A Versatile Route to 3-Benzoheteroepines Containing Group 15 and 16 Heavier Elements Involving Several Novel Ring Systems, and Their Thermal Stabilities

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The C-unsubstituted 3-benzoheteroepines (2a—g) containing group 15 (P, As, Sb, and Bi) and group 16 (S, Se, and Te) heavier elements were prepared by the reaction of the corresponding metal reagents with (*Z*,*Z*)-*o*-bis(β-lithiovinyl)benzene (5) which was derived in two steps from a common *o*-phthalaldehyde (3). The heteroepines (2) thus obtained were thermally labile towards heteroatom extrusion, and their half-lives on heating estimated from ^{1}H-NMR spectral analysis showed that the 3-benzoheteroepines (2) were far less stable than the corresponding 1-benzoheteroepines (1). The 2,4-bis(trimethylsilyl)-3-benzoheteroepines (17) containing Sb, Bi, and Te were also prepared from *o*-diiodobenzene (9) in 6 steps and were found to be more stable than the corresponding C-unsubstituted heteroepines (2).

Key words 3-benzoarsepine; 3-benzostibepine; 3-benzobismepine; 3-benzoselenepine; valence isomerization; thermal decomposition

We have already reported the syntheses of the 1-benzoheteroepines (**1**) containing group 15 (P, As, Sb, and Bi) and group 16 (S, Se, and Te) heavier elements as well as those comprising group 14 (Si, Ge, and Sn) elements by three different routes.[1—9] For instance, 1-benzophosphepine (**1a**) and 1-benzarsepine (**1b**) have been prepared by thermal valence isomerization of the corresponding 2a,7b-dihydrocyclobuta-[*b*]-1-benzoheteroles[1,2] and the 2-alkyl derivatives of group 16 1-benzoheteroepines have been obtained by intramolecular cyclization of *o*-(but-1-en-3-ynyl)phenylheterols.[3—7] In addition, all 1-benzoheteroepines (**1a**—**h**) could be synthesized from (*Z*,*Z*)-1-bromo-4-(*o*-bromophenyl)buta-1,3-diene, *via* its dilithium intermediate.[8,9] With regard to 3-benzoheteroepines, the phosphepine (**2a**),[10] tellurepine (**2g**),[11] and stannepine (**2h**)[12,13] could be prepared by the reaction of *o*-diethynylbenzene with phenylphosphane, sodium telluride, and dialkylstannanes, respectively. It has also been reported that the 3-alkyl derivatives of the 3-benzostibepine are thermally labile and can be isolated only at low temperature,[14] and the C-unsubstituted arsepine (**2a**)[10] and thiepine (**2e**)[15,16] have also been known to be too thermally unstable to be isolated, although the 3-benzothiepines having alkoxycarbonyl groups in the 2- and/or 4-positions are stable and can be isolated at room temperature.[15—19] While it was considered in heteroepine chemistry that most of heteroepines were relatively unstable and difficult to isolate, we were interested in the synthesis of 3-benzoheteroepines under mild reaction conditions. We report here on a versatile synthetic route to the C-unsubstituted group 15 and 16 3-benzoheteroepines (**2a**—**g**) and 2,4-bis(trimethylsilyl) substituted heteroepines (**17c**, **d**, **g**), all of which can be isolated at room temperature except for 3-benzobismepine (**2d**), and on the thermal stabilities of these novel heterocyclic systems.[20] In the present studies, most of the C-unsubstituted heteroepines (**2b**, **e**, **f**) and C-substituted heteroepines (**17c**, **d**, **g**) are the first isolated examples of heteroepines, and their thermal stabilities were evaluated by use of their half-lives ($t_{1/2}$ at 50 °C) estimated by ^{1}H-NMR analysis.

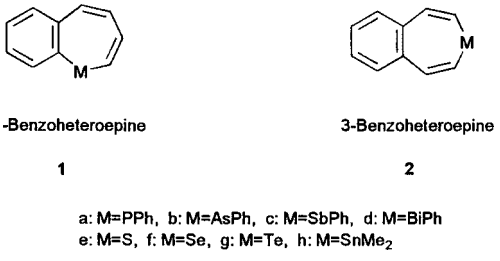

Fig. 1

Results and Discussion

Synthesis of C-Unsubstituted 3-Benzoheteroepines (2a—g) In the preceding papers,[8,9] we have shown that the 1,6-dilithium intermediate, (*Z*,*Z*)-1-lithio-4-(*o*-lithiophenyl)-1-trimethylsilylbuta-1,3-diene, generated from (*Z*,*Z*)-1-bromo-4-(*o*-bromophenyl)-1-trimethylsilylbuta-1,3-diene by treatment with *tert*-butyllithium (*t*-BuLi), reacts with electrophilic metal regents (M or MX_2: M=group 14, 15 and 16 heavier elements) to give the corresponding 2-trimethylsilyl-1-benzoheteroepines which readily afford C-unsubstituted 1-benzoheteroepines (**1**) by detrimethylsilylation with tetrabutylammonium fluoride. This result led us to examine the reaction of (*Z*,*Z*)-*o*-bis(β-lithiovinyl)benzene (**5**) which would be generated from the corresponding dibromo compound (**4**) with the metal reagents, with the aim of obtaining the title 3-benzoheteroepines (**2**).

The key starting compound, (*Z*,*Z*)-*o*-bis(β-bromovinyl)-benzene (**4**), was obtained stereoselectively in high yield (90%) by a double Wittig reaction of *o*-phthalaldehyde (**3**) with bromomethylenetriphenylphosphorane,[21,22] generated *in situ* by the reaction of bromomethyltriphenylphosphonium bromide with potassium *tert*-butoxide in tetrahydrofuran at −80 °C. The (*Z*)-stereostructure of the vinyl function in **4** was confirmed by its ^{1}H-NMR spectral data, in which two vinyl proton signals appeared at δ 6.55 (2H, d, J=10.8 Hz, β-H) and 7.11 (2H, d, J=10.8 Hz, α-H), indicating that the two vinyl groups are *cis*-form.

The dibromo compound (**4**) was treated with excess *t*-

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BuLi in anhydrous diethyl ether at −80 °C under argon atmosphere, and then with an electrophilic metal reagent [$PhPCl_2$, $PhAsCl_2$, $PhSbCl_2$, $PhBiBr_2$, $(PhSO_2)_2S$, $SeCl_4$ or $TeCl_4$] to result in ring closure, giving rise to the desired 3-benzoheteroepines (**2a**—**g**) in the yields shown in Table 1. However, most heteroepines obtained here, except for phosphepine oxide (**2a′**) are thermally labile towards heteroatom extrusion and gradually decomposed to naphthalene during isolation by column chromatography, which is the main reason for the relatively low yields in the isolation of **2** by the present reaction. When deuterium oxide was used instead of the metal reagents in the present reaction, it afforded (*Z*,*Z*)-dideuterio compound (**6**) in 45% yield. This result clearly gives evidence for the intermediacy of the 1,6-dianion species (**5**) in the present reaction. When **5** was treated with selenium or tellurium tetrachloride, the corresponding 3,3-dichloro compounds (**7f**, **g**) might be initially formed, and then dechlorination with excess *t*-BuLi would take place to give **2f** and **2g**. However, all attempts to isolate the intermediate (**7f**, **g**) failed. It would also be possible that the dichloro compounds (**7f**, **g**) thus formed may further react with the starting dilithium compound (**5**) to afford spiro-dimer (**8**), but the formation of **8** could not be observed in the reaction mixture. The phosphepine (**2a**) was susceptible to air oxidation and thus was isolated as its P-oxide (**2a′**),[10] which was, however, readily deoxygenated back to **2a** by treatment with trichlorosilane.[2]

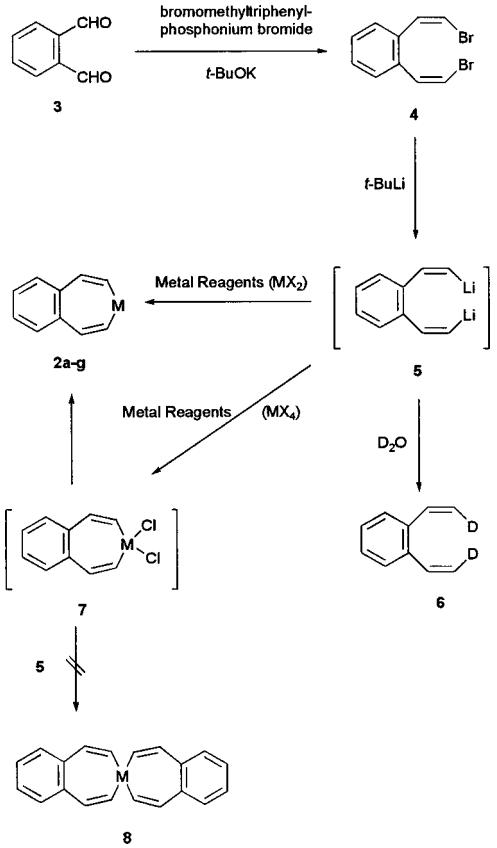

Chart 1

Synthesis of 2,4-Bis(trimethylsilyl)-3-benzoheteroepines (17c, d, g) The 3-benzobismepine (**2d**) thus obtained was extremely thermally unstable and could not be isolated, although it was detected at −20 °C by ^{1}H-NMR spectroscopy. It is well known that the stability of monocyclic heteroepines is enhanced by introduction of a bulky substituent such as a *tert*-butyl group on the α-positions on the heteroepine ring.[15,16,23—27] 1-Benzoheteroepines having a bulky trimethylsilyl group on the 2-position are also much more stable than the corresponding C-unsubstituted heteroepines (**1**).[8,9] In this context, we next performed the synthesis of the 2,4-bis(trimethylsilyl)-3-benzoheteroepines (**17**) which would be more stable than the corresponding C-unsubstituted ones.

o-Diiodobenzene (**9**) was coupled with trimethylsilylacetylene (2.5 eq) in benzene in the presence of diethylamine and a catalytic amount of a mixture of bis(triphenylphosphine)-palladium dichloride and copper(I) iodide to afford *o*-bis(trimethylsilylethynyl)benzene (**10**) in 67% yield.[28] However, treatment of **10** with diisobutylaluminum hydride (DIBAL-H) and *N*-bromosuccinimide (NBS) gave only a complex mixture, and the expected key starting compound, (*Z*,*Z*)-*o*-bis(β-bromo-β-trimethylsilylvinyl)benzene (**14**) could not be obtained. Therefore, each of the iodine moieties on **9** was transformed to a β-bromo-β-trimethylsilylvinyl group one by one to obtain **14**. Namely, diiodobenzene (**9**) was coupled with one equivalent of trimethylsilylacetylene giving rise to *o*-iodo(trimethylsilylethynyl)benzene (**11**). The ethynylbenzene (**11**) was hydraluminated with DIBAL-H in hexane,[29—31] and then brominated with NBS[8,9,32,33] to afford (*Z*)-β-bromo-*o*-iodo-β-trimethylsilylstyrene (**12**) stereoselec-

Table 1. 3-Benzoheteroepines **2** and **17**

Compound	M	Metal reagent	Yield[a] (%)	Appearance (mp/°C)	Formula	HR-MS (*m*/*z*: M^+)	
						Found	Required
2a[b]	PPh	$PhPCl_2$	13[b]	85—87[c,d]	$C_{16}H_{13}P$	236.0757	236.0755
2b	AsPh	$PhAsCl_2$	20	Oil	$C_{16}H_{13}As$	280.0123	280.0234
2c	SbPh	$PhSbCl_2$	25	76—78[c]	$C_{16}H_{13}Sb$	326.0061	326.0054
2d	BiPh	$PhBiBr_2$	20	Oil	$C_{16}H_{13}Bi$	414.0755	414.0761
2e	S	$(PhSO_2)_2S$	15	Oil	$C_{10}H_8S$	160.0483	160.0347
2f	Se	$SeCl_4$	12	Oil	$C_{10}H_8Se$	207.9661	207.979
2g	Te	$TeCl_4$	12	Oil	$C_{10}H_8Te$	257.9652	257.9695
17c	SbPh	$PhSbCl_2$	7	95—97.5[c]	$C_{22}H_{29}SbSi_2$	470.0432	470.0845
17d	BiPh	$PhBiBr_2$	10	Oil	$C_{22}H_{29}BiSi_2$	558.1551	558.1545
17g	Te	$TeCl_4$	11	Oil	$C_{22}H_{29}Si_2Te$	402.1485	402.5376

a) Isolated yields. *b*) Its 3-oxide **2a′** initially formed was deoxygenated by treatment with trichlorosilane to **2a** (see Experimental), and the yield of **2a** was calculated from **4** used. *c*) Recrystallized from MeOH. *d*) Lit.,[10] mp 86—88 °C.

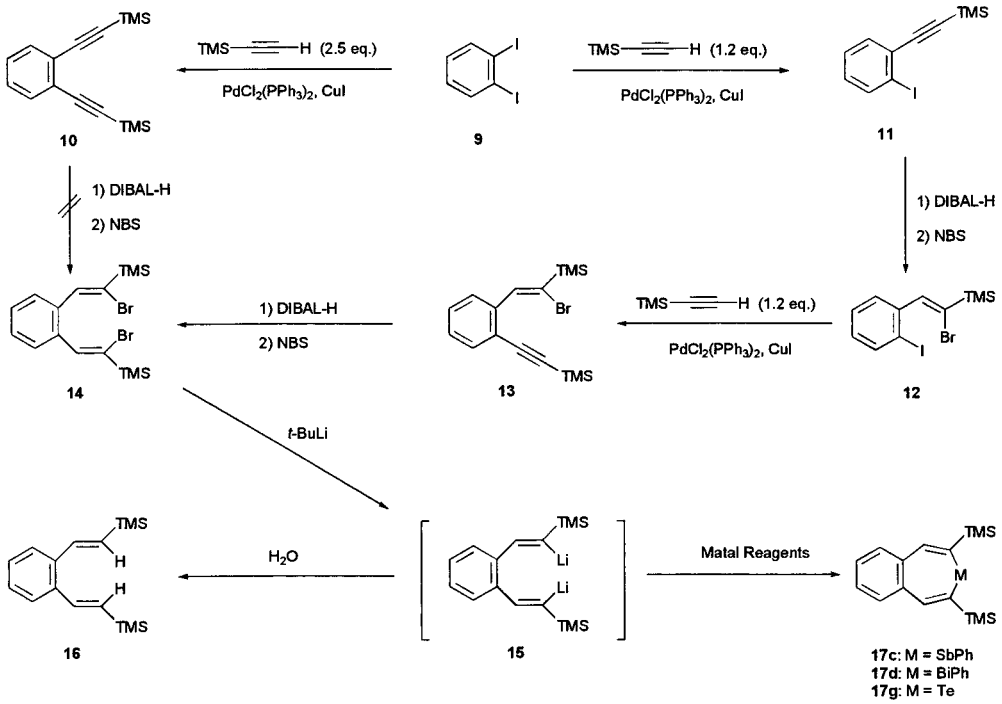

Chart 2

tively. The remaining iodine moiety on **12** was converted to a bromotrimethylsilylethenyl group by the same procedure *via* **13** to afford **14** in 39% yields from **12**. The stereochemistry of the vinyl functions for the compounds **12** and **14** was elucidated to be *Z* configuration by their ^{1}H-NMR spectral analyses; an NOE was observed between vinyl and TMS protons in the both compounds.

The dibromo compound (**14**) was treated with *t*-BuLi in anhydrous diethyl ether, then with water forming *o*-bis(β-trimethylsilylvinyl)benzene (**16**). In the ^{1}H-NMR spectrum of **16**, two vinyl protons appeared at δ 6.36 (2H, d, J=19.1 Hz, β-H) and 7.23 (2H, d, J=19.1 Hz, α-H), indicating not only that the stereochemistry of the vinyl groups on **16** is *trans*, but also that the vinyl function in parent **14** is (*Z*)-form, and the 1,6-dilithium compound (**15**) is clearly formed. These results encouraged us to perform the reaction of **15** with electrophilic reagents. Treatment of **15**, generated *in situ*, with the electrophilic metal reagents ($PhSbCl_2$, $PhBiBr_2$, and $TeCl_4$) resulted in ring closure to give 2,4-bis(trimethylsilyl)-3-benzoheteroepines (**17c**, **d**, **g**) in the yields shown in Table 1. As expected, the heteroepines (**17**) having trimethylsilyl groups are much more stable than the corresponding C-unsubstituted heteroepines (**2**), and the bismepine (**17d**) could be isolated under the usual handling at room temperature. It should be noted that the reaction of **15** with the other metal reagents [$PhPCl_2$, $PhAsCl_2$, $(PhSO_2)_2S$, or $SeCl_4$] did not give any cyclized products. These results might be attributable to the difference in the covalent bond radii of each metal, the bond length between the metals and the carbon atoms newly formed by ring closure being increased when the metal became heavier.

Structures and Thermal Stabilities of 2 and 17 Although 3-benzophosphepine (**2a**),[10] 3-benzotellurepine (**2g**),[11] and 3-alkyl- and 3-chloro-3-benzostibepine[14] have been reported, the other 3-benzoheteroepines (**2b**, **d**—**f**) and 2,4-bis(trimethylsilyl)heteroepines (**17c**, **d**, **g**) are the first isolated examples of 3-benzoheteroepines. These novel compounds were characterized mainly by their high resolution (HR)-MS and ^{1}H-NMR spectral analyses summarized in Tables 1 and 2, respectively.

Table 2. ^{1}H-NMR Spectral Data for the 3-Benzoheteroepines **2a**—**g**

Comp.	M	δ ($CDCl_3$, 400 MHz)			
		1(5)-H (2H, d)	2(4)-H (2H, d)	$J_{1,2(4,5)}$/ Hz	Ar-H (m)[c]
2a	PPh	6.64[a]	5.74[b]	12.0	6.90—7.62
2b	AsPh	7.16	6.20	11.4	7.73—8.21
2c	SbPh	7.54	6.52	12.1	7.22—7.73
2d	BiPh	8.92	7.59	11.2	7.00—8.20
2e	S	6.72	5.89	9.5	7.10—7.18
2f	Se	7.16	6.31	9.2	7.16—7.25
2g	Te	7.62	6.79	9.9	7.16—7.28

a) Double doublet, $J_{P,1(5)\text{-}H}$=12.0 Hz. *b*) Double doublet, $J_{P,2(4)\text{-}H}$=21.2 Hz. *c*) Each 9H for **2a**—**d** and each 4H for **2e**—**g**.

The chemical shifts of the heteroepine ring protons on the 3-benzoheteroepines (**2**) are sensitive to a change in the heteroatoms in analogy with 1-benzoheteroepines (**1**)[8,9] and 1-benzoheteroles.[32,33] For all 3-benzoheteroepines (**2**), the chemical shift of the proton at the 1(4)-position is higher than that of the proton at the 2(5)-position, and that of both protons is observed at lower field when the metal became heavier in the same group heteroepines; the chemical shifts (δ) of these protons increase in the order **2a** (P)<**2b** (As)<**2c** (Sb)<**2d** (Bi) and **2e** (S)<**2f** (Se)<**2g** (Te). It is also apparent that the coupling constants $J_{1,2(4,5)}$ of the group 15 heteroepines (**2a**—**d**) are somewhat larger than those of the group 16 heteroepines (**2e**—**g**).

As noted in the introductory paragraphs, most heteroepines were relatively unstable and difficult to isolate. We

Table 3. Half-lives of **1**, **2** and **17** at 50 °C in Toluene

Compound	$t_{1/2}$	Compound	$t_{1/2}$
2a (P)	82 h	**1a** (P)	28 h
2b (As)	4 min	**1b** (As)	180 min
2c (Sb)	45 min	**1c** (Sb)	48 h
2d (Bi)	<1 min	**1d** (Bi)	18 min
2e (S)	1 min	**1e** (S)	44 min
2f (Se)	4 min	**1f** (Se)	110 min
2g (Te)	48 min	**1g** (Te)	133 min
17c (Sb)	190 h		
17d (Bi)	34 min		

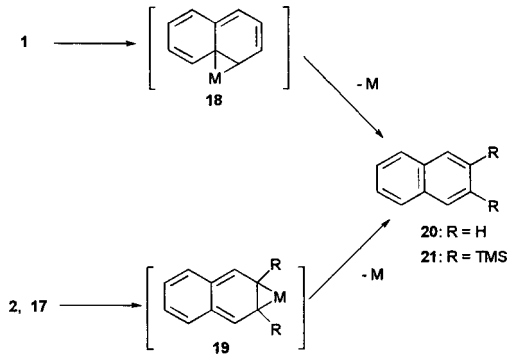

Chart 3

next studied the thermal reaction of heteroepines (**2**) and (**17**), most of which are thermally labile towards heteroatom extrusion and gradually decomposed to naphthalenes during isolation as noted earlier. The half-lives ($t_{1/2}$) of **2** and **17** estimated from ^{1}H-NMR spectral analysis are listed in Table 3, along with those of 1-benzoheteroepines (**1**).[8,9]

The 3-benzoheteroepines (**2**) are far less stable than the corresponding 1-benzoheteroepines (**1**) except for the phosphepine (**2a**) which is much more stable than the others. The widely accepted mechanism of the heteroatom extrusion in heteroepines involves valence isomerization of the seven-membered ring to the corresponding norcaradiene intermediate and following irreversible loss of the heteroatom moiety.[15,16] The differences in thermal stability between **1** and **2** may be explained by comparison of the easiness toward the transformation of the heteroepines **1** and **2** into the corresponding norcaradiene intermediates **18** and **19**, respectively. The valence isomerization of **2** into intermediary *o*-xylylene system **19** should be easier than that of **1** into bicyclo-octatetraene system **18**.[15,16] The stabilities of the group 16 heteroepines (**2e**—**g**) increase in the expected order **2e** (S)<**2f** (Se)<**2g** (Te), but there is no such pattern relative to the stabilities of the group 15 heteroepines (**2a**—**d**).

The bismepine (**17d**) having bulky trimethylsilyl groups in both of the α-positions is far more stable ($t_{1/2}$=34 min at 50 °C) than the corresponding C-unsubstituted bismepine (**2d**: $t_{1/2}$=<1 min at 50 °C), as are the monocyclic 2,7-di(*tert*-butyl)-thiepines[23—26] and -selenepines,[27] either of which are relatively stable and can be isolated although their unsubstituted derivatives are too unstable to be isolated.

In conclusion, we have demonstrated the first versatile synthesis of novel C-unsubstituted 3-benzoheteroepines containing group 15 and 16 heavier elements, most of which were new heterocyclic systems, under mild reaction conditions; all experimental manipulation to prepare them being carried out at below room temperature. The results showed that 2,4-bis(trimethylsilyl)-substituted bismepine could be isolated at room temperature, although C-unsubstituted bismepine was far more unstable to isolate. The half-lives determined by ^{1}H-NMR spectral analysis revealed that the stabilities of the group 16 heteroepines increase in the order S<Se<Te, but there is no such pattern relative to the stabilities of the group 15 heteroepines Bi<As<Sb<P.

Experimental

Melting points were determined on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. Infra red spectra were recorded on a Hitachi 270-30 spectrometer. All mass spectra including high-resolution mass spectra were recorded on a JEOL JMP-DX300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-GSX-400 (400 MHz) spectrometer, and spectral assignments were confirmed by spin-decoupling and nuclear Overhouser effect (NOE) analyses. All column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc. Japan). The metal reagents, $PhAsCl_2$,[34] $PhSbCl_2$,[35] $PhBiBr_2$,[36] and $(PhSO_2)_2S$[37] were prepared according to the literature method, and the others were purchased from Wako Pure Chemical Industries, Ltd. Japan, and were used without further purification.

(*Z*,*Z*)-*o*-Bis(β-bromovinyl)benzene (4) (Bromomethyl)triphenylphosphonium bromide (27.5 g, 63 mmol) was added in small portions to a stirred solution of potassium *tert*-butoxide (7.09 g, 63 mmol) in THF (100 ml) at −80 °C under argon atmosphere, and the mixture was warmed slowly to −30 °C. The mixture was cooled again to −80 °C, then a solution of *o*-phthalaldehyde (**3**, 2.01 g, 15 mmol) in THF (10 ml) was added dropwise to the mixture with stirring. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The mixture was diluted with water (100 ml) and the whole was extracted with CH_2Cl_2 (200 ml×2). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified with silica gel chromatography using hexane as an eluent to give **4** as a colorless oil (3.8 g, 87%). ^{1}H-NMR ($CDCl_3$) δ: 6.55 (2H, d, J=10.8 Hz, β-H), 7.11 (2H, d, J=10.8 Hz, α-H), 7.37—7.68 (4H, m, Ar-H). Electron impact (EI-MS) *m*/*z*: 286 (M^+). HR-MS *m*/*z*: 285.9016 (Calcd for $C_{10}H_8Br_2$: 285.8994).

(*Z*,*Z*)-*o*-Bis(β-deuteriovinyl)benzene (6) A solution of *t*-BuLi (1.5 M solution in pentane, 10 ml, 15 mmol) in anhydrous ether (20 ml) was added dropwise to a stirred solution of **4** (577 mg, 2 mmol) in anhydrous ether (20 ml) at −80 °C under argon atmosphere. After stirring the solution for 15 min, D_2O (99.8%, 2 ml) was added to the solution with stirring at −80 °C, and the mixture was allowed to warm to room temperature. The mixture was diluted with water (50 ml) and the whole was extracted with pentane (100 ml×3). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography using pentane as an eluent to give **6** as a colorless oil (118 mg, 45%). ^{1}H-NMR ($CDCl_3$) δ: 5.29 (2H, d, J=10.8 Hz, β-H), 6.99 (2H, dt, J=10.8 and 2.6 Hz, α-H), 7.22—7.43 (4H, m, Ar-H). HR-MS *m*/*z*: 132.1002 (Calcd for $C_{10}H_8D_2$: 132.0908)

General Procedure for the Synthesis of 3-Benzoheteroepines (2a—g) A solution of **4** (576 mg, 2 mmol) in anhydrous ether (30 ml) was added dropwise over 10 min to a stirred solution of *t*-BuLi (1.5 M solution in pentane, 10 ml, 16 mmol) in anhydrous ether (20 ml) at −80 °C under argon atmosphere. After stirring the solution for 10 min, a solution of an electrophilic metal reagent, ($PhPCl_2$ or $PhAsCl_2$: 4 mmol, 2 eq) in anhydrous ether (20 ml) or a reagent [$PhSbBr_2$, $PhBiBr_2$, $(PhSO_2)_2S$, $SeCl_4$ or $TeCl_4$: 3—4 mmol; they are insoluble in ether], was added dropwise or in small portions over 15 min with vigorous stirring at −80 °C. The mixture was allowed to warm slowly to −10 °C and stirred for an additional 3 h, and then diluted with pentane (100 ml) and water (100 ml). The insoluble substances were removed by suction filtration and the filtrate was separated. The aqueous layer was extracted with pentane (100 ml×2) and the combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography with pentane as an eluent to give the heteroepine (**2**). In the case for the preparation of phosphepine (**2a**), no **2a** was obtained, and elution of the column with a mixture of CH_2Cl_2–acetone (5 : 1) afforded 3-phenyl-3-benzophosphepine 3-oxide (**2a′**) in 38% yield. The 3-benzoheteroepines (**2**) thus obtained are listed together with the reagent used, yields, and HR-MS

analytical data in Table 1. ^{1}H-NMR spectral data are collected in Table 2.

3-Phenyl-3-benzophosphepine 3-Oxide (2a′) Colorless prisms, mp 155—156 °C (acetonitrile) (lit.,[10] 155—156 °C). ^{1}H-NMR ($CDCl_3$) δ: 6.44 (2H, dd, J=11.4 and 12.8 Hz, 2- and 4-H), 7.54 (2H, dd, J=11.4 and 34.4 Hz, 1- and 5-H) 7.75—7.45 (9H, m, Ar-H). EI-MS m/z: 252 (M^+). *Anal.* Calcd for $C_{16}H_{13}OP$: C, 76.18; H, 5.19. Found: C, 76.26; H, 5.16.

Reduction of 3-Phenyl-3-benzophosphepine 3-Oxide (2a′) with Trichlorosilane All solvents employed in this reaction were deaerated by stirring the solvents over 15 min under reduced pressure (20—100 mmHg) on cooling, and then by filling with argon at atmospheric pressure. To a solution of **2a′** (252 mg, 1 mmol) in benzene (40 ml) was added a benzene solution of $SiHCl_3$ (1.4 M, 1.9 ml, 2.7 mmol), and the mixture was heated at 80 °C for 1 h under argon atmosphere. The reaction mixture was diluted with benzene (40 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 over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was passed through a short silica gel column with hexane–benzene (10 : 1) as an eluent to give the phosphepine (**2a**: 80 mg, 34%). The spectral data for the phosphepine (**2a**) are listed in Table 1 and Table 2.

***o*-Bis(trimethylsilylethynyl)benzene (10) from 9** Bis(triphenylphosphine)palladium dichloride (480 mg, 0.68 mmol), copper(I) iodide (410 mg, 3.75 mmol), and trimethylsilylacetylene (21 ml, 150 mmol, 2.5 eq) were successively added to a stirred solution of *o*-diiodobenzene (**9**: 20 g, 60 mmol) and diethylamine (15 ml) in benzene (90 ml) in an ice-bath. The mixture was stirred for 30 min in the bath and for a further 15 h at room temperature. After concentration of the reaction mixture *in vacuo*, the resulting residue was diluted with water (100 ml) and the whole was extracted with CH_2Cl_2 (150 ml×3). The combined extracts were washed with water (150 ml×3), dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with hexane as an eluent to give **10** as a yellow oil (11.0 g, 67%), bp 141—144 °C (5 mmHg). IR λ_{max} (film) cm^{-1}: 2164 (C≡C). ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.28 (18H, s, $SiMe_3$), 7.24 and 7.46 (4H, m, Ar-H). EI-MS m/z: 270 (M^+). HR-MS m/z: 270.5247 (Calcd for $C_{16}H_{22}Si_2$: 270.5244).

***o*-Iodo(trimethylsilylethynyl)benzene (11)** Bis(triphenylphosphine)-palladium dichloride (1.55g, 2.2 mmol), copper(I) iodide (3.72 g, 34 mmol), and trimethylsilylacetylene (31 ml, 205 mmol, 1.2 eq) were successively added to a solution of *o*-diiodobenzene (**9**: 56 g, 170 mmol) and diethylamine (35 ml) in benzene (100 ml) with stirring in an ice bath. The mixture was stirred for 30 min in the bath and for a further 15 h at room temperature. After concentration of the reaction mixture *in vacuo*, the residue was diluted with water (150 ml) and the whole was extracted with CH_2Cl_2 (150 ml×3). The combined extracts were washed with water (150 ml×3), dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with hexane as an eluent to give **11** as a yellow oil (33.1 g, 65%), bp 114—119 °C (3 mmHg). IR λ_{max} (film) cm^{-1}: 2164 (C≡C). ^{1}H-NMR ($CDCl_3$, CH_2Cl_2: δ 5.30 as an internal standard) δ: 0.30 (9H, s, $SiMe_3$), 6.89—7.89 (4H, m, Ar-H). HR-MS m/z: 299.9836 (Calcd for $C_{11}H_{13}ISi$: 299.9833).

(*Z*)-β-Bromo-*o*-iodo-β-trimethylsilylstyrene (12) A solution of DIBAL-H in hexane (0.93 M, 180 ml, 167 mmol) was added dropwise to a stirred solution of **11** (33.2 g, 110 mmol) in hexane (200 ml) at room temperature under argon atmosphere, and the solution was stirred for an additional 8 h. NBS (30.0 g, 168.5 mmol) was added to the solution in small portions over 20 min with vigorous stirring in a methanol-ice bath (*ca.* −20 °C), then the stirring was continued for a further 5 h in the bath. The reaction mixture was diluted with hexane (200 ml) and water (100 ml), and insoluble substances were removed by suction filtration. The filtrate was separated and the aqueous layer was extracted with hexane (150 ml). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography with hexane as an eluent to give **12** as a pale yellow oil (27.1 g, 64.5%), bp 128—133 °C (2 mmHg). ^{1}H-NMR ($CDCl_3$, CH_2Cl_2: δ 5.30 as an internal standard) δ: 0.31 (9H, s, $SiMe_3$), 7.19 (1H, s, vinyl-H), 7.34—7.89 (4H, m, Ar-H). HR-MS m/z: 379.9098 (Calcd for $C_{11}H_{14}BrISi$: 379.9095)

(*Z*)-β-Bromo-β-trimethylsilyl-*o*-trimethylsilylethynylstyrene (13) Bis-(triphenylphosphine)palladium dichloride (0.82 g, 1.2 mmol), copper(I) iodide (0.28 g, 2.6 mmol) and trimethylsilylacetylene (12.5 ml, 89 mmol) were successively added to a stirred solution of **12** (22.5 g, 59 mmol) in diethylamine (300 ml) in an ice bath. The reaction mixture was stirred for 30 min in the bath and for a further 15 h at room temperature. After concentration of the reaction mixture *in vacuo*, the residue was diluted with water (100 ml) and the whole was extracted with CH_2Cl_2 (100 ml×3). The combined extract was washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography with hexane as an eluent to give **13** as a pale yellow oil (17.9 g, 86.2%), bp 138—142 °C (3 mmHg). IR λ_{max} (film) cm^{-1}: 2164 (C≡C). ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.26 and 0.31 (each 9H, each s, $SiMe_3$), 7.61 (1H, s, α-H), 7.32—8.04 (4H, m, Ar-H). EI-MS m/z: 350 (M^+). HR-MS m/z: 350.0524 (Calcd for $C_{16}H_{23}BrSi_2$: 350.0522).

(*Z*,*Z*)-*o*-Bis(β-bromo-β-trimethylsilylvinyl)benzene (14) from 13 A solution of DIBAL-H in hexane (0.93 M, 78 ml, 72 mmol) was added dropwise to a stirred solution of **13** (3.15 g, 9 mmol) in hexane (50 ml) under an argon atmosphere at room temperature, and the solution was stirred for additional 10 h. NBS (13.0 g, 72 mmol) was added to the solution in small portions over 15 min with vigorous stirring in a methanol-ice bath (*ca.* −20 °C), then the stirring was continued for a further 7 h in the bath. The reaction mixture was diluted with hexane (200 ml) and water (50 ml), and the insoluble substances were removed by suction filtration. The filtrate was separated and the aqueous layer was extracted with hexane (150 ml). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography with hexane as an eluent to give **14** as a yellow oil (1.8 g, 45%). ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.29 (18H, s, $SiMe_3$), 7.24 (2H, s, α-H), 7.34—7.60 (4H, m, Ar-H). EI-MS m/z: 430 (M^+). HR-MS m/z: 429.9758 (Calcd for $C_{10}H_{24}Br_2Si_2$: 429.9784).

(*E*,*E*)-*o*-Bis(β-trimethylsilylvinyl)benzene (16) A solution of **14** (650 mg, 1.52 mmol) in anhydrous ether (30 ml) was added dropwise over 10 min to a stirred solution of *t*-BuLi (1.57 M solution in pentane, 5.8 ml, 9.12 mmol) in anhydrous ether (20 ml) at −80 °C under argon atmosphere. After stirring for a further 10 min, the reaction mixture was quenched with water (5 ml). The mixture was allowed to warm to room temperature, and then diluted with pentane (100 ml) and water (50 ml). The mixture was separated, and the organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography with pentane as an eluent to give **16** as a colorless oil (213 mg, 52%). ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.18 (18H, s, $SiMe_3$), 6.35 (2H, d, J=19.1 Hz, β-H), 7.23 (2H, J=19.1 Hz, α-H), 7.18—7.47 (4H, m, Ar-H). EI-MS m/z: 274 (M^+). HR-MS m/z: 274.1579 (Calcd for $C_{16}H_{26}Si_2$: 274.1573).

General Procedure for the Synthesis of 2,4-Bis(trimethylsilyl)-3-benzoheteroepines (17c, d, g) A solution of **14** (650 mg, 1.52 mmol) in anhydrous ether (30 ml) was added dropwise over 10 min to a stirred solution of *t*-BuLi (1.57 M solution in pentane, 5.8 ml, 9.12 mmol) in anhydrous ether (20 ml) at −80 °C under argon atmosphere. After stirring the solution for 10 min at the same temperature, the electrophilic reagent ($PhSbCl_2$, $PhBiBr_2$ or $TeCl_4$: 4 mmol) was added in small portions over 15 min with vigorous stirring at −80 °C. The mixture was allowed to warm slowly to room temperature and stirred for an additional 3 h. The reaction mixture was diluted with pentane (100 ml), quenched with water (100 ml) and the insoluble substances were removed by suction filtration. The filtrate was separated and the aqueous layer was extracted with pentane (100 ml×2). The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The resulting residue was purified by silica gel column chromatography with pentane as an eluent to give **17**. The 3-benzoheteroepines (**17c**, **d**, **g**) thus obtained are listed together with the reagents used, yields, and HR-MS analytical data in Table 1. ^{1}H-NMR spectral data are shown below. **17c**: ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.29 (18H, s, $SiMe_3$), 7.93 (2H, s, 1- and 5-H), 6.81—7.01 (9H, m, Ar-H). **17d**: ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.29 (18H, s, $SiMe_3$), 8.58 (2H, s, 1- and 5-H), 6.49—6.96 (9H, m, Ar-H). **17g**: ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.23 (18H, s, $SiMe_3$), 7.71 (2H, s, 1- and 5-H), 7.18—7.25 (4H, m, Ar-H).

Thermolysis of 3-Benzoheteroepines 2 and 17 A solution of the heteroepine (**2a**—**g** or **17c**, **d**: 6—20 mg, 0.02—0.06 mmol) in d_8-toluene (0.7 ml) was heated at the temperature shown below. The disappearance of the signals for the heteroepines and the appearance of the signals for naphthalenes (**20** or **21**) were monitored by NMR integration using the signals on undeuterated toluene (benzyl group δ 2.09) contaminated in d_8-toluene as an internal standard. After the reaction was completed, the reaction mixture was purified by silica gel column chromatography with pentane as an eluent to give **20** or **21** almost quantitatively. The first-order rate constants obtained are described as follows; **2a**: 80.0 °C; $k^{353}=1.96\times10^{-4}$ s^{-1}, 89.0 °C; $k^{362}=1.91\times10^{-4}$ s^{-1}, 100.0 °C; $k^{373}=1.86\times10^{-4}$ s^{-1}, **2b**: 22.3 °C; $k^{295.3}=2.35\times10^{-4}$ s^{-1}, 30.5 °C; $k^{303.5}=2.28\times10^{-4}$ s^{-1}, 40.1 °C; $k^{313.1}=2.21\times10^{-4}$ s^{-1}, **2c**: 40.2 °C; $k^{313.2}=2.21\times10^{-4}$ s^{-1}, 50.1 °C; $k^{323.1}=2.14\times10^{-4}$ s^{-1},

60.0 °C; $k^{333}=2.08\times10^{-4}\,s^{-1}$, **2e**: 23.0 °C; $k^{296}=2.34\times10^{-4}\,s^{-1}$, 28.2 °C; $k^{301.2}=2.30\times10^{-4}\,s^{-1}$, 32.3 °C; $k^{305.3}=2.27\times10^{-4}\,s^{-1}$, **2f**: 22.8 °C; $k^{295.8}=2.34\times10^{-4}\,s^{-1}$, 30.4 °C; $k^{303.4}=2.28\times10^{-4}\,s^{-1}$, 40.1 °C; $k^{313.1}=2.21\times10^{-4}\,s^{-1}$, **2g**: 40.3 °C; $k^{313.3}=2.21\times10^{-4}\,s^{-1}$, 50.2 °C; $k^{323.2}=2.14\times10^{-4}\,s^{-1}$, 60.0 °C; $k^{333}=2.08\times10^{-4}\,s^{-1}$, **17c**: 70.0 °C; $k^{343}=2.02\times10^{-4}\,s^{-1}$, 80.0 °C; $k^{353}=1.96\times10^{-4}\,s^{-1}$, 90.0 °C; $k^{363}=1.91\times10^{-4}\,s^{-1}$, **17d**: 30.0 °C; $k^{303}=2.29\times10^{-4}\,s^{-1}$, 40.0 °C; $k^{313}=2.21\times10^{-4}\,s^{-1}$, 50.0 °C; $k^{323}=2.15\times10^{-4}\,s^{-1}$. The half lives ($t_{1/2}$) for the compounds **2a**—**c**, **e**—**f** and **17c**, **d** at 50 °C were estimated based on the rate constants at 50 °C obtained by Arrhenius plot analysis of the corresponding first-order rate constants shown above.

2,3-Bis(trimethylsilyl)naphthalene (21) Colorless oil, ^{1}H-NMR ($CDCl_3$, CH_2Cl_2, δ 5.30 as an internal standard) δ: 0.43 (18H, s, $SiMe_3$), 7.49—7.80 (4H, m, Ar-H), 8.14 (2H, m, 1- and 4-H). EI-MS *m*/*z*: 272 (M^+). HR-MS *m*/*z*: 272.1425 (Calcd for $C_{16}H_{24}Si_2$: 272.1416).

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