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SYNTHESES OF NOVEL DIBENZO[*d,f*]HETERONINS INCORPORATING GROUP 15 AND 16 HEAVIER ELEMENTS

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Abstract – Fully unsaturated dibenzo[*d,f*]heteronins incorporating Group 15 (P, As, Sb) and Group 16 (S, Se, Te) heavier elements have been prepared *via* a common 1,8-dilithium intermediate. These heteronins, except for dibenzothionin, are the first examples of fused nine-membered heterocyclic ring. Proton NMR spectra of the heteronins revealed that two olefinic bonds in the heteronin ring have the *cis* configurations and the nine-membered rings exist in a buckled, non-planar conformation.

A variety of fully unsaturated nine-membered heterocyclic rings (heteronins) such as azonines and oxonins have been prepared, and their molecular structures and aromatic character have been studied.[1] However, heteronins containing Group 15 (P, As, Sb) and Group 16 (S, Se, Te) elements have not been reported, except for dibenzothionins (**1a**)[2] and phosphonins (**2d**).[3] We recently reported the syntheses and physical properties of seven-membered (heteroepins)[4] and ten-membered (heteroecins)[5] heterocyclic compounds incorporating such heavier elements from the corresponding 1,6- and 1,9-dilithium intermediates, along with their physical properties and thermal stabilities. As part of our studies on the

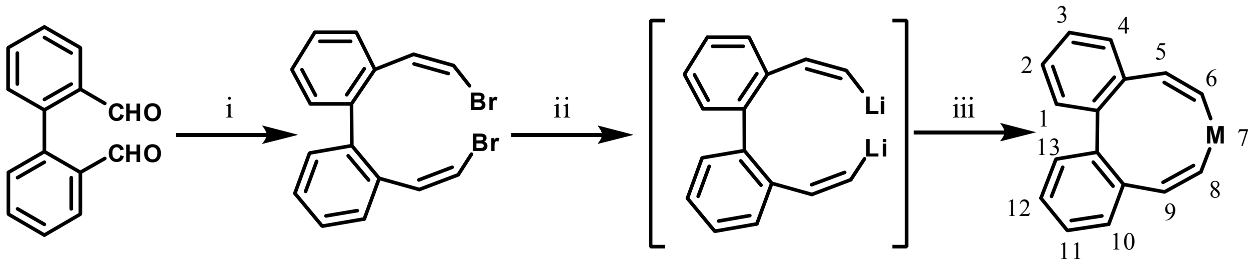
1 **2**

M = a: S, b: Se, c: Te, d: PPh, d': P(O)Ph, e: AsPh, f: SbPh

Scheme 1

Dedicated to Professor Dr Ei-ichi Negishi on the occasion of his 77th birthday synthesis of new heterocyclic compounds incorporating Group 14, 15, and 16 heavier elements, we report here the synthesis and structures of the title dibenzoheteronins (**1a-f**) from (*Z*)-2,2'-bis(2-bromovinyl)biphenyl (**4**) *via* a common 1,8-dilithium intermediate (**5**).

The key starting compound, (*Z*)-2,2'-bis(2-bromovinyl)biphenyl (**4**),[6] was prepared stereoselectively in 57% yield by a double Wittig reaction of 2,2'-diformylbiphenyl (**3**)[7] with bromomethyltriphenylphosphonium bromide.[8] In the NMR spectrum of **4**, the coupling constant of the vinylic protons ($J_{\alpha,\beta}$ = 8.1 Hz) of the bromovinyl moiety supports the all-*cis* configuration. Treatment of **4** with *tert*-butyllithium in dry ether under an argon atmosphere, and then with deuterium oxide resulted 1,8-dideuterio compound in 85% yield.[9] This result clearly shows the generation of the 1,8-dilithium species (**5**) in high efficiency. However, the reaction of **5** with electrophilic reagents such as $(PhSO_2)_2S$, $SeCl_4$, TeI_4, $PhPCl_2$, $PhAsCl_2$, and $PhSbBr_2$ gave the desired dibenzo[*d,f*]heteronins (**1a-f**) in low yields (10–17%) as the sole characterizable product.[10] The heteronins (**1**) except for phosphonin (**1d**) were stable enough to be eluted using silica gel column chromatography and isolated in pure form. The phosphorus-containing heteronin (**1d**) is susceptible to air oxidation and was isolated as its P-oxide (**1d′**).



3 **4** **5** **1**

Scheme 2. *Reagents and conditions*: i, $Ph_3P^+CH_2Br$-Br (x 2), *t*-BuOK, THF, -80 °C C to rt, 12 h, 57 %; ii, *t*-BuLi, Et_2O, -80 °C, 5 min; iii, Metal reagents [$(PhSO_2)_2S$, $SeCl_4$, TeI_4, $PhPCl_2$, $PhAsCl_2$ or $PhSbBr_2$], Et_2O, -80 to -10 °C, 2.5 h.

Table 1. Selected ^{1}H-NMR Spectroscopic Data of Heteronins (**1**) (400 MHz, $CDCl_3$: δ).

Compd.	M	6-H and 8-H (α)		5-H and 9-H (β)		$J_{5,6(8,9)}$ (Hz)	Ar
1a	S	5.86		6.52		11.0	7.12–7.40
1b	Se	6.15		6.92		11.0	7.08–7.39
1c	Te	6.45		7.40		11.0	7.02–7.39
1d′	P(O)Ph	6.07	6.15	7.09	7.40	10.6[a)] (13.9)[b)]	6.78–7.44
1e	AsPh	5.92	6.13	7.08	7.26	10.1 (13.6)	6.92–7.48
1f	SbPh	6.12	6.37	7.43	7.62	11.4 (13.9)	6.95–7.44

a) $J_{P,6(8)}$ = 13.6 and $J_{P,5(9)}$ = 35.5 Hz, b) $J_{P,6(8)}$ = 17.6 and $J_{P,5(9)}$ = 33.0 Hz.

The structures of the heteronins (**1a-c**, **d′**, **e**, **f**) obtained here were established from their spectral properties (HR-MS and ^{1}H-NMR). The ^{1}H-NMR spectroscopic data of the nine-membered ring protons for **1** are given in Table 1. The spectroscopic data [^{1}H-NMR and UV (253 nm, ε 5000, EtOH)] and mp (121–123 °C) of the thionin (**1a**) obtained here are in good accordance with those of dibenzo[*d, f*]thionin, reported by Bindra *et al.*[2] The vinyl proton signals of 6-H and 8-H as well as 5-H and 9-H for the Group 16 heteronins (**1a-c**) exhibit one AB doublet with coupling constant $J_{5,6(8,9)}$ = 11.0 Hz. This magnetic equivalence of the olefinic protons implies that **1a-c** have a symmetrical structure in solution with rapid conformational exchange on the NMR time scale, and both olefinic bonds have the *cis* configuration. It is also suggested that, because the vinyl protons of **1a-c** were observed at the relatively high field (δ 5.86–6.45 for 6-H and 8-H, δ 6.52–7.40 for 5-H and 9-H), without the deshielding associated with aromatic character, **1a-c** should be classified as non-aromatic compounds. We have already reported that the vinyl protons of non-aromatic Group 16 3-benzoheteroepins were observed at a higher field (α: δ 5.89–6.79; β: δ 6.72–7.62; $J_{\alpha,\beta}$ = 9.2–9.9 Hz),[4b] than those of aromatic Group 16 1-benzoheteroles (α: δ 7.39–8.75; β: δ 7.30–8.00; $J_{\alpha,\beta}$ = 5.5–7.0 Hz).[11] In the ^{1}H-NMR spectra of Group 15 heteronins (**1d′**, **e**, **f**), the vinyl proton signals corresponding to 5-H and 9-H as well as 6-H and 8-H were observed in different positions with the coupling constant $J_{5,6}$ = 10.1-10.6 Hz and $J_{8,9}$ = 13.6-13.9 Hz. The magnetic nonequivalence of the olefinic protons implies that these Group 15 heteronins (**1d′**, **e**, **f**) exist in buckled, non-planar conformations. It should be emphasized that both the olefinic bonds of **1d′**, C(5)–C(6) and C(8)–C(9), should have the *cis* configuration.[5] Quin has recently reported the synthesis and structure of dibenzo[*d, f*]phosphonin P-oxide (**2d′**), which have *cis* and *trans* olefinic bonds, for which two vinyl proton signals were observed at δ 6.04 ($J_{P,H}$ = 24 Hz and $J_{H,H}$ = 14 Hz) and δ 6.08 ($J_{P,H}$ = 14 Hz and $J_{H,H}$ = 4 Hz).[3a]

All the dibenzoheteronins (**1a-c**, **d′**, **e**, **f**) isolated here displayed relatively high thermal stability and remained unchanged even when heated at 110 °C for 24 h in toluene-d_8. The thermal stabilities of these dibenzoheteronins is in contrast to these of benzoheteroepins[4] and monocyclic heteronins.[1]

We have developed a general route for the synthesis of Group 15 (P, As, Sb) and Group 16 (S, Se, Te) fully unsaturated dibenzo[*d,f*]heteronins (**1**) from a common starting material, 2,2’-bis(2-bromovinyl)biphenyl (**4**) *via* 1,8-dilithium intermediate (**5**). All the heteronins obtained here exist in buckled, non-planar conformations and are classified as non-aromatic compounds.

Further studies on the molecular structures and chemical properties of these novel dibenzo[*d,f*]heteronins containing heavier elements are in progress.

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6. **4**: colorless oil; ^{1}H-NMR (400 MHz, CDCl$_3$, J = Hz): δ 6.31 (2H, d, β-H), 6.66 (2H, d, α-H), 7.21-7.89 (8H, m, Ar-H), $J_{\alpha,\beta} = 8.1$; HR-MS *m/z* 361.9327 (M$^+$, calc. for $C_{16}H_{12}Br_2$: 361.9307).
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9. 1,8-dideuterio compound: mp 73-74 °C; ^{1}H-NMR (400 MHz, CDCl$_3$, J = Hz): δ 5.08 (2H, d, β-H), 6.40 (2H, dt, α-H), 7.14-7.67 (8H, m, Ar-H), $J_{\alpha,\beta} = 8.1$, $J_{H,D} = 1.0$; HR-MS *m/z* 208.1221 (M$^+$, calc. for $C_{16}H_{12}D_2$: 208.0939).
10. **1a**: 10% yield, mp 121–123 °C (Lit.,[2] 121–122 °C); **1b**: 16% yield, mp 113–115 °C; **1c**: 14% yield, mp 155–156 °C; **1d′**: 10% yield, colorless oil; **1e**: 10% yield, colorless oil; **1f**: 17% yield, colorless

oil.

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