A Versatile Synthesis of 1-Benzoheteroepines Containing Group 14, 15, and 16 Heavier Elements *via* a Common 1,6-Dilithium Intermediate

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Fully unsaturated group 14 (Si, Ge, and Sn), group 15 (P, As, Sb, and Bi) and group 16 (S, Se, and Te) 2-trimethylsilyl-1-benzoheteroepines (16a—j), including the first isolated examples of bismepines, have been prepared by reaction of the corresponding electrophilic metal reagents (MX_2 or MX_4; M=group 14, 15, and 16 heavier elements) with the key 1,6-dilithium intermediate (9), generated from the common starting compound (*Z*,*Z*)-1-bromo-4-(2-bromophenyl)-1-trimethylsilyl-1,3-butadiene (14) by treatment with *tert*-butyllithium. The trimethylsilyl group in 16b—j was readily removed by treatment with tetrabutylammonium fluoride to give the desired C-unsubstituted 1-benzoheteroepines (1b—j). Single crystal X-ray analyses of 1d (P) and 1f (Sb) revealed that the seven-membered rings exist in boat conformations with the heteroatoms at the bows. All obtained C-unsubstituted group 15 and 16 1-benzoheteroepines (1d—j) were thermolabile in solution towards heteroatom extrusion, while heteroepines (16d—j) having the bulky trimethylsilyl group at the 2-position were much more stable than 1d—j. The half-lives of 1d—j estimated from ^{1}H-NMR spectral analysis indicate that the thermal stabilities of 1d—j decrease in the order 1f (Sb)>1d (P)>1e (As)>1g (Bi) in the group 15 heteroepines and 1j (Te)>1i (Se)>1h (S) in the group 16 heteroepines.

Key words C-unsubstituted 1-benzoheteroepine; 2-trimethylsilyl-1-benzoheteroepine; group 14, 15, 16 heavier element; 1,6-dilithium intermediate; thermal stability; X-ray crystallography

The synthesis of new fully unsaturated seven-membered heterocyclic rings (heteroepines) containing main group heavier elements other than nitrogen, oxygen or sulfur has recently received increasingly intensive study, and a variety of monocyclic and fused heteroepines containing group 14 (Si,[1] Ge,[2] and Sn[2,3]), group 15 (P,[4] As,[5] and Sb[5,6]), and group 16 (S,[7] Se,[8] and Te[9]) elements have been prepared. With regard to benzoheteroepines, up until the early 1990s, various 3-benzoheteroepines (benzo[*d*]heteroepines) containing Si,[1b] Sn,[3b] P,[4b] Sb,[5] and Te[9] had been prepared, however, 1-benzoheteroepines (benzo[*b*]heteroepines) containing main group heavier elements had not been reported, except for 1-benzothiepines.[10] Therefore, we were interested in the synthesis of such group 1-benzoheteroepines and have already reported the syntheses of several novel 1-benzoheteroepines by the two different routes shown in Chart 1.

1-Benzoheteroepines (**1**) containing group 14 (Si and Ge) and group 15 (P and As) elements have been prepared by thermal valence isomerization of the dihydrocyclobut[*b*]-1-benzoheteroles (**2**), derived from the corresponding 1-benzoheteroles *via* three steps.[11] Group 14 (Sn) and group 16 (S, Se, and Te) 2-alkyl-1-benzoheteroepines (**3**) were obtained by intramolecular cyclization of intermediates (**4**), derived from 4-alkyl-1-(2-bromophenyl)but-1-en-3-ynes *via* three steps.[12] However, these routes are fairly limited and not versatile; the latter route provides only 2-alkyl-1-benzoheteroepines and no C-unsubstituted parent rings. We report here a versatile synthetic route to group 14 (Si, Ge, and Sn), group 15 (P, As, Sb, and Bi), and group 16 (S, Se, and Te) 1-benzoheteroepines involving the first isolated examples of several C-unsubstituted parent rings, all of which can be obtained from a common starting compound, and the thermal stability of these heterocyclic rings.

Results and Discussion

Synthesis We have shown that 1,4-dilithium intermediate (**7**), formed from ethynylbenzene (**5**) *via* the (*Z*)-β-bromo-β-trimethylsilylstyrene (**6**), reacts with electrophilic metal reagents (M or MX_2, see Chart 2) to give the corresponding 1-benzoheteroles (**8**).[14] In the route to **8** from **5**, the trimethylsilyl (TMS) group is essential since it has two important roles. The presence of the TMS group induces regio- and stereo-selective formation of the (*Z*)-β-bromostyrene (**6**) from **5**, and stabilizes the key dianion intermediate (**7**). Finally, the TMS group can be readily removed to yield the C-unsubstituted parent 1-benzoheteroles (**8**). The results led us to examine application of the present synthetic route to the title 1-benzoheteroepines (**1**) *via* the 1,6-dilithium intermediate (**9**).

The present synthetic route is shown in Chart 3. *o*-Bromocinnamic acid (**10**),[15] prepared from *o*-bromoiodobenzene or *o*-bromobenzaldehyde, was brominated with bromine in carbon tetrachloride to give 2,3-dibromo-3-(2-bromophenyl)-propionic acid (**11**) in an almost quantitative yield. Treatment of the acid (**11**) with sodium hydrogencarbonate in refluxing acetone resulted in elimination with decarboxylation to give (*Z*)-β,*o*-dibromostyrene (**12**)[16] stereoselectively in 95% yield. Compound **12** was coupled[17] with trimethylsilylacetylene in diethylamine in the presence of a catalytic amount of a mixture of bis(triphenylphosphine)palladium dichloride and copper(I) iodide to afford (*Z*)-1-(2-bromophenyl)-4-trimethylsilyl-1-buten-3-yne (**13**) in 88% yield. The enyne (**13**) was hydraluminated[18] with diisobutylaluminum hydride (DIBAL-H) followed by bromination with *N*-bromosuccinimide (NBS) giving a mixture of the desired (*Z*,*Z*)-1-bromo-4-phenyl-1,3-butadiene derivative (**14**) and its (*Z*,*E*)-stereoisomer (**15**) in a ratio 10 : 1 in *ca.* 60% yield. The ratio was determined by gas-liquid chromatography analysis of the mixture and the stereochemistry of the diene functions was elucidated by ^{1}H-NMR spectral analysis [$J_{3,4}$=11.5 Hz (*cis*) for **14** and 15.8 Hz (*trans*) for **15**; nuclear Overhauser effect (NOE) was observed between 2-H and the TMS protons in

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both **14** and **15**, indicating that their C1–C2 bonds have the (*Z*)-stereochemistry]. It was difficult to separate these isomers, hence only small amounts of **14** and **15** could be isolated in a pure state by repeated column chromatography, and upon heating the mixture at *ca.* 150 °C for vacuum distillation, the (*Z*,*Z*)-isomer (**14**) isomerized to the (*E*,*Z*)-isomer (**15**). Therefore, the mixture was used in the following reaction without separation.

The key common starting compound (**14**) was treated with a large excess (5—6 mol eq) of *tert*-butyllithium in dry ether under an argon atmosphere, followed a reagent (MX_2 or MX_4, see Table 1) resulting in ring closure to form the 2-trimethylsilyl-1-benzoheteroepines (**16a**—**j**) containing group 14, 15, and 16 heavier elements, presumably *via* the 1,6-dilithium intermediate (**9**). The phosphepine (**16d**) formed in this reaction was susceptible to air oxidation and a part of it was isolated as its P-oxide (**16d′**), which was deoxygenated back to **16d** by treatment with trichlorosilane without difficulty. The TMS group in **16** was readily removed by treatment with tetrabutylammonium fluoride (TBAF) in THF containing water to give the desired C-unsubstituted 1-benzoheteroepines (**1b**—**j**) in the yields shown in Table 2, except for the silepine (**16a**), which decomposed to give no characterizable products.

Structure of the 1-Benzoheteroepines As noted in the introduction, C-unsubstituted benzosilepine (**1a**), benzogermepine (**1b**), benzophosphepine (**1d**), and benzarsepine (**1e**) have been prepared by us,[11] and benzothiepine (**1h**)[10] has been reported by manipulations at temperatures below

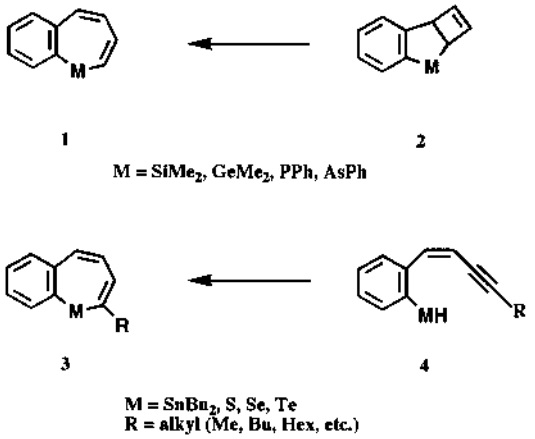

Chart 1

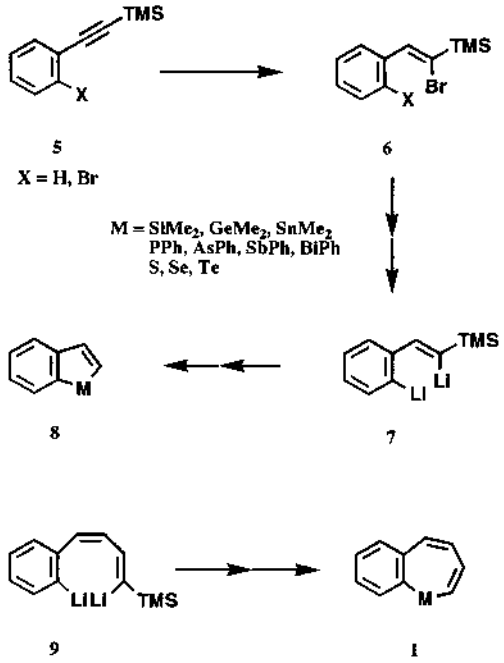

Chart 2

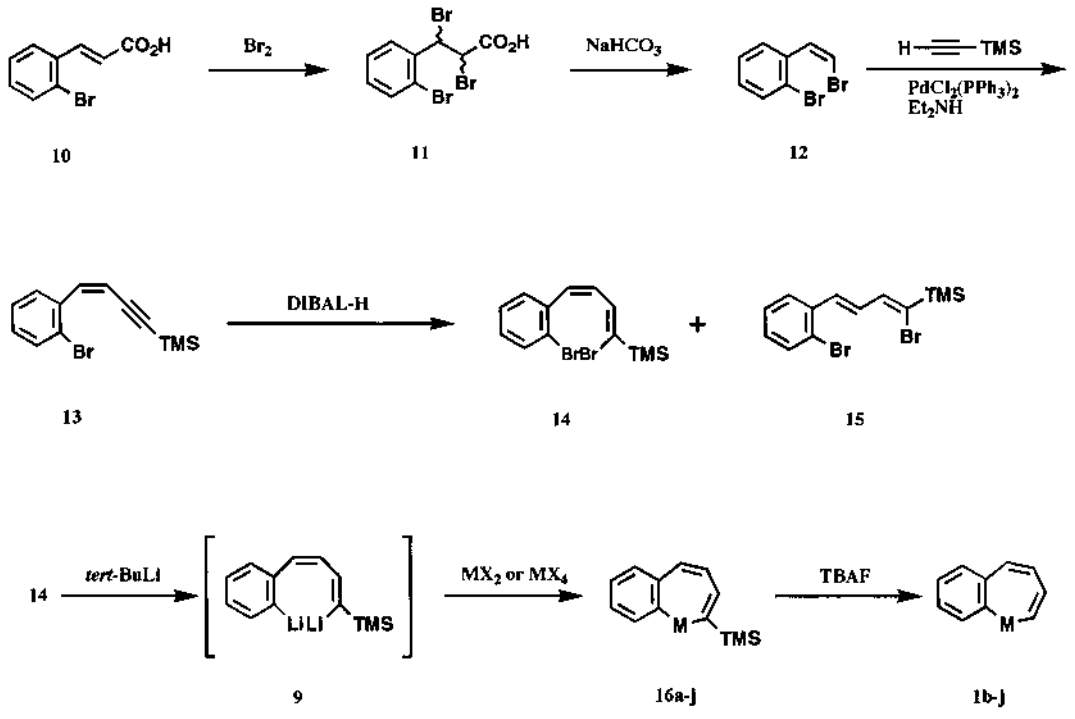

Chart 3

Table 1. 2-Trimethylsilyl-1-benzoheteroepines (**16**)

Compd. No.	M	Reagent (MX_2 or MX_4)	Yield[a] (%)	Appearance	Formula	HR-MS (*m/z*: M^+) Calcd	Found
16a	$SiMe_2$	Me_2SiCl_2	45	Oil[b]	$C_{15}H_{22}Si_2$	258.1260	258.1252
16b	$GeMe_2$	Me_2GeCl_2	47	Oil[b]	$C_{15}H_{22}GeSi$	304.0701	304.0697
16c	$SnMe_2$	Me_2SnCl_2	11	Oil[b]	$C_{15}H_{22}SiSn$	350.0513	350.0521
16d	PPh	$PhPCl_2$	12[c]	Oil[d]	$C_{19}H_{21}PSi$	308.1150	308.1149
16e	AsPh	$PhAsCl_2$	28	72—74[e]	$C_{19}H_{21}AsSi$	352.0630	352.0631[f]
16f	SbPh	$PhSbCl_2$	59	50—52[e]	$C_{19}H_{21}SbSi$	398.0450	398.0451[f]
16g	BiPh	$PhBiBr_2$	34	87—89[g]	$C_{19}H_{21}BiSi$	486.1156	486.1158[f]
16h	S	$(PhSO_2)_2S$	29	Oil[d]	$C_{13}H_{16}SSi$	232.0742	232.0743
16i	Se	$(PhSO_2)_2Se$	29	Oil[d]	$C_{13}H_{16}SSe$	280.0186	280.0192
16j	Te	$TeCl_4$	18	Oil[d]	$C_{13}H_{16}SiTe$	330.0091	330.0069

a) Isolated yields. *b*) Colorless viscous oil. *c*) A part of **16d** was isolated as its oxide (**16d′**, 28% yield) due to air oxidation. *d*) Pale yellow viscous oil. *e*) Colorless prisms from MeOH. *f*) Satisfactory elemental analyses were also obtained for the crystalline compounds (**16e**—**g**). *g*) Pale yellow prisms from MeOH.

Table 2. 1-Benzoheteroepines (**1**)

Compd. No.	M	Yield[a] (%)	Appearance	Formula	HR-MS (*m/z*: M^+) Calcd	Found
1a	$SiMe_2$	—				
1b	$GeMe_2$	68	Oil[b]	$C_{12}H_{14}Ge$	232.0305	232.0306
1c	$SnMe_2$	55	Oil[b]	$C_{12}H_{14}Sn$	278.0117	278.0115
1d	PPh	44	mp 84.5—85.5 °C[c]	$C_{16}H_{13}P$	236.0755	236.0757
1e	AsPh	83	Oil[b]	$C_{16}H_{13}As$	280.0234	280.0237
1f	SbPh	94	mp 38—39 °C[d]	$C_{16}H_{13}Sb$	326.0054	326.0055
1g	BiPh	71	Oil[e]	$C_{16}H_{13}Bi$	414.0761	414.0760
1h	S	26	Oil[e]	$C_{10}H_8S$	160.0347	160.0359
1i	Se	61	Oil[e]	$C_{10}H_8Se$	207.9790	207.9787
1j	Te	64	Oil[e]	$C_{10}H_8Te$	257.9695	257.9687

a) Isolated yields. *b*) Colorless viscous oil. *c*) Yellow prisms from EtOH. *d*) Colorless prisms from hexane. *e*) Pale yellow viscous oil.

Table 3. ^{1}H-NMR Spectral Data for the 2-Trimethylsilyl-1-benzoheteroepines (**16**)

(400 MHz, $CDCl_3$, δ)

Compd. No.	3-H (d)	4-H (dd)	5-H (d)	$J_{3,4}$ (Hz)	$J_{4,5}$ (Hz)	$SiMe_3$ (s)	Ar-H (m)	M-Me_2 (s)
16a (Si)	7.08	6.51	6.98	5.9	13.2	0.18	7.41—7.55 (4H)	0.35
16b (Ge)	6.96	6.39	6.87	5.9	13.2	0.14	7.36—7.50 (4H)	0.47
16c (Sn)	7.09	6.35	6.81	5.1	13.6	0.12	7.30—7.50 (4H)	0.39
16d (P)	7.13[a]	6.37[b]	6.77	5.8	12.5	0.29[c]	6.85—7.97 (9H)	
16e (As)	7.12	6.13	6.51	5.9	12.8	0.25	7.00—7.77 (9H)	
16f (Sb)	7.29	6.23	6.71	5.5	13.2	0.09	7.25—7.55 (9H)	
16g (Bi)	8.94	6.07	6.63	5.5	13.2	0.00	7.26—7.87 (9H)	
16h (S)	6.65	6.48	7.08	5.1	11.7	0.21	7.23—7.37 (4H)	
16i (Se)	6.86	6.42	7.03	5.1	12.5	0.19	7.16—7.44 (4H)	
16j (Te)	7.14	6.39	7.01	5.1	12.8	0.17	7.15—7.68 (4H)	

a) Double doublet, J_{P3}=18.0 Hz. *b*) Double double doublet, J_{P4}=1.1 Hz. *c*) Doublet, J_{PSiMe}=0.7 Hz.

−10 °C. However the benzostannepine (**1c**), benzostibepine (**1f**), benzobismepine (**1g**), benzoselenepine (**1i**), benzotellurepine (**1j**), and all 2-trimethylsilylbenzoheteroepines (**16a**—**j**) are new compounds, and in particular **1g** and **16g** are the first isolated examples of bismepines. The new compounds were characterized mainly by comparison of their mass (Tables 1 and 2) and ^{1}H-NMR (Tables 3 and 4) spectral data with those of the known 1-benzoheteroepines.

The chemical shifts of the heteroepine ring protons in the C-unsubstituted benzoheteroepines (**1**) are sensitive to a change in the heteroatom and some regularities exist. In same group heteroepines, 2- and 3-protons of heteroepines containing elements in higher horizontal order-rows of the periodic table resonate at lower fields than those containing elements in lower order-rows, except for the 3-proton of **1b**. Furthermore, the 2-protons always resonate at higher fields than the 3-protons. For example, the values of the chemical shifts of both the 2- and 3-protons of the group 15 heteroepines (**1d**—**g**) increase in the order **1d** (P)<**1e** (As)<**1f** (Sb)<**1g** (Bi); this tendency is in accord with the Lewis acidity of the hetero atoms. In contrast, those of the both 4- and 5-protons decrease in the reverse order. These results imply that the hetero atom in **1** acts as a π acceptor for the C2–C3 double bond but not for the C4–C5 bond. It was also apparent that the magnitude of the coupling constant between the 2- and 3-protons ($J_{2,3}$) in **1** varies with the vertical position of

Table 4. ^{1}H-NMR Spectral Data for the 1-Benzoheteroepines (**1**)

(400 MHz, $CDCl_3$, δ)

Compd. No.	M	2-H (d)	3-H (dd)	4-H (dd)	5-H (d)	$J_{2,3}$ (Hz)	$J_{3,4}$ (Hz)	$J_{4,5}$ (Hz)	Ar-H (m)	M-Me_2 (s)
1a[a]	$SiMe_2$	5.88	6.79	6.30	6.91	14.3	5.9	13.2	7.30—7.51 (4H)	0.29
1b	$GeMe_2$	5.97	6.71	6.26	6.81	13.2	5.8	13.2	7.28—7.37 (4H)	0.38
1c	$SnMe_2$	6.24	6.91	6.29	6.83	13.6	5.5	13.6	7.30—7.44 (4H)	0.36
1d	PPh	6.07[b]	6.52[b]	6.55	7.16	11.4	5.5	12.1	7.32—8.13 (9H)	
1e	AsPh	6.17	6.66	6.46	7.05	11.2	5.3	12.5	6.69—7.68 (9H)	
1f	SbPh	6.34	6.94	6.44	7.00	11.8	5.0	13.0	6.90—7.75 (9H)	
1g	BiPh	7.39	8.26	6.29	6.87	11.1	4.9	13.0	7.23—8.02 (9H)	
1h	S	5.89	6.40	6.43	7.07	8.1	5.5	12.1	7.17—7.34 (4H)	
1i	Se	6.18	6.65	6.36	7.03	8.8	5.5	12.5	7.17—7.41 (4H)	
1j	Te	6.59	7.00	6.35	7.04	9.9	5.1	12.8	7.17—7.65 (4H)	

a) The silepine was prepared by the different route previously reported by us.[11] *b*) These protons are also coupled with P: J_{P2}=12.0 Hz, J_{P3}=41.0 Hz.

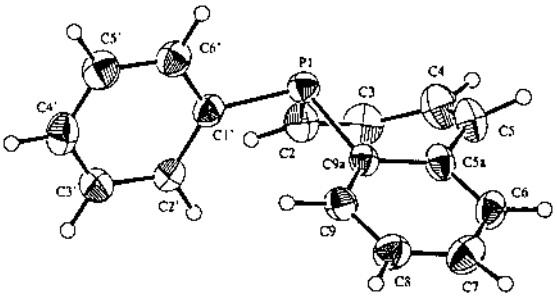

Fig. 1. ORTEP Drawing of **1d**

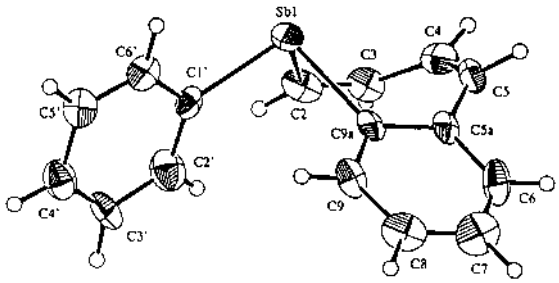

Fig. 2. ORTEP Drawing of **1f**

Selected bond lengths (Å) and angles (°) of **1d**

Bond lengths		Bond angles	
P1–C1′	1.828(6)	C1′–P1–C2	102.0(3)
P1–C2	1.797(6)	C1′–P1–C9a	103.9(3)
P1–C9a	1.829(6)	C2–P1–C9a	99.4(3)
C2–C3	1.331(8)		
C3–C4	1.46(1)		
C4–C5	1.35(1)		
C5–C5a	1.45(1)		
C5a–C9a	1.403(7)		

Selected bond lengths (Å) and angles (°) of **1f**

Bond lengths		Bond angles	
Sb1–C1′	2.14(1)	C1′–Sb1–C2	96.3(5)
Sb1–C2	2.25(2)	C1′–Sb1–C9a	93.9(4)
Sb1–C9a	2.23(1)	C2–Sb1–C9a	85.8(6)
C2–C3	1.28(2)		
C3–C4	1.47(2)		
C4–C5	1.33(2)		
C5–C5a	1.47(2)		
C5a–C9a	1.42(2)		

the elements in the periodic table, and decreases in the order: group 14 > group 15 > group 16 elements. This decreasing order is the same as that observed for vicinal coupling constants $J_{2,3}$ in group 14, 15, and 16 1-benzoheteroles.[11] These results can be explained by the variation of the electronegativity of the elements to some extent. According to a recent study by Sakurai,[1a] the magnitude of the vicinal coupling constant $J_{3,4}$ in the cyclohexatriene system, including heteroepines, is related to the bent angle (β) (Fig. 3) between the base plane (C2–C3–C5a–C9a) and the stern plane (C3–C4–C5–C5a), and the magnitude of $J_{3,4}$ should decrease when the bent angle (β) increases. The observed values of $J_{3,4}$ [**1d** (P): 5.5 Hz>**1e** (As): 5.3 Hz>**1f** (Sb): 5.0 Hz>**1g** (Bi) 4.9 Hz] imply that the angle (β) should increase in the order **1d** (P)<**1e** (As)<**1f** (Sb)<**1g** (Bi). Consequently, all of the heteroepines **1b**—**g** obtained in the present study are inferred to have a boat conformation, and the bent angle (β) should increase for higher horizontal order-row members of the periodic table, and for the elements in same group heteroepines.

The X-ray crystal structures of **1d** (P) and **1f** (Sb) are shown in Figs. 1 and 2, together with selected bond lengths and angles, which show that the seven-membered heteroepine rings exist in boat conformations with the heteroatoms at the bows, as are observed in the structures of other heteroepines such as 1,2-diazepines[19a] and 1-benzothiepine (**1h**).[19b] The analysis of thiepine (**1h**) was conducted at extreme low temperature (−140 °C) and its bond lengths and angles have also been reported. The above data for **1d**, **1f**, and **1h** indicate that with the increase in the M–C2 bond length (S–C2: 1.781 Å<P–C2: 1.797 Å<Sb–C2: 2.25 Å), the C2–M–C9a angle (C2–S–C9a: 101.1°>C2–P–C9a: 99.4°> C2–Sb–C9a: 85.8°) decreases and the boat form becomes more folded and the bent angle (β) [**1h** (S): 30.0°<**1d** (P): 30.3°<**1f** (Sb): 38.7°] increases. These alternations of the β value consistent with the estimation derived from the magnitudes of $J_{3,4}$ noted above are ascribable to the release of inner angle strain in the seven-membered ring. As to the bent angle (α) [**1h**: 49.1°, **1d**: 54.4°, **1f**: 48.6°] between the base plane and the bow (C2–M–C9a), no significant regularity was observed in the present data. Of course, the most prominent difference in their structures is the M–C bond length and the lengths of the rest of the triene-part of the heteroepine ring remain essentially the same. In addition, bond alternation is

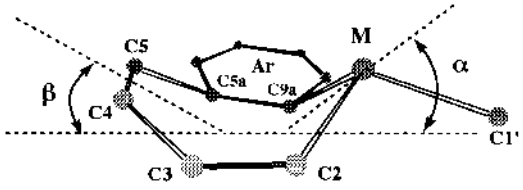

Fig. 3

Table 5. Half-Lives and Activation Energies of **1**

Compd. No.	$t_{1/2}$ min[a] at 60 °C (toluene)	*Ea*/Kcal mol^{-1}
1d (P)	519	25.0
1e (As)	67	23.0
1f (Sb)	837	26.5
1g (Bi)	7[b]	21.2
1h (S)	15[c]	23.7
1i (Se)	37	23.5
1j (Te)	433	26.3

a) The disappearance of **1** and the appearance of naphthalene were monitored by ^{1}H-NMR integration and the values of *Ea* were calculated from Arrhenius plots of the first-order rate constants obtained. *b*) 150 min at 30 °C. *c*) 478 min at 30 °C.

clearly observed in the C–C bonds of the heteroepine ring. The bond lengths of the C2–C3 (**1d**: 1.33 Å and **1f**: 1.28 Å) and C4–C5 (**1d**: 1.35 Å and **1f**: 1.33 Å) show that they are double bonds, while the bond lengths of the C3–C4 (**1d**: 1.46 Å and **1f**: 1.47 Å) and C5–C5a (**1d**: 1.45 Å and **1f**: 1.47 Å) are approximately equal to those of C(sp^2)–C(sp^2) single bonds. These bond lengths are comparable to those of cycloheptatrienes (1.33—1.46 Å). The P–C (1.80—1.83 Å) and Sb–C (2.15—2.25 Å) distances show single bond character.

Thermal Stability All C-unsubstituted group 15 and 16 1-benzoheteroepines (**1**) obtained were thermolabile in solution towards heteroatom extrusion and gradually decompose to naphthalene even at room temperature, as do 3-benzoheteroepines containing heavier elements and 1-benzothiepines involving **1h**,[7] however, in dry pure forms they can be kept for several days in a refrigerator without decomposition. The half-lives and activation energies of group 15 and 16 C-unsubstituted heteroepines (**1d**—**j**) estimated from ^{1}H-NMR spectral data are listed in Table 5. In group 15 heteroepines (**1d**—**g**), the stibepine (**1f**) is surprisingly the most stable and the stabilities of the other heteroepines decrease in the order **1d** (P)>**1e** (As)>**1g** (Bi); **1g** with the heaviest Bi atom analog being least stable. In contrast, in the group 16 heteroepines (**1h**—**j**), the stabilities decrease in the reverse order **1h** (S)<**1i** (Se)<**1j** (Te) and the heaviest Te compound (**1j**) is the most stable of the three. The group 14 heteroepines (**1a**—**c**) are relatively stable and remained largely unchanged even when heated at 110 °C in toluene for 20 h.

On the other hand, all heteroepines (**16a**—**j**) having the bulky TMS group in the 2-position are much more stable than the 2-unsubstituted heteroepines (**1**). The half-life of **16g** (Bi), presumed to be the most unstable amongst **16a**—**j**, was 82 min at 60 °C, which is about twelve times longer than that of **1g** (7 min at 60 °C), and the other trimethylsilyl-heteroepines (**16**) are relatively stable and can be kept several weeks at room temperature without decomposition even in solution, except for **16h** (S), which gradually decomposes and can be kept for only several days. It is well known that the stability of heteroepine rings is enhanced by introduction of bulky groups in α-positions. For example, monocyclic thiepines and selenepines having no bulky groups in α-positions are too unstable to be isolated, but their 2,7-di-*tert*-butyl derivatives can be isolated.[8,21] The half-life of 2-methyl-1-benzothiepine (660 min at 35 °C)[20b] is several times longer than that of the parent 1-benzothiepine (**1h**) (150 min at 30 °C) and 2-*tert*-butylthiepine is very stable in solution.[12]

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra (MS) and high-resolution mass spectra (HR-MS) were recorded on a JEOL JMP-DX300 instrument. NMR spectra were determined with a JEOL PMX-60SI (60 MHz) or JEOL JNM-GSX-400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were performed in the Microanalytical Laboratory of this Faculty by Mrs. K. Shiratori and C. Kuroda.

2,3-Dibromo-3-(2-bromophenyl)propionic Acid (11) A solution of Br_2 (16.0 g, 100 mmol) in CCl_4 (100 ml) was added dropwise over a 5 h period to a refluxing solution of *o*-bromocinnamic acid (**10**, 21.6 g, 95 mmol) in CCl_4 (500 ml). The mixture was refluxed with stirring for 2 h and then cooled in an ice bath. The resulting precipitates were collected by filtration and recrystallized from benzene to give **11**: 34.9 g, 95% yield, colorless prisms, mp 194—199 °C. ^{1}H-NMR (60 MHz, $CDCl_3$–CD_3OD) δ: 4.95 (1H, d, J=11.6 Hz, 3-H), 5.95 (1H, d, J=11.6 Hz, 2-H), 7.0—7.9 (4H, m, Ph-H). IR (KBr) cm^{-1}: 1724 (C=O). MS *m/z*: 388 (M$^+$). *Anal.* Calcd for $C_9H_7Br_3O_2$: C, 27.94; H, 1.82. Found: C, 27.67; H, 1.78.

***(Z)*-β,*o*-Dibromostyrene (12)** A mixture of **11** (32.2 g, 84 mmol), $NaHCO_3$ (21 g, 260 mmol) and acetone (400 ml) was refluxed with stirring for 12 h and then evaporated *in vacuo*. Water (200 ml) was added to the residue and the whole was extracted with ether (200 ml×2). The combined extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated *in vacuo*. The residue was vacuum-distilled to give **12**: 21.0 g, 95%, pale yellow oil, bp 101—104 °C (5 mmHg). ^{1}H-NMR (60 MHz) δ: 6.53 (1H, d, J =7.6 Hz, β-H),7.26 (1H, d, J=7.6 Hz, α-H) 7.1—8.0 (4H, m, Ph-H). HR-MS *m/z*: 259.8838 (Calcd for $C_8H_6Br_2$: 259.8837). MS *m/z*: 260 (M$^+$).

***(Z)*-1-(*o*-Bromophenyl)-4-trimethylsilyl-1-buten-3-yne (13)** Trimethylsilylacetylene (15.5 ml, 110 mmol) was added dropwise with stirring to a mixture of **12** (26.2 g, 100 mmol), bis(triphenylphosphine)palladium dichloride (345 g, 0.5 mmol), copper(I) iodide (230 mg, 1.9 mmol), and diethylamine (130 ml) in an ice bath. The mixture was further stirred for 3 h at *ca.* 0 °C then evaporated *in vacuo*. Cold water (200 ml) was added to the residue and the whole was extracted with ether (200 ml×2). The combined extract was successively washed with water (200 ml×2) and brine (200 ml), dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel with hexane to give **13**, which was further purified by vacuum-distillation. **13**: 24.5 g, 88% yield, pale yellow oil, bp 130 °C (3 mmHg). ^{1}H-NMR (400 MHz) δ: 0.17 (9H, s, $SiMe_3$), 5.83 (1H, d, J=12.0 Hz, 2-H), 7.10 (1H, d, J=12.0 Hz 1-H), 7.1—8.5 (4H, m, Ph-H). IR (neat) cm^{-1}: 2144 (C≡C). HR-MS *m/z*: 278.0127 (Calcd for $C_{13}H_{15}BrSi$: 278.0126). MS *m/z*: 278 (M$^+$)

***(Z,Z)*-1-Bromo-4-(2-bromophenyl)-1-trimethylsilyl-1,3-butadiene (14) and *(Z,E)*-Isomer (15)** A DIBAL-H hexane solution (0.93 M, 120 ml, 111.6 mmol) was added dropwise with stirring to a solution of **13** (20.6 g, 73.8 mmol) in hexane (250 ml) under an argon atmosphere at room temperature. The mixture was stirred for an additional 50 h, and then NBS (16.2 g, 91 mmol) was added in small portions over a 1.5 h period with stirring in a MeOH-ice bath (*ca.* −20 °C). After stirring for a further 6 h at the same temperature, the reaction mixture was diluted with cold water (200 ml). The separated organic layer was washed with brine, dried, and evaporated *in vacuo*. Vacuum-distillation (bp 90—94 °C, 0.02 mmHg) of the residue give a mixture of **14** and **15** (15.6 g, 59% yield, 14 : 15=10 : 1; the ratio was estimated by GLC analysis). It was difficult to separate **14** and **15** and thus the mixture was used in the following reaction without separation. However, the mixture could be separated by repeated chromatography on silica gel with hexane to give analytical samples of **14** and **15** as pale yellow oils.

14: ^{1}H-NMR (400 MHz) δ: 0.17 (9H, s, $SiMe_3$), 6.73 (1H, d, 1-H), 6.77

(1H, dd, 2-H), 7.04 (1H, d, 3-H), 7.2—7.6 (4H, m, Ph-H), $J_{2,3}$=8.4, $J_{3,4}$=11.5 Hz. HR-MS *m/z*: 357.9393 (Calcd for $C_{13}H_{16}Br_2Si$: 357.9389).

15: ^{1}H-NMR (400 MHz) δ: 0.26 (9H, s, $SiMe_3$), 6.98 (1H, d, 3-H), 7.14 (1H, d, 1-H), 7.20 (1H, dd, 2-H), 7.1—7.7 (4H, m, Ph-H), $J_{2,3}$=8.8, $J_{3,4}$=15.8 Hz. HR-MS *m/z*: 357.9388 (Calcd for $C_{13}H_{16}Br_2Si$: 357.9389).

2-Trimethylsilyl-l-benzoheteroepines (16a—j) General Procedure: A solution of **14** (720 mg, 2 mmol) in anhydrous ether (20 ml) was added dropwise over a 45 min period with stirring to a *tert*-butyllithium ether solution (1.6 M, 7.5 ml, 12 mmol) at −80 °C under an argon atmosphere, and the mixture was then warmed slowly to −20 °C with stirring and cooled again to −80 °C. A solution of a metal reagent (Me_2SiCl_2, Me_2GeCl_2, Me_2SnCl_2, $PhPCl_2$, or $PhAsCl_2$: 3 mmol) in anhydrous ether (20 ml) or a neat metal reagent [$PhSbCl_2$, $PhBiBr_2$, $(PhSO_2)_2S$, $(PhSO_2)_2Se$, or $TeCl_4$ powder: 3 mmol; since they are insoluble in ether] was added dropwise or in small portions with stirring over a 30 min period to the above reaction mixture at −80 °C. After stirring for an additional 1.5 h, the mixture was allowed to warm to room temperature and stirred for 5 h, then pentane (100 ml) and water (50 ml) were added with stirring. The layers were separated and the aqueous layer was extracted with pentane (100 ml×2). The combined organic layer was washed with brine, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel with hexane to give **16**. In the case of **16d**, further elution of the column with a mixture of CH_2Cl_2–acetone (5 : 1) afforded 1-phenyl-2-trimethylsilyl-1-benzophosphepine 1-oxide (**16d′**) in 28% yield. The 2-trimethylsilyl-1-benzoheteroepines (**16a**—**j**) thus obtained are listed together with their yields and HR-MS analytical data in Table 1. ^{1}H-NMR spectral data are collected in Table 3.

1-Phenyl-2-trimethylsilyl-1-benzophosphepine 1-Oxide (**16d′**): Colorless prisms, mp 139—140 °C (benzene). ^{1}H-NMR (400 MHz) δ: 0.40 (9H, s, $SiMe_3$), 6.35 (1H, ddd, 4-H), 6.89 (1H, d, 5-H), 7.05 (1H, dd, 3-H), 7.19—8.44 (9H, m, Ph-H), J_{P3}=42.5 Hz, J_{P4}=1.8 Hz, $J_{3,4}$=5.9 Hz, $J_{4,5}$=12.8 Hz. HR-MS *m/z*: 324.1096 (Calcd for $C_{19}H_{21}OPSi$: 324.1099). MS *m/z*: 324 (M^+). *Anal.* Calcd for $C_{19}H_{21}OPSi$: C, 70.34; H, 6.52. Found: C, 70.39; H, 6.47.

Reduction of 1-Phenyl-2-trimethylsilyl-1-benzophosphepine 1-Oxide (16d′) with Trichlorosilane All solvents employed in this reaction were deaerated by bubbling with argon gas. A $SiHCl_3$ benzene solution (1.4 M, 0.6 ml, 0.8 mmol) was added to a solution of **16d′** (97 mg, 0.3 mmol) in benzene (10 ml) and the mixture was stirred under an argon atmosphere at 80 °C for 1 h. The mixture was diluted with benzene (50 ml) and stirred with aqueous 8% NaOH (10 ml) for 5 min in an ice bath. The separated benzene layer was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–benzene (10 : 1) to give **16d**: 67 mg, 78% yield.

1-Benzoheteroepines (1b—j) General Procedure: A tetrahydrofuran (THF) solution of tetrabutylammonium fluoride (TBAF) (1.0 M, 3 mol eq) containing 5% water was added dropwise to a solution of **16** (60—70 mg) in THF (5 ml) with stirring under an argon atmosphere in an ice bath, and the reaction mixture was stirred for an additional 1.0—1.5 h except for the reaction of **16b** and **16c**, which were heated with stirring at 60 °C for 4—5 h. After addition of pentane (30 ml) and water (20 ml), the mixture was stirred for 10 min and the organic layer was separated. The aqueous layer was extracted with pentane (30 ml×2). The combined organic layer was washed with brine, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel with pentane to give **1**. However, the 2-trimethylsilyl-1-benzosilepine (**16a**) on treatment with TBAF, underwent decomposition to give no characterizable products. The 1-benzoheteroepines (**1b**—**j**) thus obtained are listed together with their yields and HR-MS analytical data in Table 2. ^{1}H-NMR spectral data are collected in Table 4.

Crystallography of 1-Benzophosphepine (1d) A single crystal (0.30×0.30×0.10 mm) of **1d** was obtained by recrystallization from EtOH. Crystal data of **1d**: $C_{16}H_{13}P$, M.W.=236.25, pale yellow prismatic, orthorhombic, space group Fdd2 (#43), a=14.118(3) Å, b=46.420(4) Å, c=7.795(3) Å, V=5108(1) Å^3, Z=16, D_{calc}=1.229 g/cm^3, μ(CuK_α)=16.70 cm^{-1}. The R (R_w) value of **1d** was 0.044 (0.083). The data were collected on a Rigaku AFC7R diffractometer at 20±1 °C using graphite monochromated CuK_α (λ=1.54178 Å) radiation. The structure was solved by direct methods[22] and expanded using Fourier techniques.[23] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[24]

Crystallography of 1-Benzostibepine (1f) A single crystal (0.40×0.10×0.10 mm) of **1f** was obtained by recrystallization from hexane. Crystal data of **1f**: $C_{16}H_{13}Sb$, M.W.=327.03, colorless, prismatic, orthorhombic, space group $Pna2_1$(#33), a=7.305(2) Å, b=29.655(5) Å, c=6.161(2) Å, V=1334(1) Å^3, Z=4, D_{calc}=1.627 g/cm^3, μ(CuK_α)=161.25 cm^{-1}. The R (R_w) value of **1f** was 0.038 (0.060). The data were collected on a Rigaku AFC7R diffractometer at 20±1 °C using graphite monochromated CuK_α (λ=1.54178 Å) radiation. The structure was solved by heavy-atom Patterson methods[25] and expanded using Fourier techniques.[23] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[24]

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