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SYNTHESIS AND STRUCTURE OF NOVEL DIBENZO[*b,i*]-1-OXA-6-HETEROECINES CONTAINING GROUP 15 HEAVIER ELEMENTS

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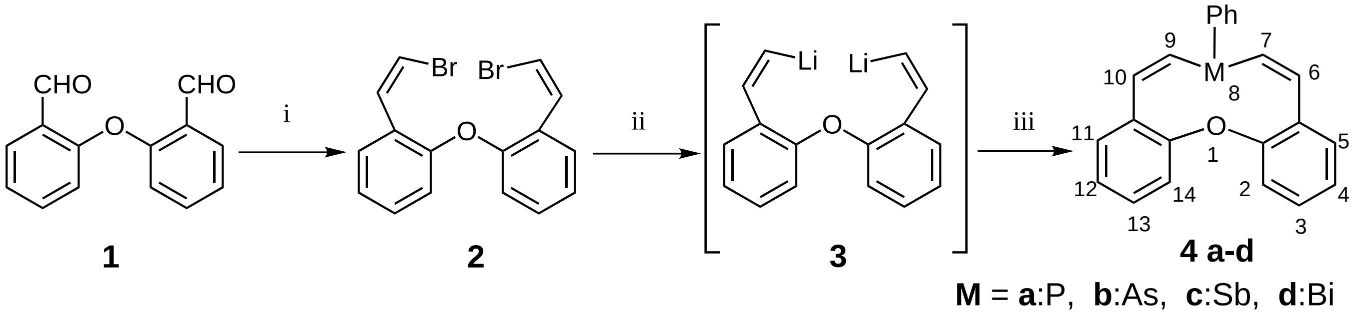
Abstract — A series of novel dibenzo[*b,i*]-1-oxa-6-heteroecines (**4a-d**) containing Group 15 heavier elements (P, As, Sb, and Bi) have been prepared *via* common 1,9-dilithium intermediate (**3**). Single crystal X-Ray analysis of oxastibecine (**4c**) reveals that the two olefinic bonds in the ring system are both *cis* configuration and the distance between the antimony and oxygen atoms is shorter than the sum of the van der Waals radiis of each element, indicating the presence of a transannular interaction between the oxygen and hetero atoms.

Considerable effort has recently been directed toward the synthesis of new heterocyclic ring systems with heavier elements other than nitrogen, oxygen, or sulfur, and the syntheses of a variety of new, fully unsaturated five- (heteroles)[1,2] and seven-membered rings (heteroepines)[1a-d,3,4] containing Group 14 (Si, Ge, and Sn), Group 15 (P, As, Sb, and Bi), and Group 16 (Se and Te) elements, as well as their physical properties and thermal stabilities,[4] have been reported. However, fully unsaturated larger rings than heteroepines containing such heavier elements have not been prepared, except for nine-membered phosphonines.[5] On the other hand, the transannular interactions between heavier elements and a nitrogen, oxygen or sulfur atom have been observed in a large number of fully or partially saturated eight-,[6] nine-,[7] and ten-membered[8] heterocyclic compounds, in which the distance between the two hetero atoms is significantly shorter than the sum of the van der Waals radii of the each elements in the crystalline structure. This interaction can be attributed to the formation of hypervalent compound of the heavier elements.[9] As part of our studies on the synthesis of new heterocyclic rings containing heavier elements, we report here the synthesis and structures of the title 1,6-diheteroecines (**4a-d**) having group 15 heavier elements (P, As, Sb, and Bi) from bis(2-(*Z*)-β-bromovinylphenyl) ether (**2**) *via* a common 1,9-dilithium intermediate (**3**).

The key starting bis(2-(*Z*)-β-bromovinylphenyl) ether (**2**)[10] was prepared stereoselectively in 76% yield by a double Wittig reaction of bis(2-formylphenyl) ether (**1**) with bromomethylene-triphenylphosphorane,[11] as illustrated. The dibromo compound (**2**) was treated with *tert*-butyllithium in dry ether under an argon



Scheme 1 *Reagents and conditions*: i, $Ph_3P^+CH_2Br$ ^-Br (X 2), Bu^tOK, THF, -80 °C to rt,12 h, 76 %; ii, Bu^tLi, Et_2O, -80 °C, 5 min; iii, Metal reagents ($PhPCl_2$, $PhAsCl_2$, $PhSbBr_2$ or $PhBiBr_2$), Et_2O, -80 to -10 °C, 2.5 h.

atmosphere, and then with dihalogeno metal reagents ($PhPCl_2$, $PhAsCl_2$, $PhSbBr_2$ and $PhBiBr_2$) to result in ring closure, giving rise to the desired dibenzo[*b*, *i*]-1-oxa-6-heteroecines (**4a-d**) as the sole characterizable products,[12] presumably *via* the 1,9-dilithium intermediate (**3**). The phosphorus-containing diheteroecine (**4a**) is susceptible to air oxidation and was isolated as its *P*-oxide (**4a'**), which was, however, easily deoxygenated to **4a** by treatment with trichlorosilane in benzene. The 1,6-diheteroecines (**4a-c**) were stable enough to be eluted from a silica gel column and isolated as stable crystalline compounds, except for oxabismecine (**4d**) which underwent decomposition during chromatographic isolation (silica gel or alumina) and could be purified only by repeated recrystallization from methanol. The diheteroecines (**4a-c**) were thermally stable and remained unchanged even when heated at 110 °C for 24 h in toluene, while the oxabismecine (**4d**) decomposed gradually to unspecified products at the same temperature.

The structures of the 1,6-diheteroecines (**4**) obtained here were established by their HR-MS, ^1H NMR spectral and single crystal X-Ray analyses. The ^1H NMR spectroscopic data of the ten-membered ring protons in **4** are given in Table 1. The chemical shifts are sensitive to change in the heteroatom, and in all of the 1,6-diheteroecines (**4**), the signals of 7-H and 9-H (6-H and 10-H) on the ten-membered ring appear to be equivalent with the coupling constant of $J_{6,7(9,10)}$ = 12.1-13.6 Hz. This magnetic equivalence of the olefinic protons implies that these 1,6-diheteroecines have a symmetrical structure in solution, and both of the olefinic bonds should be *cis* configuration.

Table 1 Selected ^1H NMR Spectroscopic Data of 1,6-Diheteroecines (**4**).(400 MHz, $CDCl_3$ at 32 °C: δ)

Compd.	M	7- and 9-H	6- and 10-H	$J_{6,7(9,10)}$ in Hz
4a'	P(O)Ph	6.06	7.13	13.6 *a)*
4a	PPh	6.01	6.81	13.6 *b)*
4b	AsPh	6.33	7.03	12.5
4c	SbPh	6.65	7.32	12.8
4d	BiPh	7.27	8.28	12.1

a) $J_{P,7(9)}$ = 13.9 and $J_{p,6(10)}$ = 42.1 Hz, *b*) $J_{P,7(9)}$ = 23.5 and $J_{P,6(10)}$ = 12.5 Hz.

In order to confirm the stereochemistry of **4**, single crystal X-Ray analysis of the oxastibecine (**4c**) was performed (Figure 1).[13] The result reveals that, in contrast with the structure in solution, **4c** lies in a

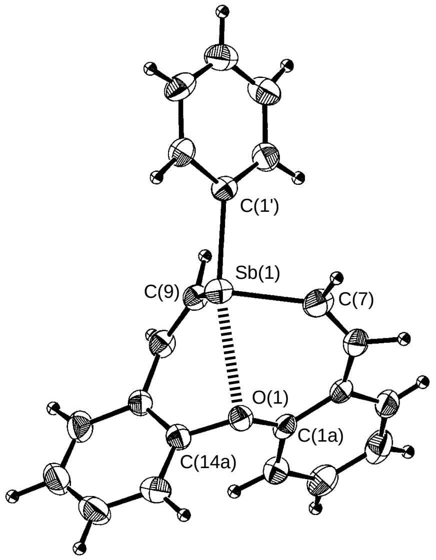


Figure 1 ORTEP drawing of **4c**. Selected bond distances (Å) and angles (°): Sb(1)---O(1) 2.83, Sb(1)-C(7) 2.112(6), Sb(1)-C(9) 2.136(4), Sb(1)-C(1') 2.164(4), O(1)-Sb(1)-C(1') 156.6(2), C(7)-Sb-C(9) 100.8(2), C(7)-Sb-C(1') 93.5(2), C(9)-Sb-C(1') 91.5(2), C(1a)-O(1)-C(14a) 117.1(3).

dissymmetrical structure in the solid state. Either of the olefinic bonds of the 6- and 9-position adopts *cis* configuration, unlike those of the phosphonines[5] and 1,6-dithiecine,[14] both of which have one *trans* olefinic bond in their ring system. The overall geometry around the antimony atom is pseudo trigonal bipyramidal (TBP) with that the C(1') of the phenyl substituent on antimony and the oxygen atom lie approximately *trans* to each other and the O---Sb—C(1') angle is 156.6 °. Most of the bond distances are unexceptional; however, the distance between the antimony and oxygen atoms (2.83 Å) is much shorter than the sum of the van der Waals radii of the oxygen and antimony atoms (3.60 Å), and larger than that of the covalent bond radiis of them (2.02 Å).[15] This result shows the presence of an intramolecular nonbonded interaction between the oxygen and antimony atoms.

In summary, we have succeeded in preparation of new 1-oxa-6-heteroecines containing group 15 heavier elements, and revealed that the two olefinic bonds in the ring system are both *cis* configuration and a transannular interaction is presented between the oxygen and antimony atoms by means of the single crystal X-Ray analysis of **4c**.

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REFERENCES AND NOTES

1. For reviews; (a) K. Dimroth, in 'Comprehensive Heterocyclic Chemistry', ed. by A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, Vol. 1, pp. 493-357; (b) R. E. Atkinson, *ibid.*, Vol. 1, pp. 539-561; (c) D. A. Armitage, *ibid.*, Vol. 1, pp. 573-627; (d) C. W. Bird, G. W. H. Cheesman, and A. -B Förnfeldt, *ibid.*, Vol. 4, pp. 935-971; (e) J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, 1990, **90**, 215; (f) F. Mathey, *Chem. Rev.*, 1988, **88**, 429.
2. J. Kurita, M. Ishii, S. Yasuike, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1309; J. Kurita, M. Ishii, S. Yasuike, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1994, **42**, 1437; S. Yasuike, J. Kurita, and T. Tsuchiya, *Heterocycles*, 1997, **45**, 1891.

3. Y. Nakadaira, R. Sato, and H. Sakurai, *Organometallics*, 1991, **10**, 435; Y. Nakadaira, R. Sato, and H. Sakurai, *J. Organomet. Chem.*, 1992, **441**, 411; T. Nishinaga, K. Komatsu, and N. Sugita, *J. Org. Chem.*, 1995, **60**, 1309; G. Märkl and W. Burger, *Angew. Chem., Int. Ed., Engl.*, 1984, **23**, 894; A. J. Ashe, L. Goossen, J. W. Kanpf, and H. Konishi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1642.
4. S. Yasuike, H. Ohta, S. Shiratori, J. Kurita, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1817; S. Yasuike, T. Kiharada, J. Kurita, and T. Tsuchiya, *Chem. Commun.*, 1996, 2183; H. Sashida, K. Itoh, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1995, **43**, 19; S. Yasuike, S. Shiratori, J. Kurita, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1999, **47**, 1108, and references cited therein.
5. L. D. Quin, E. D. Middlemas, and N. S. Rao, *J. Org. Chem.*, 1982, **47**, 905; N. S. Rao and L. D. Quin, *J. Am. Chem. Soc.*, 1983, **105**, 5960.
6. For examples; K.-y. Akiba, K. Takee, Y. Shimizu, and K. Ohkata, *J. Am. Chem. Soc.*, 1986, **108**, 6320; K.-y. Akiba, K. Okada, and K. Ohkata, *Tetrahedron Lett.*, 1986, **27**, 5221; K. Ohkata, M. Ohnishi, and K.-y. Akiba, *ibid.*, 1988, **29**, 5401; K. Ohkata, S. Takemoto, M. Ohnishi, and K.-y. Akiba, *ibid.*, 1989, **30**, 4841; J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483; H. Fujiwara, T. Uehara, and N. Furukawa, *J. Am. Chem. Soc.*, 1995, **117**, 6388; M. Minoura, Y. Kanamori, A. Miyake, and K.-y. Akiba, *Chem. Lett.*, 1999, 861, and references cited therein.
7. M. Kuti, J. Rábai, I. Kapovits, A. Kucsman, L. Pàrkànyi, Gy. Argay, and A. Kálmán, *J. Mol. Struct.*, 1994, **318**, 161.
8. J. J. H. Edema, R. Libbers, A. Ridder, R. M. Kellogg, and A. L. Spek, *J. Orgamomet. Chem.*, 1994, **464**, 127; A. Saxena and J. P. Tandon, *Polyhedron*, 1984, **3**, 681.
9. K.-y. Akiba, in 'Chemistry of Hypervalent Compounds', ed. by K.-y. Akiba, Wiley-VCH, New York, 1998, pp.1-48; K.-y. Akiba, Y. Itoh, K. Tamao, T. Nagano, and N. Furukawa, 'Chemistry of Hypervalent Organic Compounds', Kikan Kagaku Sosetu, Vol. 34, Gakkai Shuppan Center, Tokyo, 1998.
10. Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. **2:** oil, ^{1}H NMR (400 MHz, $CDCl_3$, J= Hz) δ 6.47(2H, d, β-H), 7.26(2H, d, α-H), 6.78-8.01(8H, m, Ar-H), $J_{\alpha,\beta}$ 8.1; HR-MS *m/z* 377.9264 (M^+, Calc. for $C_{16}H_{12}Br_2O$: 377.9256).
11. M. Matsumoto and K. Kuroda, *Tetrahedron Lett.*, 1980, **21**,4021; M. A. Romero and A. G. Fallis, *Tetrahedron Lett.*, 1994, **35**, 4711.
12. **4a'**: 78 % yield, mp 242-246℃; **4a**: 59 % yield from **4a'**, mp 161-163 ℃; **4b**: 32 % yield, mp 164-166 ℃; **4c**: 39 % yield, mp 143-146 ℃; **4d**: 29 % yield, mp 111-116 ℃.
13. *Crystal data* for **4c**: $C_{22}H_{17}OSb$, M = 419.13, orthorhombic, a = 11.883(1), b = 21.114(3), c = 7.1974(6) Å, V= 1805.7(4) Å^3, T = 296±1 K, space group $P2_12_12_1$ (no. 19), Z=4, μ(Mo-Kα) = 15.39 cm^{-1}. The R (R_W) value of **4c** was 0.023 (0.028). The data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα (λ=0.71069 Å). All of the structures were solved by direct method (program MITHRIL84) and expanded using Fourier technique (program DIRDIF84).
14. P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*,1971, 947.
15. J. Emsley, 'The Elements', 3rd edn., Clarendon press, Oxford, 1998.