C 35.37 (35.68), H 8.16 (8.37), Cl 17.40 (17.12). ^1H NMR (C_6D_6, 80 MHz): δ 0.25 (s, Me_3Si), 2.71 (s, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 22.5 MHz): δ 0.48 (s, Me_3Si), 44.36 (s, CH_2). Mass spectrum (70 eV, scan at 140°C): selected m/e (abundance) 391 (20%) [$(M-Me)^+$], 371 (100%) [$(M-Cl)^+$], 336 (5%) [$(Me_3SiCH_2)_3As^+$], 249 (10%) [$(Me_3SiCH_2)_2As^+$], 145 (20%) [$AsCl_2^+$], 73 (60%) [Me_3Si^+].

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