1,3-Thiaphosphole and 1,3-thiarsole are aromatic

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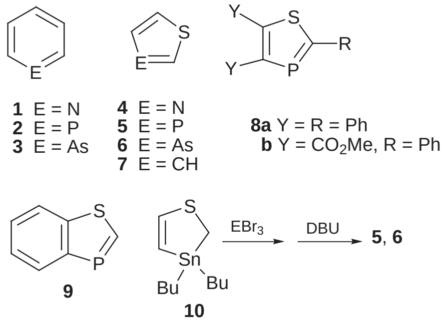
Treatment of 3,3-dibutyl-2,3-dihydro-1,3-thiastannole with either PBr_3 or $AsCl_3$ followed by DBU affords 1,3-thiaphosphole or 1,3-thiarsole, respectively.

Studies on the series pyridine (**1**), phosphabenzene (**2**) and arsabenzene (**3**) have contributed handsomely to our understanding of the concepts of aromaticity and multiple bonding between carbon and the heavier main group atoms.[1–4] 1,3-Thiazole (**4**),[5] 1,3-thiaphosphole (**5**) and 1,3-thiarsole (**6**) form a similar series of aromatic heterocycles. Heavily substituted derivatives of **5**, *e.g.* **8**[6] and **9**,[7] have been prepared although thiarsole remains unknown. A preparation of the unsubstituted heterocycles is desirable and would allow study of the intrinsic properties of the parent rings. We now report on a one step synthesis of **5** and **6** and on some properties of the compounds.

Our synthesis is analogous to the original preparation of **2** and **3**.[3] Heating 3,3-dibutyl-2,3-dihydro-1,3-thiastannole (**10**)[8] in tetraglyme with 1 equiv. of PBr_3 followed by treatment with DBU allows distillation of **5** in 10% yield (Scheme 1). Similar treatment of **10** with $AsBr_3$ followed by DBU allows distillation of **6** in 22% yield. Compounds **5** and **6** are air sensitive liquids which are most conveniently handled in dilute solutions.

The ^{1}H NMR spectra of **4**, **5** and **6** (Table 1) show very low field signals, downfield from those of thiophene (**7**). The most characteristic feature of the spectra is the particularly low field signals due to protons which are adjacent to the group 15 heteroatoms. This shift, which is also shown by the series **1–3**, is apparently caused by the large magnetic anisotropies of the π-bound group 15 heteratoms.[9] However the low field signals for the more remote protons H(5) of **5** and **6** are probably due to the effects of an aromatic ring current.[10] The ^{13}C NMR chemical shifts for C(2) and C(4) also occur at low field as is typical of carbon atoms which are π-bound to heavier group 15 elements.[9,11] Lastly, the ^{31}P shift of **5** (δ 211.3) is virtually identical to those of **8** and **9** which indicates **5** has a π-bound phosphorus(III).[12]



Scheme 1

Table 1 Comparison of the ^{1}H and ^{13}C NMR parameters of thiophene (**7**), 1,3-thiazole (**4**), 1,3-thiaphosphole (**5**) and 1,3-thiarsole (**6**)[a,b]

	Compound			
Parameter	**7**	**4**	**5**[c]	**6**
$\delta_{H(2)}$	7.35	8.88	8.87 (J_{PH} 35.7 Hz)	9.93
$\delta_{H(4)}$	7.13	7.98	8.16 (J_{PH} 43.4 Hz)	8.94
$\delta_{H(5)}$	7.35	7.41	8.37 J_{PH} 9.1 Hz)	8.48
$J_{H(2)\,H(4)}$/Hz	0.9	0	2.2	2.2
$J_{H(2)\,H(5)}$/Hz	3.0	2.0	1.4	1.4
$J_{H(4)\,H(5)}$/Hz	5.0	3.2	6.9	7.0
$\delta_{C(2)}$	124.2	152.7	153.8 (J_{CP} 60.4 Hz)	167.9
$\delta_{C(4)}$	126.2	143.4	144.6 (J_{CP} 51.3 Hz)	155.7
$\delta_{C(5)}$	124.2	118.6	138.8 (J_{CP} 15.4 Hz)	139.5

[a] Solvent $CDCl_3$. [b] ^{1}H NMR (400 MHz) and ^{13}C NMR (126 MHz). [c] ^{31}P NMR (162 MHz), δ 211.3.

The mass spectra of **4**, **5** and **6** show intense molecular ions which are the base peaks. Like **2** and **3**[3] the major daughter peaks for thiaphosphole and thiarsole are due to loss of acetylene. The loss of HCE (E = N, P, As) is rather less important for **5** and **6** than for **4**.[13]

The UV spectrum of 1,3-thiazole shows intense peaks at 208 (2550) and 233 nm (3750),[14] which have been assigned to $\pi\rightarrow\pi^*$ excitations. The spectrum of **5** in hexane shows peaks at 215 (12,000), 249 (3000) and 274 nm (5000), while that of **6** shows peaks at 225 (14,000), 267 (6200) and 290 nm (9800). The progressive red shift of the corresponding bands with increasing atomic number of the heteroatoms corresponds to a smaller gap between the bonding and antibonding orbitals for the heavier heterocycles. This trend is confirmed by performing Hartree–Fock level *ab initio* molecular orbital calculations for **5**[15] and **6** with the RHF/6-31+G* basis set.[16] The optimized structural parameters of **5** listed in Table 2 do not differ significantly from those reported for the X-ray structures of the substituted derivative **8**. The calculated structures are consistent with those of planar aromatic heterocycles.

Since acid catalyzed proton isotopic exchange is the simplest aromatic substitution reaction,[17] it was of interest to examine the behavior of **5** and **6** in deuteroacids. Compound **5** is rapidly destroyed by CF_3CO_2D, but shows no H/D exchange on extended heating in CH_3CO_2D. Heating **6** with excess CH_3CO_2D–$CDCl_3$ (1 : 2) to 100 °C for 22 h leads to the incorporation of two deuterium atoms.[18] The rate of exchange at C(2) is 1.5 times faster than at C(4) with no detectable exchange at C(5). Under identical conditions thiophene does not show exchange[19] but the more reactive indole shows H/D exchange at C(3) at a similar rate.[20] Thus like arsabenzene,[21] 1,3-thiaarsole shows the reactivity of a highly activated aromatic ring.

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Table 2 Selected bond lengths for **8b** compared with the calculated bond lengths for **5** and **6**.

	Bond length/Å		
Bond	**8b** (E = P)[a]	**5** (E = P)	**6** (E = As)
S(1)–C(2)	1.70	1.71	1.70
C(2)–E(3)	1.72	1.69	1.79
E(3)–C(4)	1.76	1.78	1.88
C(4)–C(5)	1.36	1.35	1.34
C(5)–S(1)	1.71	1.72	1.72

[a] Ref 7(*c*).

Notes and references

† *Experimental procedure* for **6**: A solution of $AsBr_3$ (0.96 g, 3.65 mmol) in 2 ml of tetraglyme was added to a solution of **10** (0.98 g, 3.21 mmol) in 4 ml of tetraglyme at −30 °C. The mixture was heated to 85 °C for 15 h and then cooled to 60 °C. DBU (1.00 ml, 6.69 mmol) was added and the mixture was stirred for 3 h at this temperature. Pot-to-pot distillation (0.01 torr, 25 °C) gave the desired product as a yellow liquid (100 mg, 22%). Compound **6** is extremely air sensitive and brief exposure leads to a white intractable precipitate; *m/z* 146 (100%), 120 (51), 75 (13), 45 (19). Compound **5** was prepared in the same manner; *m/z* 102 (100%), 76 (47), 57 (24), 45 (29).

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