A versatile synthesis of the group 15 and 16 3-benzoheteroepines involving the first isolated examples of several *C*-unsubstituted 3-benzoheteroepines

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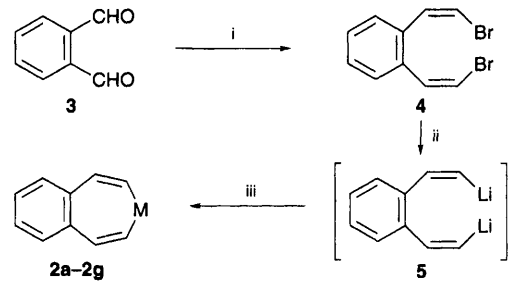
Group 15 (P, As, Sb and Bi) and group 16 (S, Se and Te) 3-benzoheteroepines 2, involving the first isolated examples of several *C*-unsubstituted fully unsaturated 3-benzoheteroepines, are prepared in two steps from (*Z*,*Z*)-*o*-bis(β-bromovinyl)benzene 4 and their thermal stabilities examined.

1-Benzoheteroepines **1** containing group 15 (P, As, Sb and Bi) and group 16 (S, Se and Te) elements, as well as those containing group 14 (Si, Ge, Sn), have been prepared by various routes. Flash vacuum pyrolysis of 2*a*, 7*b*-dihydrocyclobuta[*b*]-1-benzoheteroles results in valence isomerization with ring-opening to give the 1-benzophosphepine **1a** and 1-benzarsepine **1b**,[1] and the 2-substituted group 16 1-benzoheteroepines have been obtained by intramolecular cyclization of *o*-(but-1-en-3-ynyl)phenylheterols.[2] Furthermore, we have also shown that the 1-benzoheteroepines **1a–g** can be prepared from 1-bromo-4-(*o*-bromophenyl)buta-1,3-dienes *via* their 1,6-dilithium intermediates.[3] However, with regard to the group 15 and 16 3-benzoheteroepines **2**, only a few examples have been reported, although the 3-benzoheteroepines containing group 14 (Si[4] and Sn[5]) elements are known. The phosphepine **2a**,[6] tellurepine **2g**[7] and 3-alkyl-3-benzostibepines[8] have been prepared starting from *o*-diethynylbenzene. The *C*-unsubstituted arsepine **2b**[6,8] and thiepine **2e**[9] have been reported to be too thermally unstable to be isolated, although the 3-benzothiepines having alkoxycarbonyl groups in the 2- and/or 4-position are more stable and can be isolated.[9] We report here a versatile synthetic route to the group 15 and 16, 3-benzoheteroepines **2**, which can be prepared from a common starting material, and on the thermal stabilities of these heteroepine rings. The compounds **2b,e** and **f** are the first isolated examples of 3-benzarsepines, parent 3-benzothiepine and 3-benzoselenepines, respectively.

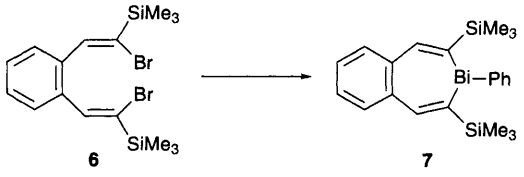
The key common starting (*Z*,*Z*)-*o*-bis(β-bromovinyl)benzene **4**† could be obtained stereoselectively in high yield (*ca.* 90%) by a double Wittig reaction of *o*-phthalaldehyde with bromomethylenetriphenylphosphorane,[10] generated *in situ* by treatment of bromomethyltriphenylphosphonium bromide with potassium *tert*-butoxide in THF at −80 °C. The dibromo compound **4** was treated with *tert*-butyllithium in dry diethyl ether at −80 °C, and then with a metal reagent [$PhPCl_2$, $PhAsCl_2$, $PhSbCl_2$, $PhBiBr_2$, $(PhSO_2)_2S$, $SeCl_4$ or $TeCl_4$] resulting in ring closure giving the desired 3-benzoheteroepines **2a–g** in 15–40% isolated yields,‡ presumably *via* the 1,6-dilithium intermediate **5**.

The bismepine **2d** was extremely thermally unstable and thus not isolated, although it was detected at −20 °C by ^{1}H NMR spectroscopy. It is known that the stability of heteroepine rings is enhanced by the introduction of bulky groups in α-positions.[9,11] Therefore, the 2,4-bis(trimethylsilyl)bismepine **7** was prepared by treatment of the dibromo compound **6**, obtained from *o*-diiodobenzene in four steps,§ with *tert*-butyllithium followed by dibromophenylbismuth.¶ As expected, the bismepine **7** was slightly more stable and could be isolated.

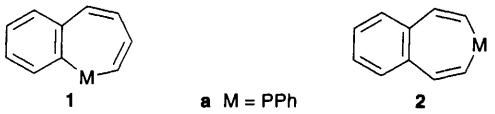
The ^{1}H NMR spectroscopic data of the seven-membered ring protons of **2** is given in Table 1. The chemical shifts are sensitive to a change in the heteroatom and some patterns are



Scheme 1 *Reagents and conditions*: i, $Ph_3P^+CH_2BrBr^-$, Bu^{t}OK, THF, −80 °C, 2 h, −80 °C to room temp., 8 h; ii, Bu^{t}Li, Et_2O, argon, −80 °C, 20 min; iii, $PhPCl_2$, $PhAsCl_2$, $PhSbCl_2$, $PhBiBr_2$, $(PhSO_2)_2S$, $SeCl_4$ or $TeCl_4$, Et_2O, argon, −80 °C to room temp., 3 h



Scheme 2



a M = PPh
b M = AsPh
c M = SbPh
d M = BiPh
e M = S
f M = Se
g M = Te

Table 1 Selected ^{1}H NMR spectroscopic data of **2**

Compd. 2	M	δ (CDCl$_3$, 400 MHz) 1-H (5-H)	2-H (4-H)	$J_{1,2}$/Hz
a	PPh	6.64	5.74	12.0
b	AsPh	7.16	6.20	11.4
c	SbPh	7.57	6.52	12.1
d	BiPh	8.92	7.59	11.2
e	S	6.72	5.89	9.5
f	Se	7.16	6.31	9.2
g	Te	7.62	6.79	9.9

Table 2 Half-lives of **2** and **1** at 50 °C in toluene

Compd.	$t_{1/2}$
2a	82 h
2b	4 min
2c	45 min
2d	< 1 min
2e	1 min
2f	4 min
2g	48 min
1a	28 h
1b	180 min
1c	48 h
1d	18 min
1e	44 min
1f	110 min
1g	133 min

observed, in analogy with 1-benzoheteroepines[3] and 1-benzometalloles.[12] The protons at position 1 resonate at higher field than protons at position 2. In the same heteroepine group, both the 1- and 2-protons of the heteroepines containing elements from the higher horizontal rows of the periodic table resonate at lower fields than those containing elements in lower rows. The values of the chemical shifts of these protons increase in the order **2a**(P) < **2b**(As) < **2c**(Sb) < **2d**(Bi) and **2e**(S) < **2f**(Se) < **2g**(Te). The values of the coupling constants ($J_{1,2}$) of the group 15 heteroepines are somewhat larger than those of the group 16 heteroepines.

All benzoheteroepines **2** are thermally labile towards heteroatom extrusion and gradually decomposed to naphthalene even during isolation by column chromatography, as are the 1-benzoheteroepines **1**. The half-lives of **2** estimated from ^{1}H NMR spectral analysis are listed in Table 2, together with those of **1**. The 3-benzoheteroepines **2** are far less stable than the corresponding 1-benzoheteroepines **1**, except for the phosphepine **2a**, which is surprisingly much more stable than the others. The bismepine **7** having the bulky trimethylsilyl groups in both α-positions is much more stable ($t_{1/2}$ = 34 min at 50 °C) than the *C*-unsubstituted bismepine **2d** ($t_{1/2}$ = < 1 min at 50 °C). The stabilities of the group 16 heteroepines decrease in the expected order **4g**(Te) > **4f**(Se) > **4e**(S), but there is no pattern to the stabilities of the group 15 benzoheteroepines.

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Footnotes

† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. *Selected data* for **4**: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (2 H, d, *J* 10.8 Hz, β-H), 7.11 (2 H, d, *J* 10.8 Hz, α-H), 7.37 and 7.68 (each 2 H, dd, *J* 5.5 and 3.3 Hz, Ph-H).

‡ The phosphepine **2a** was susceptible to air oxidation and was thus isolated as its P-oxide, which was, however, readily deoxygenated back to **2a** by treatment with trichlorosilane. The benzoheteroepines were obtained as oils except for **2a** (mp 155–156 °C) and **2c** (mp 76–78 °C). The group 16 heteroepines **2e–g** were also formed by treatment of S, Se or Te powder, but in lower yields (5–10%).

§ Although (*Z*)-β-bromo-β-(trimethylsilyl)styrene can be prepared in two steps from iodobenzene *via* (trimethylsilylethynyl)benzene,[3,12] *o*-bis-(trimethylsilylethynyl)benzene obtained from *o*-diiodobenzene did not give the desired divinyl compound **6**, therefore each of the bromo groups in diiodobenzene was converted to the vinyl group one by one to give **6**.

¶ *Selected data* for **7**: 15% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (18 H, s, TMS-H), 6.49–6.96 (9 H, m, Ph-H) and 9.58 (2 H, s, 1- and 5-H).

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