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Arsenous chloride-free synthesis of cyclic tertiary organoarsines from arylarsine oxides and di-Grignard reagents

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ABSTRACT

The growing importance of triarylarsines as ligands for transition metal catalysis has sparked recent interest in new synthetic routes to tertiary arsines that avoid hazardous arsenous chloride reagents. However, safer methods for the synthesis of lesser explored arsine heterocycles, especially those containing As–C(sp^3) bonds, remain lacking. We demonstrate for the first time that bench stable, less hazardous, arylarsine(III) oxides are effective substitutes for their corresponding chlorides in the one-pot construction of cyclic tertiary organoarsines from di-Grignard reagents. Several known and novel heterocycles have been prepared in reasonable yields, accommodating variations in both the diorganomagnesium reagent and electrophile, making this a modular approach to cyclic arsine assembly.

Introduction

Organoarsines have found application in coordination chemistry [1], materials science [2] and recently in chemotherapy as potential drug delivery and anti-cancer agents [3]. Triaryl arsines in particular are now well established as valuable ligands for transition metal catalysis, demonstrating superiority to analogous phosphines in many cases [4]. Although tertiary organoarsines are traditionally prepared *via* the combination of arsenic chlorides (or other halides) with organometallic reagents or nucleophilic arenes, a major drawback to this approach is the inherent toxicity associated with the As–Cl bond [5]. It is well known that arsenic compounds (or metabolites thereof) generally exhibit toxicity [6], however, most arsenous chlorides are additionally characterized by alarming acute effects based on their rapid *in vivo* covalent binding to thiol-containing enzymes and proteins [7]. These hazards are exacerbated by the often semi-volatility of arsenous(III) chlorides, which have historically been exploited as blistering and vomiting agents in chemical warfare (e.g., Lewisite, Ph_2AsCl, $PhAsCl_2$ and Adamsite) [5]. As such, tertiary organoarsine syntheses that avoid this reagent class have received some interest [8], particularly for the construction of acyclic triarylarsines *via* As–C(sp^2) cross-coupling [4d,9].

In our own search for alternate methods of As–C bond formation, we turned our attention to seminal work by Blicke with arylarsine(III) oxides **1** (Scheme 1) [10]. In contrast to the noxious arsenous chlorides, oxides **1** are generally bench-stable, non-hygroscopic solids that can be safely handled in the laboratory and are resistant to atmospheric oxidation [11]. These compounds (arsenous acid anhydrides) were shown to react with aryl Grignard reagents at ambient temperature to yield dimers **2** after addition of the carbanion (Scheme 1a) [10a]. Attempts to achieve a second Grignard addition were carried out with phenylarsine oxide **3** at elevated temperature (Scheme 1b) [10a]. In the two examples reported (both shown), the product ratio was highly dependent on the concentration of the Grignard regent: a large excess (8 equiv) was required to favour the second addition, enabling triphenylarsine to be obtained in near quantitative yield.

Although anhydrous arylarsine oxides are often depicted as containing a π-bond (As=O), spectroscopic experiments have shown their existence in solid state and solution as well-defined oligomers: $(ArAsO)_x$ [12]. Thus, the formation of a tertiary organoarsine from **1** (or **3**) likely involves the sequential cleavage of two As–O σ-bonds. In this way, arsine oxides could be considered as direct synthetic equivalents of arsenous chlorides.

Encouraged by these findings, we became interested in investigating arsine oxides as safer substitutes for arsenous chlorides in

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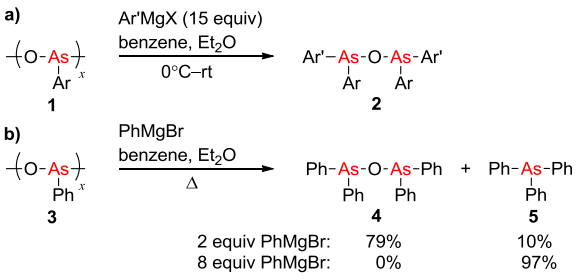


Scheme 1. Previous organoarsine syntheses using arylarsine oxides as electrophiles [**10a**].

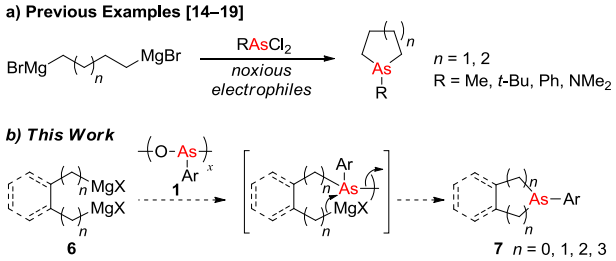
the preparation of (semi)saturated arsine heterocycles **7** from di-Grignard reagents (Scheme 2). Analogous cyclic phosphines and their derived dimers have proven highly effective in ligand-assisted catalysis and asymmetric variants [13], and thus safer and wider access to molecular class **7** was of interest to expand the repertoire of useful arsine ligands beyond the standard triaryl species.

Based on Blicke's results (Scheme 1b) [10a], we proposed that di-Grignard reagents **6** would be ideal nucleophiles to react with oxides **1**, given that the second (and evidently most challenging) As–C bond forming event could occur in an intramolecular mode (Scheme 2b). An additional advantage offered by this approach over stepwise processes was the ability to form the desired heterocycles in a single-pot, avoiding the isolation and purification of organoarsine intermediates.

Results and discussion

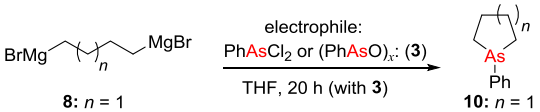
The commercially available phenylarsine oxide **3** was selected as a model electrophile to begin our investigations. Although **3** is an oligomeric material, it dissolves readily in standard organic solvents ($x = 4$ in benzene, CCl_4 and camphor) [12a]. Arsenous chlorides have been used as electrophiles in previous syntheses of cyclic arsines from di-Grignard reagents (Scheme 2a) [14], therefore, by selecting known arsacycles **10** and **11** as initial targets for reaction optimization, a direct comparison could be made between the performance of $(PhAsO)_x$ and its corresponding dichloride (Table 1). Previous results from the literature using $PhAsCl_2$ are therefore included (entries 1–6) [15–19].

Our opening experiment was performed using an equimolar quantity of di-Grignard reagent **8** with a 20 h reaction time (entry 7). Following aqueous work-up, the desired arsolane **10** was isolated in 12% yield after elution through silica gel with hexanes. The remaining material consisted of a complex mixture of unidentified polar components. Encouraged by our immediate success in the formation of **10**, we proceeded to examine the effect of temperature variations: mixing the reactants at −78 °C gave a similar yield



Scheme 2. Proposed synthesis of cyclic arsines from arylarsine oxides and di-Grignard reagents.

Table 1
Reaction optimization for the synthesis of arsolane **10** and arsinane **11** from $(PhAsO)_x$.



Entry [Ref.]	*n*	Equiv Grignard	Electrophile	Temp (°C)	Product	Yield (%)[a]
1 [15]	1	1.0	$PhAsCl_2$	rt-reflux[b]	**10**	18
2 [16]	1	1.1	$PhAsCl_2$	10-rt	**10**	28
3 [17]	1	3.2	$PhAsCl_2$	10-rt	**10**	66
4 [18]	2	1.3	$PhAsCl_2$	rt-reflux[b]	**11**	32
5 [19]	2	1.4	$PhAsCl_2$	0-rt[b]	**11**	31
6 [17]	2	3.2	$PhAsCl_2$	10-rt	**11**	53
7	1	1.0	$(PhAsO)_x$	0-rt	**10**	12
8	1	1.0	$(PhAsO)_x$	-78-rt	**10**	13
9	1	1.0	$(PhAsO)_x$	-78-reflux	**10**	4
10	1	1.0	$(PhAsO)_x$	-78-rt[c]	**10**	10
11	1	3.0	$(PhAsO)_x$	-78-rt	**10**	39[d]
12	1	5.0	$(PhAsO)_x$	-78-rt	**10**	42
13	2	5.0	$(PhAsO)_x$	-78-rt	**11**	9
14	2	5.0	$(PhAsO)_x$	0-rt	**11**	36

[a] Isolated yield based on electrophile.
[b] Et_2O used as solvent.
[c] Reaction time was 70 h.
[d] Yield determined by ^1H NMR with DMSO as internal standard.

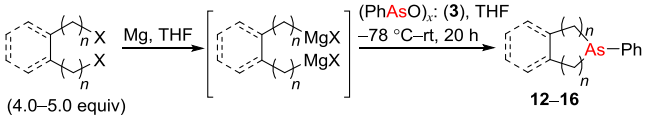
(entry 8), while heating the reaction at reflux was detrimental (entry 9), possibly due to polymerization of the arsine oxide [12b]. An extension of the reaction time to 70 h did not result in an improvement (entry 10), establishing that the low yields were not merely a result of a slow Grignard addition.

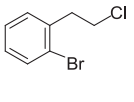
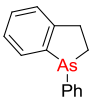
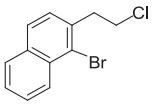
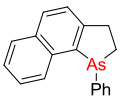
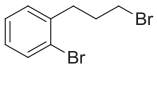
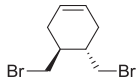
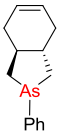
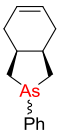
Comparison of previous literature yields using $PhAsCl_2$ reveals a significant advantage from employing an excess of the di-Grignard reagent (entries 3 and 6) [17]. This also proved to be the case in our experiments when the equivalents of **8**, relative to $(PhAsO)_x$, were increased 3- and 5-fold (entries 11 and 12). From the latter reaction (entry 12), **10** was isolated in an acceptable 42% yield. Translation to the six-membered homologue with an excess of di-Grignard reagent **9** occurred smoothly when the addition was performed at 0 °C, allowing **11** to be obtained in a similar yield (36%, entry 14).

Although it is evident that the previously optimized yields of **10** and **11** from the dichloride electrophile are higher than obtained here with $(PhAsO)_x$ (entry 3 versus 12; entry 6 versus 14), we believe that the benefits of avoiding hazardous $PhAsCl_2$ outweighs these current discrepancies. Importantly, the current reactions are also amenable to larger-scale preparations. The arsine oxide can be weighed in the air with no special precautions. As an example, we have prepared 0.8 g of **10** from the reaction between 1.5 g of **3** and the di-Grignard reagent **8** (42% yield, entry 12).

With phenylarsine oxide established as a viable synthon to cyclic arsines, we explored the synthesis of additional heterocycles using fused di-Grignard reagents (Table 2). Phenyl- and naphthyl-fused bis-nucleophiles performed adequately in the cyclization, giving five-membered arsacycles **12** and **13** in 44% and 41% yields respectively (entries 1 and 2). These results compare well with that obtained for the non-aromatic analogue **10** (Table 1, entry 12). The standard flash chromatographic purification with hexanes was carried out to isolate the analogous six-membered arsine (deoxo)-**14**, (entry 3), however the product was found to be contaminated with non-volatile hydrocarbons derived from Grignard hydrolysis and Wurtz-coupling processes. Thus, subsequent treatment with H_2O_2 [15] was performed to isolate the more polar oxide derivative **14** in an overall 26% yield. It should be noted that desymmetrized

Table 2
Synthesis of arsine heterocycles **12**–**16** from carbocyclic-fused di-Grignard reagents.



Entry	Di-Grignard precursor[a]	Product		Yield (%)[b]
1			(**12**)[c]	44
2			(**13**)[c]	41
3			(**14**)[c]	26[d,e]
4	 (racemic)		(**15**)[c]	36
5			(**16**)	41 (dr = 1:1)

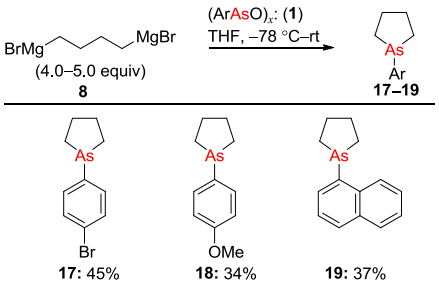
[a] See the experimental section for Grignard formation conditions.
[b] Isolated yield based on **3**.
[c] Racemic mixture.
[d] Reaction performed from 0 °C-rt.
[e] Overall isolated yield after oxidation with H_2O_2.

heterocycles **12**–**14** have been obtained as racemic mixtures due to the newly installed arsenic stereocenter. Additionally, both *trans*- and *cis*-cyclohexene-fused di-Grignard reagents reacted productively under the standard conditions (entries 4 and 5). The racemic *trans* product **15**, which exhibits solely backbone chirality, was isolated in 36% yield, while its *cis* isomer **16**, bearing an additional stereocenter at arsenic, was obtained after silica gel chromatography in 41% yield as a 1:1 mixture of the two *meso* compounds.

Although the yields obtained for known compounds **12** and (deoxo)-**14** are modest (Table 2, entries 1 and 3), they are both superior to the previous three-step procedures (25% and 17% yields respectively) [20,21], which involve Friedel–Crafts cyclization and again use hazardous $PhAsCl_2$ as starting material. Furthermore, we have fully characterized these compounds for the first time.

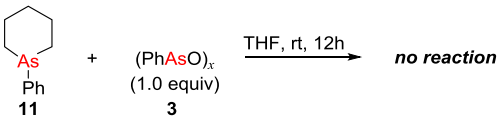
Importantly, this methodology can also be applied to arylarsine oxides of electronic and steric variability (Scheme 3). Utilizing di-Grignard reagent **8** under the established conditions, novel arsolanes **17**–**19**, bearing 4-bromophenyl, 4-methoxyphenyl and 1-naphthyl substituents, were readily obtained in comparable yields (34–45%) to their phenyl analogue. The marginally lower yield of **18** was presumably a result of the electron-donating methoxy group, decreasing the reactivity of the electrophile.

As a first step to understanding why excess Grignard reagent is required for satisfactory double As–C bond formation, we carried out a control experiment to determine whether the cyclic arsine(III) products were sufficiently nucleophilic to react *in situ* with their oxide precursors (Eq (1)) [22]. Accordingly, exemplary substrate **11**



Scheme 3. Preparation of novel arsolanes **17**–**19** from various arylarsine oxides.

was treated with **3** under the standard conditions of heterocycle formation. NMR spectroscopic analysis of the resultant mixture showed no reaction had occurred. This result clearly shows that the general requirement for excess Grignard reagent is not a consequence of a competing reaction between the formed heterocycle and the remaining $(ArAsO)_x$. Given that we have also shown that longer reaction times do not increase the yield of the di-Grignard cyclization (Table 1, entry 10), we currently speculate that a higher concentration of the Grignard reagent activates the electrophile by Lewis acid coordination and/or affects the degree of $(ArAsO)_x$ association in solution. Further studies are required to validate these arguments.

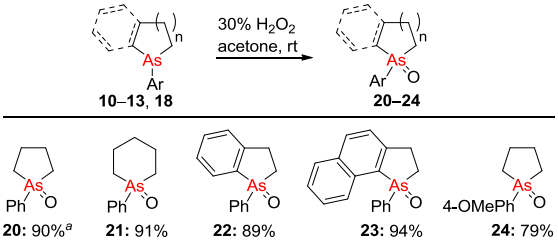


(1)

In the course of this work, we found all arylarsine(III) heterocycles to be relatively stable compounds; no oxidation or decomposition was observed during work-up and chromatographic purification, without special precautions to exclude atmospheric oxygen and moisture. Selected compounds were nonetheless readily converted to their As(V) analogues by oxidation with H_2O_2 [15] (Scheme 4). No As–C(sp^3) bond cleavage was detected in these reactions, as has been observed for some acyclic arsines [12c].

Conclusion

In conclusion, we have demonstrated that arylarsine oxides can be utilized as synthetic equivalents to their dichloride counterparts in combination with di-Grignard reagents, allowing the preparation of cyclic tertiary organoarsines in a significantly less hazardous manner than previously possible. Extension to carbocyclic-fused di-Grignard reagents has enabled access to several novel arsacycles, including those with backbone and arsenic chirality, maintaining acceptable yields throughout. Modular electronic and steric alteration of the peripheral aryl substituent has also been shown to be possible. Conveniently, these arylarsine heterocycles are stable to



Scheme 4. Oxidation of selected cyclic arsines. [a] Previously reported in 96% yield but was not fully characterized [15].

air and moisture, but can be readily oxidized to their As(V) analogues, which offer potential opportunities for functionalization *via* α-lithiation chemistry [23], including oxidative dimerization [24] to novel bisarsines. Further studies in our laboratory will include the examination of solvent effects and/or Lewis acid additives on the cyclization efficiency, the resolution of chiral racemates **12**–**15** and potential applications of the cyclic arsines and derived dimers in transition metal catalysis.

Experimental

General information

All reactions were carried out under an atmosphere of N_2 in oven-dried glassware with magnetic stirring. Thin layer chromatography (TLC) was performed on aluminium-backed 0.20 mm silica gel plates. Visualization was accomplished with UV light or an aqueous ceric ammonium molybdate solution. Flash chromatography was performed under positive air pressure using Silica Gel 60 of 230–400 mesh (40–63 μm). Infrared (IR) spectra were obtained with neat samples on a Shimadzu IRAffinity-1 FTIR Spectrometer. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 300 MHz spectrometer, a Varian Inova 500 MHz spectrometer or a Varian VNMRS PS54 500 MHz spectrometer. All spectra were acquired in $CDCl_3$ and are reported relative to tetramethylsilane (^{1}H: $\delta = 0.00$ ppm) and solvent resonance (^{13}C: $\delta = 77.0$ ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (d = doublet, t = triplet, m = multiplet), coupling constant (Hz), integration and assignment. Low resolution mass spectrometry (MS) was performed on a Shimadzu LC-2010 Electrospray Ionization (ES) Mass Spectrometer or on a Shimadzu QP-5050 Electron Impact (EI) Spectrometer. High resolution mass spectrometry (HRMS) was performed on a Waters Quadrupole-Time of Flight (QTOF) Xevo ES Spectrometer with Leucine-Enkephalin as an internal standard or on a Fison/VG Autospec-TOF EI Spectrometer at 70 eV with a source temperature of 250 °C.

Nitrogen (N_2) was dried by passage through self-indicating silica gel (blue, 2–4 mm bead size). Known halogenated Grignard precursors unavailable commercially were prepared according to literature methods cited within. Grignard reagents were prepared from Mg turnings that were freshly washed with 1 M HCl, followed sequentially by water, EtOH, THF and Et_2O before being dried under high vacuum. Phenylarsine oxide $(PhAsO)_x$ and anhydrous tetrahydrofuran were purchased and used as received. The known 4-bromo- [25], 4-methoxy-[10b] and 1-napthylarsine oxides [10b] were prepared in two steps from the corresponding anilines *via* diazonium salt activation in the presence of arsenic trioxide [26], then reduction of the arsonic acids with an iodine/ascorbic acid system [12d]. All other reagents and solvents were purchased reagent grade and used without further purification.

*Synthesis of 1-phenylarsolane (**10**)*

A suspension of Mg (2.215 g, 91.12 mmol) and 1,4-dibromobutane (9.838 g, 45.56 mmol) in THF (70 mL) was stirred at rt for 1 h. The resulting dark grey solution was added dropwise to a solution of $(PhAsO)_x$ (1.532 g, 9.11 mmol) in THF (70 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (50 mL) was slowly added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving **10** [17] (803 mg, 42%) as a colorless oil. This compound has been fully characterized previously [17]. NMR data for the sample prepared herein was consistent with the published data, with the exception that the quaternary aromatic carbon [As–C(sp^2)] was significantly further downfield than previously reported (lit: $\delta = 132.5$ [17], our sample: $\delta = 143.3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.76–1.98 (m, 8H), 7.22–7.30 (m, 3H), 7.40–7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 27.4, 30.4, 127.3, 128.3, 131.5, 143.3.

*Synthesis of 1-phenylarsinane (**11**)*

A suspension of 1,5-dibromopentane (684 mg, 2.97 mmol) and Mg (145 mg, 5.97 mmol) in THF (6.3 mL) was stirred at rt for 1.5 h. The mixture, containing a small amount of unreacted Mg, was cooled to 0 °C and a solution of $(PhAsO)_x$ (100 mg, 0.595 mmol) in THF (4.2 mL) was added dropwise. The mixture was allowed to warm to rt and stirred for 20 h. The reaction was quenched with water (10 mL) and the product extracted with EtOAc (20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), concentrated, and subjected to column chromatography (hexanes) affording **11** [17] (48 mg, 36%) as a colorless oil. This compound has been fully characterized previously [17]. NMR data for the sample prepared herein was consistent with the published data, with the exception that the quaternary aromatic carbon [As–C(sp^2)] was significantly further downfield than previously reported (lit: $\delta = 132.5$ [17], our sample: $\delta = 141.8$). The identity of the sample prepared herein was also confirmed by high resolution mass spectrometry. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.34–1.96 (m, 10H), 7.21–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.7, 24.4, 29.0, 127.5, 128.7, 132.0, 141.8; MS (EI+): 222 (90%) $[M]^+$, 152 (100%) $[M-(CH_2)_5]^+$; HRMS (ES+): calcd for $C_{11}H_{16}As$ 223.0463, found 223.0459.

*Synthesis of 1-phenyl-2,3-dihydro-1H-arsindole (**12**)*

A suspension of 1-bromo-2-(2-chloroethyl)benzene [27] (5.00 g, 22.78 mmol) and Mg (1.108 g, 45.56 mmol) in THF (50 mL) was heated at reflux for 2 h. After cooling to rt, the resulting solution was added dropwise to a solution of $(PhAsO)_x$ (766 mg, 4.56 mmol) in THF (50 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (50 mL) was slowly added and the mixture was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving **12** [20] (523 mg, 44%) as a colorless oil. This compound has not been fully characterized previously. FTIR: *ν* 3384, 3046, 2360, 1435, 872, 765, 733, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.08–2.26 (m, 2H), 3.15–3.35 (m, 2H), 7.19–7.21 (m, 5H), 7.20–7.36 (m, 3H), 7.65 (d, $J = 6.6$ Hz, 1H); ^{13}C NMR (CDCl3, 75 MHz): δ 26.7, 36.4, 125.0, 126.5, 127.7, 128.3, 128.6, 131.8, 131.9, 140.9, 142.7, 150.8; MS (EI+): 256 (77%) $[M]^+$, 227 (40%), 179 (100%); HRMS (ES+): calcd for $C_{14}H_{14}As$ 257.0311, found 257.0321.

*Synthesis of 1-bromo-2-(2-chloroethyl)naphthalene (novel precursor to **13**)*

A mixture of 2-(1-bromonaphthalen-2-yl)ethanol [28] (25.00 g, 99.55 mmol) and PCl_5 (31.10 g, 149.33 mmol) in $CHCl_3$ (200 mL) was heated at reflux for 4 h. Upon cooling to rt, water (100 mL) was added dropwise and the mixture was diluted with CH_2Cl_2 (200 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were dried ($MgSO_4$) then concentrated *in vacuo* and the residue subjected to silica gel chromatography. Elution with hexanes gave 1-bromo-2-(2-chloroethyl)naphthalene (25.50 g, 95%) as a pale yellow solid. mp: 42–43 °C; FTIR: *ν* 1321, 1259, 967, 817, 759, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.44 (t, $J = 7.5$ Hz, 2H), 3.82

(t, J = 7.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 40.7, 43.3, 124.5, 126.5, 127.5, 127.7, 127.9, 128.2, 128.6, 132.7, 133.8, 135.7; MS (EI+): 270 (99%) [M, ^{81}Br/^{35}Cl]$^+$, 268 (100%) [M, ^{79}Br/^{35}Cl]$^+$; HRMS (EI+): calcd for $C_{12}H_{10}{}^{79}Br^{35}Cl$ 267.9654, found 267.9657.

*Synthesis of 1-phenyl-2,3-dihydro-1H-benzo[g]arsindole (**13**)*

A suspension of Mg (1.45 g, 59.5 mmol) and 1-bromo-2-(2-chloroethyl)naphthalene (8.02 g, 29.76 mmol) in THF (70 mL) was heated at reflux for 12 h. After cooling to rt, the dark grey/brown solution was added dropwise to a solution of $(PhAsO)_x$ (1.00 g, 5.95 mmol) in THF (70 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (50 mL) was slowly added and the mixture was extracted with Et_2O (3 × 50 mL). The combined extracts were dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving **13** (746 mg, 41%) as a colorless oil. FTIR: ν 3047, 2961, 2916, 2849, 1432, 1023, 810, 773, 734, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.21–2.27 (m, 1H), 2.32–2.38 (m, 1H), 3.48–3.51 (m, 2H), 7.14–7.19 (m, 5H), 7.41–7.49 (m, 3H), 7.81–7.86 (m, 2H), 7.93–7.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 26.1, 37.9, 123.6, 125.2, 126.7, 127.9, 128.27, 128.33, 128.7, 129.4, 132.1, 132.4, 135.3, 140.6, 140.7, 149.5; MS (ES+): 307 (30%) $[M+H]^+$, 323 (100%) $[M + NH_4]^+$; HRMS (ES+): calcd for $C_{18}H_{16}As$ 307.0468, found 307.0481.

*Synthesis of 1-phenyl-1,2,3,4-tetrahydroarsinoline-1-oxide (**14**)*

A suspension of Mg (785 mg, 32.31 mmol) and 1-bromo-2-(3-bromopropyl)benzene [29] (4.49 g, 16.15 mmol) in THF (10 mL) was stirred at rt for 12 h. The mixture was cooled to 0 °C and a solution of $(PhAsO)_x$ (679 mg, 4.04 mmol) in THF (10 mL) was added dropwise. The mixture was allowed to warm to rt and stirred for 20 h. The reaction was quenched with water (10 mL) and the product extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), concentrated and subjected to column chromatography (petroleum ether) giving a mixture of 1-phenyl-1,2,3,4-tetrahydroarsinoline (deoxo-**14**) and a Wurtz coupling-derived Grignard hydrolysis side product: 1,6-diphenylhexane (387 mg total). The mixture was taken up in acetone (10 mL) and H_2O_2 (30% aqueous, 167 mg total, 1.43 mmol H_2O_2) was added and the solution was stirred at rt for 12 h. The solution was concentrated under reduced pressure and the residual solid was triturated with hexanes to provide **14** (340 mg, 26%) as a white foam. FTIR: ν 3363, 2930, 1697, 1438, 1269, 1262, 1087, 1066, 996, 874, 852, 802, 773, 743, 716 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.20–2.28 (m, 1H), 2.30–2.40 (m, 1H), 2.52–2.60 (m, 1H), 2.70–2.78 (m, 1H), 2.88–2.96 (m, 1H), 3.04–3.12 (m, 1H), 7.24–7.72 (m, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.1, 30.9, 32.2, 128.1, 129.3, 129.5, 130.0, 130.7, 132.2, 132.3, 132.5, 134.5, 145.2; MS (ES+): 287 (95%) $[M+H]^+$, 572 (100%) $[2M + H]^+$; HRMS (ES+): calcd for $C_{15}H_{16}AsO$ 287.0417, found 287.0405.

*Synthesis of (rac)-trans-4,5-bis(bromomethyl)cyclohex-1-ene (novel precursor to **15**)*

To a solution of (*rac*)-*trans*-4,5-bis(hydroxymethyl)cyclohex-1-ene [30] (13.25 g, 93.17 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added sequentially NEt_3 (32.3 mL, 232.91 mmol) and MsCl (15.9 mL, 204.97 mmol) and the resulting suspension was allowed to warm to rt and stirred for 3 h. Water (50 mL) was slowly added and the mixture was extracted with EtOAc (3 × 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated. The crude dimesylate was taken up in THF (100 mL) and LiBr (37.00 g, 426.05 mmol) was added. The resulting solution was then heated between 40 and 50 °C for 48 h. Water (50 mL) was added and the mixture was extracted with EtOAc (3 × 50 mL). The combined extracts were dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving (*rac*)-*trans*-4,5-bis(bromomethyl)cyclohex-1-ene (15.05 g, 60% over two steps) as a yellow oil. FTIR: ν 3027, 2898, 1430, 1276, 1223, 1034, 978, 924, 850, 768, 668, 607 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.98–2.25 (m, 6H), 3.45–3.53 (m, 2H), 3.60–3.67 (m, 2H), 5.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.4, 36.2, 37.8, 125.0; MS (EI+): 270 (3%) [M, ^{81}Br]$^+$, 268 (6%) [M, ^{81}Br/^{79}Br]$^+$, 266 (3%) [M, ^{79}Br]$^+$, 189 (45%) [M−Br, ^{81}Br]$^+$, 187 (49%) [M−Br, ^{79}Br]$^+$, 107 (100%).

*Synthesis of (rac)-trans-2-phenyl-2,3,3a,4,7,7a-hexahydro-1H-isoarsindole (**15**)*

A suspension of Mg (0.363 g, 14.93 mmol) and (*rac*)-*trans*-4,5-bis(bromomethyl)cyclohex-1-ene (1.000 g, 3.73 mmol) in THF (4 mL) was stirred at rt for 1 h. The supernatant liquid was added dropwise to a solution of $(PhAsO)_x$ (0.125 g, 0.74 mmol) in THF (4 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (5 mL) was slowly added and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving **15** (69 mg, 36%) as a colorless oil. FTIR: ν 3858, 3019, 2900, 1701, 1559, 1507, 1043, 774, 731, 694, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.39–1.68 (m, 4H), 1.79–1.94 (m, 2H), 2.22–2.45 (m, 3H), 2.50–2.57 (m, 1H), 5.61 (s, 2H),7.21–7.32 (m, 3H), 7.42–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 33.9, 34.4, 35.2, 35.3, 43.3, 44.0, 126.6, 126.7, 127.4, 128.4, 131.6, 143.5; MS (ES+): 261 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{14}H_{18}As$ 261.0624, found 261.0634.

*Synthesis of (meso)-(2r,3aR,7aS)-2-phenyl-2,3,3a,4,7,7a-hexahydro-1H-isoarsindole (**16r**) and (meso)-(2s,3aR,7aS)-2-phenyl-2,3,3a,4,7,7a-hexahydro-1H-isoarsindole (**16s**)*

A suspension of Mg (0.308 g, 12.67 mmol) and (*meso*)-(4*R*,5*S*)-4,5-bis(bromomethyl)cyclohex-1-ene [31] (0.850 g, 3.17 mmol) in THF (3.4 mL) was stirred at rt for 1 h. The supernatant liquid was added dropwise to a solution of $(PhAsO)_x$ (0.107 g, 0.64 mmol) in THF (3.4 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (5 mL) was slowly added and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving an inseparable mixture of *meso*-diastereomers **16s** and **16r** (67 mg, dr = 1:1, 41% combined yield) as a colorless oil. FTIR: ν 3741, 2915, 1653, 1540, 1038, 880, 732, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, as mixture): δ 1.65–2.40 (m, 20H), 5.48 (s, 2H), 5.62 (s, 2H), 7.17–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz, as mixture): δ 27.9, 28.7, 31.1, 31.8, 39.6, 39.7, 124.7, 125.2, 126.8, 127.4, 128.3, 128.4, 130.5, 131.7, 143.4, 145.6; MS (ES+): 261 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{14}H_{18}As$ 261.0624, found 261.0616.

*Synthesis of 1-(4-bromophenyl)arsolane (**17**)*

A suspension of Mg (470 mg, 19.33 mmol) and 1,4-dibromobutane (1.386 g, 6.42 mmol) in THF (12.8 mL) was stirred at rt for 16 h. The supernatant liquid was added dropwise to a solution of $(4\text{-}BrPhAsO)_x$ (406.7 mg, 1.65 mmol) in THF (16.5 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. The reaction was quenched by the slow addition of saturated NH_4Cl (10 mL), then water (20 mL) was added and the product was extracted with Et_2O (2 × 20 mL). The combined organic extracts

were washed with brine (20 mL), dried (Na_2SO_4), concentrated and subjected to column chromatography (petroleum ether) giving **17** (211.5 mg, 45%) as a colorless oil. FTIR: *ν* 3331, 2917, 1653, 1479, 1377, 1043, 1007, 799, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): *δ* 1.72–2.04 (m, 8H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 27.5, 30.4, 121.6, 131.2, 133.1, 142.2; MS (EI+): 288 (11%) [M, $^{81}Br]^+$, 286 (11%) [M, $^{79}Br]^+$, 232 (15%), 230 (19%), 71 (100%); HRMS (EI+): calcd for $C_{10}H_{12}As^{79}Br$ 285.9338, found 285.9349.

*Synthesis of 1-(4-methoxyphenyl)arsolane (**18**)*

A suspension of Mg (245 mg, 10.10 mmol) and 1,4-dibromobutane (1.090 g, 5.05 mmol) in THF (5 mL) was stirred at rt for 1 h. The resulting dark grey solution was added dropwise to a solution of $(4\text{-OMePhAsO})_x$ (200 mg, 1.01 mmol) in THF (9 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (5 mL) was slowly added and the mixture was extracted with EtOAc (2 × 10 mL). The combined extracts were washed with brine (10 mL), dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving **18** (81.4 mg, 34%) as a colorless oil. FTIR: *ν* 3320, 2925, 2317, 1700, 1653, 1507, 1044, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 1.73–1.95 (m, 8H), 3.77 (s, 3H), 6.85 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 27.7, 30.5, 55.2, 114.1, 132.9, 133.6, 159.4; MS (ES+): 239 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{11}H_{16}AsO$ 239.0417, found 239.0424.

*Synthesis of 1-(naphthalen-1-yl)arsolane (**19**)*

A suspension of Mg (223 mg, 9.17 mmol) and 1,4-dibromobutane (990 mg, 4.59 mmol) in THF (5 mL) was stirred at rt for 1 h. The resulting dark grey solution was added dropwise to a solution of $(1\text{-naphthylAsO})_x$ (200 mg, 0.92 mmol) in THF (9 mL) at −78 °C and the mixture was allowed to warm to rt and stirred for 20 h. Water (20 mL) was slowly added and the mixture was extracted with EtOAc (2 × 20 mL). The combined extracts were washed with brine (20 mL), dried ($MgSO_4$), concentrated and subjected to column chromatography (hexanes) giving **19** (87.6 mg, 37%) as a colorless oil. FTIR: *ν* 3741, 2927, 1701, 1255, 1022, 947, 787, 770, 649 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 1.73–1.86 (m, 4H), 1.97–2.09 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.41–7.55 (m, 3H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.80 (d, $J = 7.6$ Hz, 1H), 8.30 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 26.3, 30.3, 125.2, 125.55, 125.57, 126.7, 127.2, 127.9, 128.8, 133.9, 135.4, 140.5; MS (ES+): 259 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{14}H_{16}As$ 259.0468, found 259.0468.

*Synthesis of 1-phenylarsolane-1-oxide (**20**)*

Based on a literature procedure [15], to a solution of **10** (700 mg, 3.36 mmol) in acetone (10 mL) was added H_2O_2 (30% aqueous, 573 mg total, 5.05 mmol H_2O_2) and the solution was stirred at rt for 12 h. The solution was concentrated under reduced pressure and the residue subjected to column chromatography (EtOAc to 20% NEt_3/EtOAc) to afford **20** [15] (678 mg, 90%) as a colorless oil. This compound has not been fully characterized previously. FTIR: *ν* 3321, 2971, 2874, 1439, 1378, 1089, 1048, 879, 863, 740, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 1.97–2.05 (m, 2H), 2.13–2.28 (m, 6H), 7.50–7.60 (m, 3H), 7.72–7.78 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 25.9, 29.2, 129.1, 129.5, 131.7, 134.8; MS (EI+): 224 (25%) $[M]^+$, 169 (100%); HRMS (ES+): calcd for $C_{10}H_{14}OAs$ 225.0261, found 225.0255.

*Synthesis of 1-phenylarsinane-1-oxide (**21**)*

To a solution of **11** (220 mg, 0.99 mmol) in acetone (5 mL) was added H_2O_2 (30% aqueous, 112 mg total, 0.99 mmol H_2O_2) and the solution was stirred at rt for 12 h. The solution was concentrated under reduced pressure and the residue was subjected to column chromatography (10:20:70 MeOH:NEt_3:EtOAc to 20:20:60 MeOH:NEt_3:EtOAc) to give **21** (210 mg, 91%) as a yellow oil. FTIR: *ν* 3335, 2922, 2853, 1434, 1089, 1021, 930, 887, 863, 809, 747, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 1.58–2.42 (m, 10H), 7.50–7.58 (m, 3H), 7.76–7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 23.3, 25.4, 29.5, 129.2, 129.9, 131.8, 133.6; MS (ES+): 239 (40%) $[M+H]^+$, 477 (100%) $[2M + H]^+$; HRMS (ES+): calcd for $C_{11}H_{16}AsO$, 239.0417 found 239.0420.

*Synthesis of 1-phenyl-2,3-dihydro-1H-arsindole-1-oxide (**22**)*

To a solution of **12** (500 mg, 1.92 mmol) in acetone (10 mL) was added H_2O_2 (30% aqueous, 327 mg total, 2.88 mmol H_2O_2) and the solution was stirred at rt for 12 h. The solution was concentrated under reduced pressure and the residue subjected to column chromatography (EtOAc to 20% NEt_3/EtOAc) to give **22** (468 mg, 89%) as a colorless oil. FTIR: *ν* 3323, 3056, 1653, 1437, 1086, 866, 740, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 2.50–2.62 (m, 2H), 3.36–3.42 (m, 1H), 3.55–3.61 (m, 1H), 7.39–7.57 (m, 5H), 7.65 (d, $J = 7.5$ Hz, 2H), 7.71 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 27.5, 29.7, 127.2, 128.5, 129.4, 129.8, 130.3, 132.1, 132.6, 132.7, 134.4, 146.3; MS (ES+): 273 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{14}H_{14}OAs$ 273.0261, found 273.0251.

*Synthesis of 1-phenyl-2,3-dihydro-1H-benzo[g]arsindole-1-oxide (**23**)*

To a solution of **13** (400 mg, 1.31 mmol) in acetone (10 mL) was added H_2O_2 (30% aqueous, 222 mg total, 1.96 mmol H_2O_2) and the solution was stirred at rt for 12 h. The solution was concentrated under reduced pressure and the residual solid was triturated with cold CH_2Cl_2 providing **23** (394 mg, 94%) as a white solid. mp: 106–107 °C; FTIR: *ν* 3104, 2830, 845, 811, 744, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 2.62–2.68 (m, 1H), 2.76–2.82 (m, 1H), 3.53–3.59 (m, 1H), 3.71–3.77 (m, 1H), 7.46–7.51 (m, 6H), 7.70 (d, $J = 7.5$ Hz, 2H), 7.90 (d, $J = 7.5$ Hz, 1H), 7.98 (d, $J = 7.5$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 27.1, 30.2, 124.3, 126.0, 126.6, 128.1, 128.3, 128.7, 129.3, 129.9, 132.0, 132.1, 133.0, 133.5, 134.5, 146.4; MS (ES+): 323 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{18}H_{16}AsO$ 323.0417, found 323.0425.

*Synthesis of 1-(4-methoxyphenyl)arsolane-1-oxide (**24**)*

To a solution of **18** (39.8 mg, 0.17 mmol) in acetone (1.2 mL) was added H_2O_2 (30% aqueous, 19.2 mg total, 0.17 mmol H_2O_2) and the solution was stirred at rt for 30 min. The solution was concentrated under reduced pressure and the residue subjected to column chromatography (CH_2Cl_2 to 10% MeOH/CH_2Cl_2) to give **24** (33 mg, 79%) as a colorless oil. FTIR: *ν* 3353, 2941, 1507, 1090, 1019, 884, 868, 821, 794, 752, 608 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): *δ* 1.96–2.25 (m, 8H), 3.86 (s, 3H), 7.04 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): *δ* 25.9, 29.3, 55.4, 114.9, 125.3, 131.2, 162.4; MS (ES+): 255 (100%) $[M+H]^+$; HRMS (ES+): calcd for $C_{11}H_{16}AsO_2$ 255.0366, found 255.0360.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.03.006.

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