Synthesis and characterization of triarylborthiins, $Ar_3B_3S_3$ ($Ar = 4\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, $2\text{-}MeC_6H_4$, $4\text{-}EtC_6H_4$, and $3,5\text{-}Me_2C_6H_3$)

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Abstract

The air/moisture-sensitive triarylborthiins, $Ar_3B_3S_3$ ($Ar = 4\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, $2\text{-}MeC_6H_4$, $4\text{-}EtC_6H_4$, and $3,5\text{-}Me_2C_6H_3$), have been prepared by the reaction of $ArBBr_2$ with HgS in benzene at reflux and have been characterized by ^{11}B NMR and IR spectroscopy and mass spectrometry. The substituted aryl derivatives are less air-stable than $Ph_3B_3S_3$, and in air significantly decompose to boron–oxygen species within minutes; the approximate order of air-stability is ($Ar =$) Ph > $3,5\text{-}Me_2C_6H_3$ > 4-EtC_6H_4 > $4\text{-}MeC_6H_4$ > $3\text{-}MeC_6H_4$ > $2\text{-}MeC_6H_4$. $ArBBr_2$ compounds have been prepared by the reaction of ArHgBr with BBr_3; their ^{11}B, ^{13}C, and ^{1}H NMR data are presented. NMR (^{13}C, ^{1}H) data are also reported for the ArHgBr species prepared by reaction of ArMgBr with $HgBr_2$.

Key words: Boron; Aryl; Borthiin; Nuclear magnetic resonance; Sulfur; Heterocycles

1. Introduction

The first report of a six-membered ring consisting of alternating boron and sulphur atoms with substituents at boron (borthiins) was made by Wiberg and Sturm in 1953 [1], although such rings were first prepared, without being recognised by Stock and Blix in 1901 [2]. The heterocyclic ring structure was confirmed later by single crystal X-ray diffraction studies of $Br_3B_3S_3$ [3,4]. To date, about a dozen substituted borthiins are known, and their stabilities depend upon the steric or electronic effects of the substituents [5,6]. Triphenylborthiin has been prepared from phenylboron dihalides by using H_2S, Na_2S, HgS, $^tBu_2S$, or $(Me_2Si)_3S_3$ as the sulphur containing reagent [7–11]. We report below the results of exploring the general utility of the HgS–$PhBBr_2$ reaction for the synthesis of substituted triarylborthiins, $Ar_3B_3S_3$ ($Ar = 4\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$, 2-MeC_6H_4, $4\text{-}EtC_6H_4$, and $3,5\text{-}Me_2C_6H_3$). General synthetic routes to substituted arylboron dibromides have

been reported, and these involve the interaction of BBr_3 with $ArSiMe_3$, $Ar_3B_3O_3$, or ArHgBr [12–16]; we obtained the necessary arylboron dibromides from ArHgBr.

2. Results and discussion

The substituted arylmercury (II) bromides, prepared in moderate yields as white air-stable crystalline solids by established methods [17,18], gave satisfactory elemental analyses and had melting points in agreement with literature values. Previously unreported NMR (^{1}H, ^{13}C) data are given in Table 1. The ^{199}Hg satellites can be observed in the proton spectra on the methyl resonances of $2\text{-}MeC_6H_4HgBr$ ($^4J = 20$ Hz) and $3,5\text{-}Me_2C_6H_3HgBr$ ($^5J = 10$ Hz). The magnitudes of the coupling constants are consistent with previous reports [19]. The $^{13}C\text{-}\{^1H\}$ spectra show ^{199}Hg coupling to aromatic carbons but not to substituent methyl or ethyl carbons. An assignment of the spectrum of $3,5\text{-}Me_2C_6H_3HgBr$, which shows four aromatic signals at 156.3, 138.7, 133.1, and 131.3 ppm and a methyl signal at 21.4 ppm, was made with the help of a DEPT

experiment that identified the non-hydrogen bearing carbons as those at 156.3 and 138.7 ppm. The ^{199}Hg satellites are apparent for all the aromatic signals except for that at lowest field. The $^nJ(^{13}C^{199}Hg)$ coupling constants are in the ranges quoted for PhHgBr [20], and the DEPT experiment confirmed that coupling to the *meta* (substituted) carbon is larger than that to the *ortho* carbon with $^3J > {}^2J > {}^4J$. The ^1J interaction (expected to be *ca.* 1–2.6 kHz [20]) was not discernible above the noise level for the weak (no nuclear-Overhauser enhancement) downfield signal.

Reaction of a suspension of the arylmercury(II) bromide in toluene at 80–90°C with one equivalent of BBr$_3$ afforded the arylboron dibromides in reasonable yields. The arylboron dibromides are all colourless volatile liquids or low-melting distillable solids, which fume in air, in which they are rapidly hydrolysed to the corresponding triarylboroxine. With the exception of 2-MeC$_6$H$_4$BBr$_2$, the arylboron dibromides have been

previously reported, but characterization was limited to physical data for 4-MeC$_6$H$_4$BBr$_2$ and 3,5-Me$_2$C$_6$H$_3$-BBr$_2$ [12,21] and to ^{11}B and ^{1}H NMR data for 4-Me-C$_6$H$_4$BBr$_2$ and 3-MeC$_6$H$_4$BBr$_2$ [16]. Physical data and NMR data (^{11}B, ^{13}C, ^{1}H) are given in Tables 1 and 2, respectively, and where relevant are consistent with the available literature data.

The interaction of ArBBr$_2$ with a suspension of HgS in benzene under reflux affords the substituted triarylborthiin as a pale-yellow/off-white solid in generally excellent yields. The reaction of 2-MeC$_6$H$_4$BBr$_2$ with HgS was not clean, and the product, (2-MeC$_6$H$_4$)$_3$B$_3$S$_3$, was contaminated by another (unidentified) boron containing species. The difficulty encountered in preparing (2-MeC$_6$H$_4$)$_3$B$_3$S$_3$ might be attributed to a strong destabilizing steric interaction between the *ortho*-methyl hydrogen atoms and the heterocyclic sulphur atoms in the co-planar conformation that would allow maximum overlap of the aryl π-system with the "va-

TABLE 1. NMR data for ArHgBr, ArBBr$_2$ and Ar$_3$B$_3$S$_3$ compounds [a]

2-MeC$_6$H$_4$HgBr	$\delta(^1$H): 2.3 (s, 3H, ^4J = 20 Hz); 7.1–7.4 (m, 4H)
	$\delta(^{13}$C): Me: 26.2; Ar: 126.1 (J = 193 Hz), 129.2 (J = 31 Hz), 130.3 (J = 154 Hz), 135.6 (J = 110 Hz), 142.1, 155.4.
3-MeC$_6$H$_4$HgBr	$\delta(^1$H): 2.3 (s, 3H); 7.0–7.3 (m, 4H).
	$\delta(^{13}$C): Me: 21.7; Ar: 129.2, 130.5 (J = 40 Hz), 132.8 (J = 116 Hz), 136.4, 139.2, 153.1.
4-MeC$_6$H$_4$HgBr	$\delta(^1$H): 2.3 (s, 3H); 7.2–7.4 (m, 4H).
	$\delta(^{13}$C): Me: 21.1; Ar: 130.0 (J = 200 Hz), 135.5 (J = 154 Hz), 139.7, 156.3
3,5-Me$_2$C$_6$H$_3$HgBr	$\delta(^1$H): 2.3 (s, 6H, ^5J = 10 Hz); 6.9 (2H); 7.3 (1H).
	$\delta(^{13}$C): Me: 21.4; Ar: 131.3 (^4J = 50 Hz), 133.1 (^2J = 115 Hz), 138.7 (^3J = 210 Hz), 156.3.
4-EtC$_6$H$_4$HgBr	$\delta(^1$H): 1.2 (t, 3H); 2.65 (q, 2H); 7.1–7.3 (m, 4H).
	$\delta(^{13}$C): Me: 15.4; CH$_2$: 28.7; Ar: 128.9 (J = 193 Hz), 135.5 (J = 135 Hz), 145.9, 156.3.
2-MeC$_6$H$_4$BBr$_2$	$\delta(^{11}$B): +57.7.
	$\delta(^1$H): 2.6 (3H); 7.1–7.5 (m, 4H) 7.9 d, (4H).
	$\delta(^{13}$C): Me: 24.3; Ar: 125.5, 131.4, 133.6 (×2 coincidence?), 136.1, 143.3.
3-MeC$_6$H$_4$BBr$_2$	$\delta(^{11}$B): +56.9; (+57.0 in C$_6$D$_6$)
	$\delta(^1$H): 2.6 (3H); 7.4 t (1H); 7.6 d, (1H); 8.2 (2H).
	$\delta(^{13}$C): Me: 21.5; Ar: 128.7, 135.2 (×2 coincidence?), 136.4, 137.8, 138.4.
4-MeC$_6$H$_4$BBr$_2$	$\delta(^{11}$B): +55.9.
	$\delta(^1$H): 2.45 (3H); 7.25 (2H); 8.1 (2H).
	$\delta(^{13}$C): Me: 22.1; Ar: 128.8, 129.5, 137.8, 146.8.
3,5-Me$_2$C$_6$H$_3$BBr$_2$	$\delta(^{11}$B): +56.7; (+57.1 in C$_6$D$_6$)
	$\delta(^1$H): 2.5 (6H); 7.35 (1H); 7.9 (2H).
	$\delta(^{13}$C): Me: 21.4; Ar: 128.3, 135.5, 137.1, 137.6.
4-EtC$_6$H$_4$BBr$_2$	$\delta(^{11}$B): +56.1; (+56.1 in C$_6$D$_6$).
	$\delta(^1$H): 1.2 (t, 3H); 2.65 (q, 2H); 7.2 (d, 2H); 8.1 (d, 2H).
	$\delta(^{13}$C): Me: 14.85; CH$_2$: 29.2; Ar: 127.6, 128.2, 138.0, 152.7.
(2-MeC$_6$H$_4$)$_3$B$_3$S$_3$	$\delta(^{11}$B): +62.2; (+65.4 also strong)
(3-MeC$_6$H$_4$)$_3$B$_3$S$_3$	$\delta(^{11}$B): +60.4;
	$\delta(^1$H): 2.1 (3H); 6.9–7.2 (m, 2H); 8.0 (m, 2H).
(4-MeC$_6$H$_4$)$_3$B$_3$S$_3$	$\delta(^{11}$B): +59.9;
	$\delta(^1$H): 2.05 (3H); 7.1 (d, 2H, $J \approx$ 7 Hz), 8.15 (d, 2H).
(3,5-Me$_2$C$_6$H$_3$)$_3$B$_3$S$_3$	$\delta(^{11}$B): +60.4;
	$\delta(^1$H): 2.1 (6H); 6.85 (1H), 7.9 (2H).
(4-EtC$_6$H$_4$)$_3$B$_3$S$_3$	$\delta(^{11}$B): +59.7;
	$\delta(^1$H): 1.1 (q, 3H, $J \approx$ 7 Hz); 2.35 (t, 2H); 7.1 (d, $J \approx$ 7 Hz), 8.4 (d).

[a] Unless otherwise stated ArHgBr and ArBBr$_2$ recorded in CDCl$_3$; Ar$_3$B$_3$S$_3$ recorded in C$_6$D$_6$. In ArHgBr spectra J refers to ^nJ (^{199}Hg^{1}H) or ^nJ (^{199}Hg^{13}C) spin–spin coupling.

TABLE 2. Physical data for $ArBBr_2$ and $Ar_3B_3S_3$

Compound	M.Pt/°C	Bpt [a]/°C	% yield
$2\text{-}MeC_6H_4BBr_2$	–	65–70(0.15)	56
$3\text{-}MeC_6H_4BBr_2$	–	90–100(0.15)	60
$4\text{-}MeC_6H_4BBr_2$	70	135(2)	64
$3,5\text{-}Me_2C_6H_3BBr_2$	60	110(2)	[b]
$4\text{-}EtC_6H_4BBr_2$	–	155(2)	[b]
$(2\text{-}MeC_6H_4)_3B_3S_3$	130	–	81 [c]
$(3\text{-}MeC_6H_4)_3B_3S_3$	150–160	–	73
$(4\text{-}MeC_6H_4)_3B_3S_3$	142–5	–	95
$(3,5\text{-}Me_2C_6H_3)_3B_3S_3$	153	–	79
$(4\text{-}EtC_6H_4)_3B_3S_3$	25–30	–	80

[a] mmHg in parentheses; [b] not accurately recorded but ca. 60%; [c] crude yield.

cant" boron p orbital. All the substituted triarylborthiins were readily hydrolysed in air to the corresponding triarylboroxine, but could be manipulated successfully in an inert-atmosphere glove-box. They were successfully characterized by IR and NMR (^{11}B, ^{1}H) spectroscopy and mass spectrometry. The IR spectra (Table 3), obtained with Nujol mulls (glove-box), all showed a moderate intensity triplet at ca. 1000 cm^{-1} that was previously assigned as a B–S stretch [9,22]. When samples are exposed to air these bands rapidly disappear from the spectra, and new bands characteristic of triarylboroxines appear within minutes. The order of stability of the substituted triarylborthiins to air, as judged from the IR spectra, was found to be (Ar =) Ph > $3,5\text{-}Me_2C_6H_3$ > $4\text{-}EtC_6H_4$ > $4\text{-}MeC_6H_4$ > $3\text{-}MeC_6H_4$ > $2\text{-}MeC_6H_4$. The electron-releasing inductive effect of the methyl or ethyl groups has little effect on the π-interaction at boron, and weakly activates the triarylborthiin towards decomposition. The ^{11}B NMR

spectra of reaction mixtures after a few hours reaction show two peaks at chemical shifts corresponding to the starting materials and products, with the $Ar_3B_3S_3$ resonance appearing ca. 4 ppm downfield of the related $ArBBr_2$ signal and consistent with data reported for $Ph_3B_3S_3$ and $PhBBr_2$ [23]. The ^{11}B spectra of the isolated products, except $(2\text{-}MeC_6H_4)_3B_3S_3$, always showed this downfield signal as the major peak. For $(2\text{-}MeC_6H_4)_3B_3S_3$ however, an additional signal was also observed at even lower field. The chemical shift of the additional signal is in the region expected for $(2\text{-}MeC_6H_4)_3B$ or for $(2\text{-}MeC_6H_4B)_2S_3$ which could be possible decomposition products of the unstable triarylborthiin [7,23]. The mass spectra of the triarylborthiins (Table 3) all show similar fragmentation patterns, which are characterized by a weak molecular ion peak, $[Ar_3B_3S_3]^+$. The parent peak is invariably owing to $[ArBS]^+$ and the dimer $[Ar_2B_2S_2]^+$ is also reasonably strong. These breakdown patterns are significantly different from that reported for $Ph_3B_3S_3$ (which is sufficiently stable to be handled for short periods in air without decomposition), for which a strong molecular ion peak is seen. Overall the substituted triarylborthiins have molecular ion peaks of similar intensity to those of the Br, MeS, and MeO borthiin derivatives, which again indicates that the substituted arylborthiins are less stable than $Ph_3B_3S_3$ [24]. Interestingly, $[M - 16]^+$, $[M - 32]^+$, and $[M - 48]^+$ ions (tentatively assigned to the unreported heterocycles $[Ar_3B_3S_2O]^+$ and $[Ar_3B_3SO_2]^+$, and to $[Ar_3B_3O_3]^+$) were also consistently present, and these ions presumably arise from partial hydrolysis of the sample during transfer (in air) to the probe. A high-resolution mass spectrum confirmed the assignment of M^+ for $(3,5\text{-}Me_2C_6H_3)_3B_3S_3$.

TABLE 3. MS [a] and IR [b] data for $Ar_3B_3S_3$ compounds

$(2\text{-}MeC_6H_4)_3B_3S_3$	MS: 402 (M^+), 1%; 386 ($M^+ - 1S + 1O$), 2%; 370 ($M^+ - 2S + 2O$), 7%; 354 ($M^+ - 3S + 3O$), 50%; 268 ($M^+ - ArBS$), 20%; 262, 35%; 202, 35%; 144, 48%; 134 ($ArBS^+$), 100%; 117 ($ArBO^+$), 80%; 91 (Ar^+), 65%. IR: 1595m, 1566w, 1342s, 1189s, 1040m, 1010m, 986s, 940m, 866s, 741s, 687m, 625m, 602w.
$(3\text{-}MeC_6H_4)_3B_3S_3$	MS: 402 (M^+), 1%; 386 ($M^+ - 1S + 1O$), 2%; 370 ($M^+ - 25 + 20$), 3%; 354 ($M^+ - 3S + 3O$), 25%; 268 ($M^+ - ArBS$) 25%; 202, 60%; 166, 40%; 134 ($ArBS^+$), 100%; 117 ($ArBO^+$), 28%; 91 (Ar^+), 70%. IR: 1595w, 1573w, 1376m, 1242s, 1179w, 1162s, 1028m, 1011m, 982m, 931m, 780m, 766m, 691m, 630w.
$(4\text{-}MeC_6H_4)_3B_3S_3$	MS: 402 (M^+), 5%; 386 ($M^+ - 1S + 1O$), 14%; 370 ($M^+ - 2S + 2O$), 31%; 354 ($M^+ - 3S + 3O$), 99%; 268 ($M^+ - ArBS$) 49%; 262, 32%; 252, 10%; 193, 81%; 160, 15%; 144, 28%; 134 ($ArBS^+$), 100%; 117 ($ArBO^+$), 78%; 91 (Ar^+), 86%; 65, 34⟨ IR: 1606s, 1348s, 1200w, 1182s, 1021m, 1001m, 987m, 866m, 803m, 773m, 733m, 684m.
$(3,5\text{-}Me_2C_6H_3)_3B_3S_3$	MS: 444 (M^+), 10%; 428 ($M^+ - 1S + 1O$), 20%; 412 ($M^+ - 2S + 2O$), 22%; 396 ($M^+ - 3S + 3O$), 65%; 296 ($M^+ - ArBS$), 85%; 281, 20%; 222, 70%; 148 ($ArBS^+$), 100%; 133 ($ArBOH^+$), 75%; 115, 52%; 105 (Ar^+), 50%. IR: 1598m, 1351s, 1284m, 1265m, 1223w, 1196w, 1172m, 1035m, 1008m, 994w, 952w, 859m, 731s, 695m.
$(4\text{-}EtC_6H_4)_3B_3S_3$	MS: 444 (M^+), 1%; 428 ($M^+ - 1S + 1O$), 5%; 412 ($M^+ - 2S + 2O$), 5%; 396 ($M^+ - 3S + 3O$), 3%; 296 ($M^+ - ArBS$), 62%; 221, 66%; 174, 7%; 148 ($ArBS^+$), 88%; 133 ($ArBOH^+$), 100%; 116,17%; 105 (Ar^+), 12%. IR: 1605s, 1405m, 1351s, 1214m, 1183m, 1110w, 1054m, 1016m, 989s, 910m, 869s, 828s, 756m, 698w.

[a] MS data presented as m/e (assignement), relative intensity %.
[b] IR data from Nujol mull (cm^{-1}).

3. Experimental details

3.1. General

Reactions were carried out by standard Schlenk techniques under N_2, and all solvents were dried before use. The compounds BBr_3, $HgBr_2$, HgS, Mg, and aryl bromides were obtained commercially. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer as Nujol mulls (prepared in a glove-box) or by use of standard liquid cells with NaCl windows. Melting points were obtained with an Electrothermal Melting Point apparatus within a glove box. Mass spectra were recorded on a Finnigan 1020 GC mass spectrometer. Multi-element NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer operating at 250 MHz for ^{1}H, 62.9 MHz for ^{13}C-$\{^1$H$\}$ and 80.25 MHz for ^{11}B-$\{^1$H$\}$. Chemical shifts (δ) are given in ppm with positive values towards high frequency (downfield) from $SiMe_4$ for ^{1}H and ^{13}C-$\{^1$H$\}$, and from $BF_3 \cdot OEt_2$ for ^{11}B-$\{^1$H$\}$.

3.2. Preparation of $3,5$-$Me_2C_6H_3HgBr$

To the Grignard reagent ($3,5$-$Me_2C_6H_3MgBr$), prepared from $1,3,5$-$Me_2C_6H_3Br$ (18.52g; 0.1 mol) and Mg (2.46g; 0.1 mol) in dry THF (80 cm^3) was added a solution of $HgBr_2$ (36.09g; 0.1 mol) in dry THF (80 cm^3). The mixture was stirred and heated under reflux for 24 h, and then poured into cold water (500 cm^3). The solid was filtered off and extracted with $CHCl_3$ (2 l in total). The combined extracts were evaporated to dryness on a rotary evaporator, and the residue was washed with acetone (50 cm^3) to leave an analytically pure-white solid (26.2 g; 68%). Mpt. 197°C. Anal. Found: C, 24.9; H, 2.3. C_8H_9BrHg, calc.: C, 24.92; H, 2.35%.

Yields and melting points of the other ArHgBr compounds are as follows: 2-MeC_6H_4HgBr, 57%, 173–174°C (Ref. [17] 169.5°C); 3-MeC_6H_4HgBr, 66%, 187–189°C (Ref. [17] 184°C); 4-MeC_6H_4HgBr, 43%, 224–227°C (Ref. [17] 231°C); 4-EtC_6H_4HgBr, 50%, 249–250°C (Ref. [25] 227–28°C).

3.3. Preparation of $3,5$-$Me_2C_6H_3BBr_2$

BBr_3 (12.61 g; 0.05 mol) in toluene (30 cm^3) was added to a stirred suspension of $3,5$-$Me_2C_6H_3HgBr$ (19.31 g; 0.05 mol) in toluene (85 cm^3). The mixture was kept at 90°C for 24 h, allowed to cool to room temperature, and then filtered to remove $HgBr_2$. Toluene was removed from the filtrate under vacuum (room temperature/2 mm Hg) and the product (ca. 8.2 g; 60%) was obtained as a light-brown solid by distillation of the residue (110°C/2 mm Hg) in a bulb-to-bulb distillation apparatus. Physical data for the other

ArBBr$_2$ compounds are given in Table 2. NMR data are given in Table 1.

3.4. Preparation of $(3,5$-$Me_2C_6H_3)_3B_3S_3$

To a solution of $(3,5$-$Me_2C_6H_3)BBr_2$ (3.23 g; 11.7 mmol) in dry benzene (60 cm^3) was added HgS (2.93 g; 12.6 mmol). The red suspension was refluxed for 24 h (reddish off-white suspension) and allowed to cool to room temperature before being filtered to remove $HgBr_2$. The filtrate was evaporated to dryness to afford the product (1.37 g; 79%) as an off-white solid. Mpt. 153°C. The ^{11}B and ^{1}H NMR data are reported in Table 1. MS and IR data are given in Table 3. High resolution MS: M$^+$ ($^{12}C_{24}{}^1H_{27}{}^{11}B_3{}^{32}S_3^+$) obs. 444.1518 $+/-$ 0.004, calc. 444.1554.

Acknowledgments

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