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A convenient way of making arsoxanes $(RAsO)_n$, X-ray crystal structure of $(m\text{-}F_3CC_6H_4AsO)_4$

Hongsui Sun, Brain O. Patrick and William R. Cullen*

Department of Chemistry, The University of British Columbia 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada

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The reactions of RLi (R = t-Bu, *m*-$F_3CC_6H_4$) with bis(dimethylamino)chloroarsine in diethyl ether at room temperature result in the formation of t-butyl-bis(dimethylamino)arsine (1) and *m*-trifluromethylphenyl-bis(dimethylamino)arsine (2). Compounds 1 and 2 were hydrolysed in water solution in the presence of sodium carbonate to give the oxides $(t\text{-}BuAsO)_n$ (3) and $(m\text{-}F_3CC_6H_4AsO)_n$ (4) respectively. The X-ray crystal structure of 4 shows the molecule to be cyclotetrameric with pyramidal arsenic. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: t-butylarsarsoxane; t-butylarsine oxide; *m*-trifluromethylphenylarsoxane; *m*-trifluromethylphenylarsine oxide; arsine; arsenic; crystal structure; NMR; arsine oxide

INTRODUCTION

Arsoxanes $(RAsO)_n$, especially methylarsoxane, commonly known as methylarsine oxide $(MeAsO)_n$, have been of great interest for biological studies.[1–6] Arsoxanes are also reported to be attractive oxygen-transfer agents in organometallic oxidation.[7] Studies related to the use of organocycloarsoxanes multidentate ligands have been reviewed by Sheldrick and Muller.[8] Methylarsoxane was first synthesized by Baeyer[9] in 1858. NMR studies[10,11] suggested that arsoxanes $(RAsO)_n$ are associated as trimers ($R = C_2H_5$, C_3H_7, $n\text{-}C_4H_9$) or tetramer ($R = CH_3$). Phenylarsine oxide $(PhAsO)_n$ was reported to be tetrameric $(PhAsO)_4$.[12,13] The cyclic tetramer structures $(RAsO)_4$ have been confirmed previously by X-ray structure analysis for R = mesityl,[14] Me,[15] and C_6H_5.[16]

The most commonly used methods for making arsoxanes are the reduction of the arsonic acid, usually by using sulfur dioxide, and hydrolysis of organoarsenic dihalides. The former method is the best choice if the arsonic acid itself is readily available, as in the case for methylarsine oxide and phenylarsine oxide. In this communication, we report a convenient general method for preparing arsoxanes and the X-ray crystal structure of *m*-trifluromethylphenylarsanoxane.

RESULTS AND DISCUSSION

Synthesis of the compounds

t-Butyl lithium and *m*-trifluromethylphenyl lithium react with bis(dimethylamino)chloroarsine in diethyl ether at room temperature to give t-butyl-bis(dimethylamino)arsine (**1**) and *m*-trifluromethylphenyl-bis(dimethylamino)arsine (**2**) respectively (Scheme 1). Both compounds **1** and **2** are colourless liquid, and can be easily separated from the reaction mixture by fractional distillation at low pressure. These two compounds are not very stable towards air and moisture but can be handled by using Schlenk techniques.

Compounds **1** and **2** were hydrolysed in sodium carbonate solution to give the oxides $(t\text{-}BuAsO)_n$ (**3**) and $(m\text{-}F_3CC_6H_4AsO)_n$ (**4**) respectively. Compounds **3** and **4** are not very soluble in water. Compound **3** is easily soluble in most common organic solvents; **4** is soluble in benzene, toluene, chloroform and acetonitrile.

The route for making arsoxanes as shown in Scheme 1 is straightforward and affords good yields. Irgolic and co-workers[17] showed that this route is also good for making arsonic acids.

NMR spectra and mass spectrometry

The ^1H NMR and ^{13}C NMR spectra of compound **1** showed appropriate signals for t-butyl and *N*-methyl groups. The split resonances for the t-butyl group in compound **3** indicate that **3** may be a mixture of oligomers (trimer, tetramer, etc.) in chloroform solution. The mass spectrum of **3** showed a parent peak for the tetrameric form $(t\text{-}BuAsO)_4$ and the peaks corresponding to consecutive loss of t-butyl

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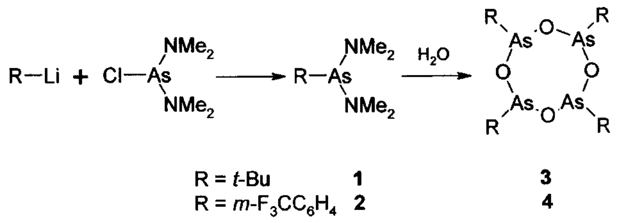
*Correspondence to: William R. Cullen, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada.
E-mail: wrc@chem.ubc.ca



Scheme 1.

groups [$M_4 - \text{t-Bu}$], [$M_4 - 2 \times \text{t-Bu}$], [$M_4 - 3 \times \text{t-Bu}$] and [$M_4 - 4 \times \text{t-Bu}$]. Therefore, the backbone of the cycloarsoxane is considered stable. Other oligomers of t-butylarsanoxane, such as the trimer $(\text{t-BuAsO})_3$ were not observed in the mass spectrum.

The NMR spectra of compound **4** also showed the oligomer. The mass spectrum of **4** gave signals for the tetramer $(m\text{-}F_3CC_6H_4AsO)_4$: and trimer $(m\text{-}F_3CC_6H_4AsO)_3$, as well as [$M_4 - F_3CC_6H_4$], [$M_3 - F_3CC_6H_4$] and [$M_2 - F_3CC_6H_4$].

Solid-state structure of 4

Clear, colourless prism crystals of **4** were obtained from an acetonitrile solution of the compound. The ORTEP diagram and selected bond lengths and bond angles are shown in Fig. 1.

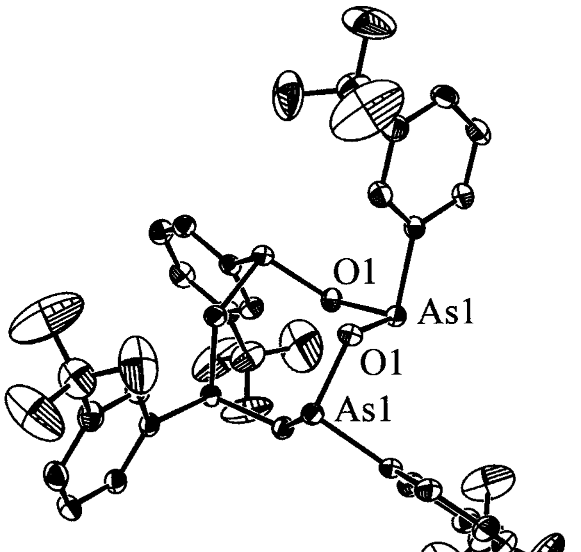


Figure 1. The molecular structure of compound **4**; for clarity, hydrogen atoms are omitted and only the major component (43%) of the disordered CF_3 group is shown. Selected bond lengths (Å) and bond angles (°): As–O1 1.7970(9), As–C1 1.9648(13), As–O(1)^{i} 1.8049(9); O1–As–C1 93.35(5), O1–As–O1^{i} 99.37(5), O1^{i}–As–C1 98.33(5), As–O–As^{ii} 124.09(5). Symmetry operations: i: $\frac{3}{4} - y$, $\frac{3}{4} + x$, $1\frac{3}{4} - z$; ii: $-\frac{3}{4} + y$, $\frac{3}{4} - x$, $1\frac{3}{4} - z$.

The structure of **4** shows that the molecule is a cyclotetramer, i.e. an eight-membered ring with alternating arsenic and oxygen atoms. This is consistent with its mass spectrum. The arsenic atoms exist in a distorted pyramidal geometry defined by two oxygen atoms and the carbon atom from the phenyl group; the lone pair occupies the fourth position in the tetrahedral arrangement of four electron pairs. The lone pair pushes the three bonds down, so that the angles subtended at arsenic are significantly less than the ideal tetrahedral angle. This leaves the arsenic atom as a potential Lewis base towards transition metals. This tetrameric *m*-trifluromethylphenyl-arsanoxane, exhibiting a boat–chair conformation in the solid-state structure, has similar features to those early reported examples.[15,16]

EXPERIMENTAL DETAILS

General considerations

All manipulations were conducted by using standard Schlenk techniques under a dry nitrogen atmosphere unless stated otherwise. Anhydrous diethyl ether and benzene were dried and freshly distilled from sodium benzophenone ketyl under nitrogen. Hexane was dried over CaH_2. NMR spectra were recorded on a Bruker AV 300 spectrometer at ambient temperature. Chemical shifts are given in parts per million relative to tetramethylsilane, with the solvent signal as a secondary standard, and coupling constants are given in hertz. Mass spectra were obtained on a Kratos MS-50 spectrometer operating in the electron ionization mode. Elemental analyses were carried out with a Carlo Erba Elemental Analyzer EA 1108. Bis(dimethylamino)chloroarsine was prepared according to the literature.[18]

Synthesis of t-butyl-bis(dimethylamino)arsine (1)

A solution of bis(dimethylamino)chloroarsine (4.8 ml, 37 mmol) in dry diethyl ether (30 ml) was cooled to −78 °C. To the above solution, t-butyl lithium (1.7 M pentane solution, 24 ml, 40 mmol) was added slowly. A white precipitate formed immediately. The reaction mixture was left stirring overnight; meanwhile, the temperature was increased to room temperature. The filtrate was distilled at reduced pressure, giving a colourless liquid at 28 °C/0.1 Torr. Yield 80%. ^1H NMR ($CDCl_3$) δ 1.02 (s, 9H), 2.54 (s, 12H).

Synthesis of *m*-trifluromethylphenyl-bis(dimethylamino)arsine
(2)

m-Bromobenzyltrifluoride (16.1 g, 71 mmol) in 60 ml diethyl ether was cooled to −65 °C, and to the solution was added *n*-BuLi (1.6 M hexane solution, 44 ml, 71 mmol) slowly. The resulting solution was stirred at −65 °C for 15 min. The stirring solution was slowly warmed to 0 °C over 1 h and kept at that temperature for 30 min, then it was cooled to −70 °C. Bis(dimethylamino)chloroarsine (9.2 ml, 71 mmol) was introduced. The mixture was stirred overnight and work-up as for compound **1**. **2** was obtained as a colourless liquid, 88–89 °C/6 Torr. Yield 67%. ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 12H), 7.39 (t, $J = 7.6$, 1H), 7.48 (d, $J = 7.8$, 1H), 7.65 (d, $J = 7.4$, 1H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 144.3, 135.4, 130.8 (q, $J = 0.4$), 128.6, 126.1, 125.3, 122.5, 42.6.

Synthesis of t-butylarsoxane $(t\text{-}BuAsO)_4$ (3)

To compound **1** (6.0 g, 27.3 mmol), 20 ml water and about a gram amount of sodium carbonate were added. White precipitate began to form in a few minutes. After stirring for 1 h, all volatiles were removed *in vacuo*, leaving a white solid. Extraction with hot benzene gave 3.9 g of **3**. Yield 98%. Recrystallization in hexane gave colourless crystals that turned to white powder after losing solvent. ^{1}H NMR ($CDCl_3$) δ 1.0 (m. 12H); ^{13}C NMR ($CDCl_3$) δ 25 (b). m/z: 592 $[M_4]^+$, 535 $[M_4 - Bu]^+$, 479 $[M_4 - 2Bu]^+$, 423 $[M_4 - 3Bu]^+$, 367 $[M_4 - 4Bu]^+$, 57 $[Bu]^+$.

Synthesis of *m*-trifluromethylphenylarsoxane (4)

4 was obtained following a procedure similar to that described for **3**. Yield 61%. Anal. Found: C, 35.85; H, 1.53. Calc. for $C_7H_4AsF_3O$: C, 35.62; H, 1.71%. ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 1H), 7.66 (t, 1H), 7.86 (d, 1H), 7.98 (s, b, 1H); m/z: 944 $[M_4]^+$, 799 $[M_4 - F_3CC_6H_5]^+$, 708 $[M_3]^+$, 563 $[M_3 - F_3CC_6H_5]^+$, 327 $[M_2 - F_3CC_6H_5]^+$.

X-ray crystallographic study

The data were collected at a temperature of 173(2) K on a Bruker X8 APEX diffractometer with graphite monochromated Mo Kα radiation. Data were collected and integrated using the Bruker SAINT[19] software package and were corrected for absorption effects using the multi-scan technique (SADABS[20]). The structure was solved by direct methods[21] and refined on F^2 using SHELXTL.[22] The molecule resides on a 4_1 screw axis, with a quarter molecule defining the asymmetric unit, and the rest related by crystallographic symmetry. The CF_3 moiety is disordered and was modelled over three orientations. $C_{28}H_{16}As_4F_{12}O_4$, $M = 944.09$, tetragonal, $I4_1/a$, $a = 19.3627(5)$, $c = 8.6403(5)$ Å, $V = 3239.4(2)$ Å^3, $Z = 4$, 1913 unique data ($\theta_{max} = 27.8°$), $R = 0.018$, $wR = 0.041$. CCDC deposition number: 239 627.

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