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Syntheses of the Group 15 1-Benzoheteroepines, Dibenzo[*b,d*]heteroepines and Dibenzo[*b,f*]heteroepines involving the First Isolated Examples of Arsepines and Bismepines

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The *C*-unsubstituted fully unsaturated Group 15 (P, As, Sb and Bi) 1-benzoheteroepines **6**, dibenzo[*b,d*]heteroepines **8** and dibenzo[*b,f*] heteroepines **10** have been prepared from the dibromo compounds **3**, **7** and **9** having a 1,6-dibromohexatriene system, and their thermal stabilities have been examined.

Considerable attention has recently been focused on the synthesis of new fully unsaturated seven-membered heterocyclic rings (heteroepines) containing a heavier element other than nitrogen, oxygen or sulfur and a variety fo monocyclic and benzo-fused heteroepines containing Group 14 (Si,[1] Ge[2] and Sn[2,3]) and Group 16 (Se[4,5] and Te[5,6]) elements have been prepared. With regard to the Group 15 heteroepines, several phosphepines (monocyclic,[7] 1-benzo-.[8] 3-benzo-[9] and dibenzo[*b,f*]-[10]) are known; however, heteroepines containing other elements have not been reported except for 3-benzostibepines.[11] Although 3-benzoarsepines have been detected by spectroscopy at a low temperature, they are thermally too unstable to be isolated.[9,11] We report here on the syntheses of the Group 15 (P, As, Sb and Bi) 1-benzoheteroepines, dibenzo[*b,d*]heteroepines and dibenzo[*b,f*]heteroepines and on the thermal stability of these novel heterocyclic rings.

Treatment of (*Z*)-*o*, β-dibromostyrene **1**[12] with trimethylsilylacetylene in the presence of a catalytic amount of bis(triphenylphosphine) palladium dichloride–copper(I) iodide[13] gave the but-1-en-3-yne **2** in 95% yield.† The enyne **2** was hydraluminated with diisobutylaluminium hydride

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† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. Selected data for compound **2**: bp 130 °C (3 mmHg); IR ν_{max}/cm^{-1} (neat) 2144; ^{1}H NMR (100 MHz, CDCl$_3$) δ 0.17 (9H, s, SiMe$_3$), 5.83 (1H, d, *J* 12 Hz, 2-H), 7.10 (1H, d, *J* 12 Hz, 1-H), 7.11–7.70 and 8.52 (3H, m, and 1H, m, Ph-H). Compound **3**: oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.17 (9H, s, SiMe$_3$), 6.73 (1H, d, 4-H), 6.77 (1H, dd, 3-H), 7.04 (1H, d, 2-H), 7.11–7.62 (4H, m, Ph-H), $J_{2,3}$ 7.0, $J_{3,4}$ 11.5 Hz. GLC and ^{1}H NMR analysis of the bromination product mixture showed that it contained three stereoisomers; *Z,Z* (**3**) (50%), *E,Z* (22%) and *Z,E* (5%) isomers. Separation was difficult and only small amounts of **3** and the *Z,E*-isomer ($J_{3,4}$ 15.8 Hz) could be isolated in a pure state. Also on heating **3** at 150–160 °C for distillation, **3** isomerized to the *Z,E*-isomer. Therefore, the mixture was used in the following reaction without separation.

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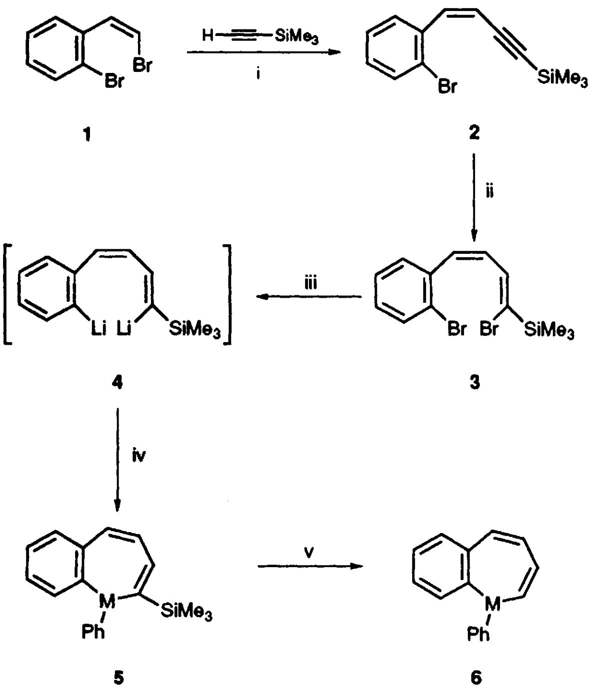


a; M = P
b; M = As
c; M = Sb
d; M = Bi

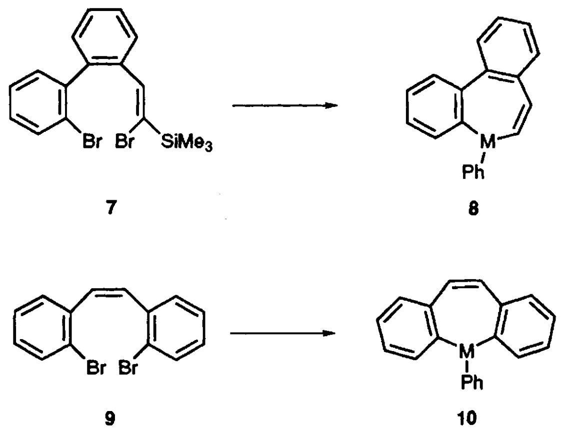
Scheme 1 *Reagents and conditions*: i, $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH, 0 °C, 3 h; ii, DIBAL-H, hexane, room temp., 36 h; NBS, −20 °C, 5 h; iii, Bu^tLi, Et_2O, −80 °C, 2 h; iv, $PhPCl_2$, $PhAsCl_2$, $PhSbCl_2$ or $PhBiBr_2$, −80 °C to room temp., 5 h; v, TBAF, THF-H_2O (3%), room temp., 10–12 h for **5a–c**, 0 °C, 3 h for **5d**

Table 1 Selected ^1H NMR spectroscopic data of **6**

		δ ($CDCl_3$, 400 MHz)[a]			
Compd.	M	2-H	3-H	4-H	5-H
6a	P	6.07	6.52	6.55	7.16
6b	As	6.17	6.66	6.46	7.05
6c	Sb	6.34	6.94	6.44	7.00
6d	Bi	7.39	8.26	6.29	6.87

[a] $J_{2,3}$ 11.1–11.8; $J_{3,4}$ 4.9–5.5; $J_{4,5}$ 12.1–13.0 Hz.

(DIBAL-H) in hexane,[14] followed by bromination with *N*-bromosuccimide (NBS) to give the (*Z*,*Z*)-1-bromobuta-1,3-diene **3** in *ca.* 50% yield as the major product along with other stereoisoemrs.† The key common starting compound **3** was treated with *tert*-butyllithium and then with dihalogeno reagents ($PhPCl_2$, $PhAsCl_2$, $PhSbCl_2$ and $PhBiBr_2$), resulting in ring closure forming the 2-trimethylsilyl-1-benzoheteroepines **5**,‡ presumably *via* the 1,6-dilithium intermediate **4**. We have recently shown[15] that the 1,4-dilithium intermediate derived from (*Z*)-β-bromo-β-trimethylsilylstyrene by treatment with butyllithium reacts with dihalogeno reagents to afford the corresponding 1-benzoheteroles; this result led us to examine the present synthetic route. The trimethylsilyl group in **5** was readily removed by treatment with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran containing water to give the desired *C*-unsubstituted 1-phenyl-1-benzoheteroepines **6a–d** in moderate yields.§



a; M = P
b; M = As
c; M = Sb
d; M = Bi

Scheme 2

Table 2 Half-lives and activation energies of **6**

Compd.	$t_{\frac{1}{2}}$/min[a]	E_a/kJ mol^{-1}[b]
6a	519	104.6
6b	67	96.2
6c	837	110.9
6d	7	88.7

[a] At 60 °C in toluene. [b] The disappearance of **6** and the appearance of naphthalene were monitored by ^1H NMR integration and the values of E_a were calculated from Arrhenius plots of the first-order rate constants obtained.

Although the phosphepine **6a** is known,[8] the other heteroepines **6b–d** are novel ring systems: in particular, **6b** and **6d** are the first isolated examples of arsepines and bismepines. The ^1H NMR spectroscopic data of the seven-membered ring protons of 6 are given in Table 1. The chemical shifts are sensitive to a change in the heteroatom and some patterns are observed. The chemical shifts of both 2- and 3-protons increase in the order **6a**(P) < **6b**(As) < **6c**(Sb) < **6d**(Bi), and the 2-protons resonate at higher field than the 3-protons, analogous to the behaviour of the Group 15 1-benzoheteroles;[15] with the exception of **6d**, the chemical shifts of both 4- and 5-protons decrease in the above order, and the 5-protons resonate at the lowest field of the four ring protons.

All heteroepines **6** are thermolabile, as are the Group 16 heteroepines[4–6] and borepines,[16] and gradually decomposed to naphthalene even during isolation by column chromatography using hexane as an eluent. The half-lives and activation energies of **6** estimated from ^1H NMR data are listed in Table 2. The stibepine **6c** is surprisingly the most stable and the stabilities of the other heteroepines decrease in the expected order **6a**(P) > **6b**(As) > **6d**(Bi). The heteroepines **5**

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‡ Selected data for **5a**: 12% yield, oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (9H, d, $SiMe_3$), 6.37 (1H, ddd, 4-H), 6.77 (1H, d, 5-H), 7.13 (1H, dd, 3-H), 6.85–7.97 (9H, m, Ph-H), $J_{P,Me}$ 0.7, $J_{P,3}$ 18.0, $J_{P,4}$ 1.1, $J_{3,4}$ 5.8, $J_{4,5}$ 12.5 Hz; **5b**: 35% yield, mp 72–74 °C, ^1H NMR δ 0.25 (9H, s, $SiMe_3$), 6.13 (1H, dd, 4-H), 6.51 (1H, d, 5-H), 7.12 (1H, d, 3-H), $J_{3,4}$ 5.9, $J_{4,5}$ 12.8 Hz; **5c**: 63% yield mp 50–52 °C; **5d**: 40% yield, mp 87–88.5 °C.

§ Selected data for **6a**: 55% yield, mp 84–85 °C (lit.[8] mp 84–85 °C); **6b**: 85% yield, oil; **6c**: 94% yield, mp 38–39 °C; **6d**: 71% yield, oil.

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having the bulky trimethylsilyl group in the 2-position are much more stable than **6**; for example, the half-life of **5d**(Bi) ($t_{\frac{1}{2}}$ = 82 min at 60 °C) is about twelve times longer than that of **6d**, and **5a**(P) and **5c**(Sb) can be kept for several weeks at room temperture without decomposition even in solution. It is known[17] that the stability of heteroepine rings is enhanced by introduction of bulky groups in α-positions.

Similarly, the *C*-unsubstituted dibenzo[*b,d*]heteroepines **8a–d** and dibenzo[*b,f*]heteroepines **10a–d** were obtained from the dibromovinylbiphenyl **7**¶ and *cis-o,o'*-dibromostilbene **9**[18] having a 1,6-dibromohexatriene system.‖ The dibenzoheteroepines **8** and **10** are hitherto unknown hetero-systems, except for the dibenzo[*b,f*]phosphepine **10a**,[10] which may be prepared from its 10,11-dihydro derivative. The ^{1}H NMR spectra of **8** also show that the 7-protons (δ, **8a**: 7.00; **8b**: 7.21; **8c**: 7.50; **8d**: 8.70) resonate at lower fields than the 6-protons (δ, **8a**: 6.71; **8b**: 6.85; **8c**: 7.01; **8d**: 8.14) and the values of chemical shifts of both 6- and 7-protons increase in the order **81**(P) < **8b**(As) < **8c**(Sb) < **8d**(Bi), analogous to the 2- and 3-protons of the 1-benzoheteroepines **6**. The dibenzoheteroepines **8** and **10** are thermally far more stable than the benzoheteroepiens **6** and remained unchanged even when heated at 60 °C for 20 h in toluene.

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¶ Compound **7** was prepared in *ca.* 70% yield from 2-iodo-2'-bromobiphenyl by coupling with trimethylsilylacetylene, followed by hydroalumination with DIBAL-H and bromination with NBS: bp 163–165 °C (3 mmHg); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.08 (9H, s, $SiMe_3$), 6.96 (1H, s, vinylic H), 7.13–7.90 (8H, m, Ph-H).

‖ Compounds **8** were obtained from **7** in 45–55% yields *via* the corresponding 6-trimethylsilyldibenzo[*b,d*]heteroepiens and compounds **10** were obtained from **9** in 60–70% yields. Selected data for **8a**: mp 201–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (1H, dd, 6-H), 7.00 (1H, dd, 7-H), 6.52–7.78 (13H, m, Ph-H), $J_{P,6}$ 6.6, $J_{P,7}$ 19.8, $J_{6,7}$ 12.1 Hz; **8b**: mp 184–187 °C; **8c**: mp 151–153 °C; **8d**: mp 98–110 °C (decomp.); **10a**: mp 141–143 °C (lit.[10] 135–136 °C); **10b**: mp 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (2H, s, 10- and 11-H), 7.24–7.45 (13H, m, Ph-H); **10c**: mp 142–144 °C; **10d**: 168–170 °C.

References

1 T. J. Barton, W. E. Volz and J. L. Johnson, *J. Org. Chem.*, 1971, **36**, 3365; L. Birkofer and H. Haddad, *Chem. Ber.*, 1972, **105**, 2101; Y. Nakadaira, R. Sato and H. Sakurai, *Organometallics*, 1991, **10**, 435.

2 Y. Nakadaira, R. Sato and H. Sakurai, *J. Organomet. Chem.*, 1992, **441**, 411.

3 A. J. Leusing, W. Drenth, J. G. Noltes and G. J. M. van der Kerk, *Tetrahedron Lett.*, 1967, 1263; A. J. Leusink, H. A. Budding and J. G. Noltes, *J. Organomet. Chem.*, 1970, 24, 375; G. Axelrad and D. F. Halpern, *J. Chem. Soc., Dalton Trans.*, 1971, 291.

4 K. Sindelar, J. Metysova and M. Protiva, *Collect. Czech. Chem. Commun.*, 1969, **34**, 3801; H. Hori, S. Yamazaki, K. Yamamoto and I. Murata, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 424.

5 H. Sashida, K. Ito and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1493.

6 H. Sashida, H. Kurahashi and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1991, 802.

7 G. Märkl and H. Schubert, *Tetrahedron Lett.*, 1970, 1273; G. Märkl and W. Burger, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 894; G. Keglvich, F. Janke, J. Brlik, I. Pentnehazy, G. Toth and L. Toke, *Phosphorus Sulfur Silicon*, 1989, **46**, 69; G. Märkl, K. Hohenwarter, M. L. Ziegler and B. Nuber, *Tetrahedron Lett.*, 1990, **31**, 4849.

8 J. Kurita, S. Shiratori, S. Yasuike and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1991, 1227.

9 G. Märkl and W. Burger, *Tetrahedron Lett.*, 1983, **24**, 2545.

10 Y. Segall, E. Shirin and I. Granoth, *Phosphorus Sulfur*, 1980, **8**, 243.

11 A. J. Ashe III, L. Goossen, J. W. Kampf and H. Konishi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1642.

12 V. Glamb and H. Alper, *Tetrahedron Lett.*, 1983, **24**, 2965.

13 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627.

14 J. J. Eisch and M. W. Foxton, *J. Org. Chem.*, 1971, **36**, 3520; G. Zweifel and W. Lewis, *J. Org. Chem.*, 1978, **43**, 2739; R. B. Miller and G. McGravey, *J. Org. Chem.*, 1978, **43**, 4424.

15 J. Kurita, M. Ishii, S. Yasuike and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1309.

16 Y. Nakadaira, R. Sato and H. Sakurai, *Chem. Lett.*, 1987, 1451; A. J. Ashe III and F. J. Drone, *J. Am. Chem. Soc.*, 1987, **109**, 1879; S. M. van der Kerk, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1981, **215**, 303.

17 I. Murata and T. Tatsuoka, *Tetrahedron Lett.*, 1975, 2697; K. Nishino, K. Matsui, Y. Abo, Y. Ikutani and I. Murata, *Chem. Express*, 1990, **5**, 863.

18 R. Dierck and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 266.