1-Benzostannepines: first synthesis and novel conversion into 1-benzo-borepines, -stibepines and -tellurepines[1]

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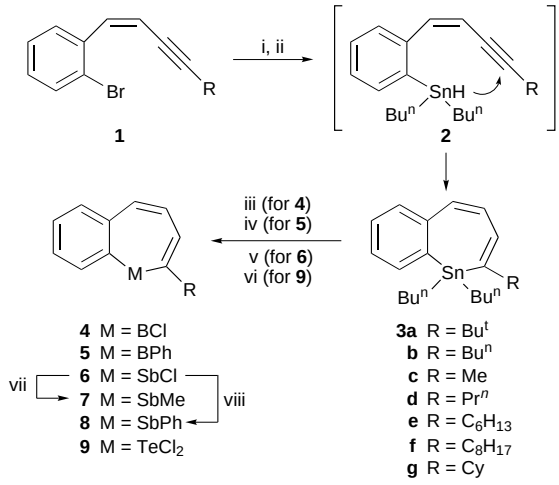
2-Alkyl-1-benzostannepines 3 were prepared in one pot from (*Z*)-1-(*o*-bromophenyl)but-1-en-3-ynes 1 *via* tin hydride intermediates 2 and easily converted into 1-benzo-borepines 4 and 5, -stibepines 6, 7 and 8, and -tellurepines 9 by tin–metal exchange reaction in moderate to good yields.

3-Benzostannepines,[2] fully unsaturated seven-membered tin-containing heterocycles, were synthesized by hydrostannation of *o*-diethynylbenzenes more than 30 years ago. Monocyclic,[3] thiophene ring-,[4] pyrrole ring-[5] and cyclopentane ring-fused[6] stannepines have also been prepared by extension of this reaction. It is well-known that these parent stannepines can be converted into the corresponding derivatives of borepine[2b,3b,4–7] and stibepine.[8] However, no 1-benzostannepines **3**, a theoretically possible structural isomer, have been prepared until now, in spite of much synthetic effort. Recently, we reported the synthesis of 1-benzotellurepines **9**,[9] novel tellurium-containing seven-membered heterocycles, *via* the successive intramolecular addition of telluroles to a triple bond. In our continuing studies[10] on the synthesis of new heterocyclic ring systems using efficient intramolecular cyclization reactions with a participating acetylenic group, we herein describe the preparation of novel stable 1-benzostannepines **3** and the transformation of **3** into 1-benzoborepines **4** and **5**, 1-benzostibepines **6**, **7** and **8**, and also 1-benzotellurepines **9**; the former compounds are new heterocyclic ring systems.

(*Z*)-1-(*o*-Bromophenyl)but-1-en-3-ynes **1**[11] were lithiated with Bu^tLi in the presence of tetramethylethylenediamine in *n*-hexane, followed by hydrostannation with Bu^n_2ClSnH[12] to give the desired 2-alkyl-1-benzostannepines **3**‡ as a sole product in 30–40% yield. The intermolecular hydrostannation of acetylene compounds induced by radical initiators,[13] transition metal catalysts,[14] base catalysts[2] or Lewis acid catalysts[15] to form vinylstannanes has been given extensive attention, and this hydrostannation frequently proceeds in the absence of a catalyst.[16] Therefore, the stannepines **3** may probably be obtained by the intramolecular *endo*-mode ring closure of stannyl hydride intermediates **2** at the sp carbon of the ethynyl moiety, as shown in Scheme 1. These compounds are quite stable and are not sensitive to air, light or even moisture.



Scheme 1 *Reagents and conditions*: i, Bu^tLi (2.2 equiv.), $Me_2NC_2H_4NMe_2$, hexane, −80 °C, then room temp., 3 h; ii, Bu^n_2SnHCl, room temp., 1 h; iii, BCl_3 (1 equiv.), hexane, room temp., 1 h; iv, $PhBCl_2$ (1 equiv.), hexane, room temp., 1 h; v, $SbCl_3$ (1 equiv.), $CHCl_3$, room temp., 30 min; vi, $TeCl_4$ (1 equiv.), PhH, room temp., 1 h; vii, MeLi (1.2 equiv.), Et_2O, −20 °C, 30 min; PhLi (1.2 equiv.), Et_2O, −20 °C, 30 min

The reaction of the 1-stannepine **3a** with 1.0 equiv. of BCl_3 in *n*-hexane at room temperature afforded 2-*tert*-butyl-1-chloro-1-benzoborepine **4a**,§ which could be purified by distillation under reduced pressure in spite of being air- and moisture-sensitive. A 1-phenyl derivative **5a** was similarly obtained.

The stannepines **3a**,**b** also reacted readily with 1.0 equiv. of $SbCl_3$ in $CHCl_3$ at 0 °C to give the corresponding 1-chlorostibepines **6a**,**b**¶ almost quantitatively, but these compounds were too unstable to be isolated. Thus, we have examined the conversion of **6** to the Sb-alkyl or -phenyl substituted derivatives. Treatment of the 1-chlorostibepines **6**, which were freshly prepared without purification after removal of the solvent and $Bu^n_2SnCl_2$ under reduced pressure, with a small excess of MeLi in Et_2O at −20 °C gave the 1-methylstibepines **7**. The phenyl derivative **8** was prepared in a similar manner. Compounds **7** and **8**‖ were more stable than the 1-chloro derivatives **6**, and could be chromatographed on silica gel, contrary to our expectation. However, the 3-alkyl-3-benzostibepines are thermally labile. The structure of **6** was determined by comparison of its NMR spectra with those of **7** and **8**.

1,1-Dichlorotellurepines **9a**,**b** were formed from the parent stannepines **3** by tin–tellurium replacement reaction in 77–82% yield and were identical with authentic samples.[11] To the best of our knowledge, this tin–tellurium exchange reaction, accompanied by fission of a tin–carbon single bond and the simultaneous formation of a tellurium–carbon bond, is a new discovery.

Monocyclic fully unsaturated borepines, 3-benzoborepines and other ring-fused derivatives have now been recognized and established as aromatic compounds[4–7,17] by ^1H and ^{13}C NMR spectropic studies, molecular orbital calculations and X-ray crystal analyses. The ^1H NMR chemical shift values of the borepine ring protons in **4** and **5** appear rather lower than those of the other seven-membered heterocycles obtained in this work; in particular, the proton signals of 4-H of **4** and **5** are shifted 0.34–0.64 ppm downfield. These results suggest that the 1-borepines **4** and **5** are aromatic.

Further detailed studies on the ring transformation and reactivities of these novel 1-benzostannepines and its analogues, and on the aromaticity of the 1-benzoborepines, are in progress.

Notes and References

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‡ All new compounds exhibited satisfactory spectroscopic data. *Selected data* for **3a**: 39%, colorless oil; δ_H(400 MHz, $CDCl_3$) 0.97, 1.21–1.48 and 1.59–1.68 (6 H, t, *J* 7.3, 8 H, m, 4 H, $Bu^n \times 2$), 1.14 (9 H, s, Bu^t), 6.25 (1 H, dd, *J* 5.9 and 13.6, 4-H), 6.53 (1 H, d, *J* 5.9, 3-H), 6.84 (1 H, d, *J* 13.6, 5-H), 7.31–7.37 and 7.51–7.53 (3 H, m, and 1 H, m, Ar-H); δ_C(100 MHz,

$CDCl_3$) 10.55 (t), 13.64 (q), 27.36 (t), 29.43 (t), 30.59 (q), 38.37 (s), 127.03 (d), 127.81 (d), 128.32 (d), 128.40 (d), 130.24 (d), 134.45 (d), 134.49 (d), 142.81 (s), 143.85 (s), 163.29 (s); HRMS: Calc. for $C_{22}H_{34}Sn$ (M^+) 418.1682. Found 418.1775. For **3b**: 33%. For **3c**: 24%. For **3d**: 23%. For **3e** 37%. For **3f**: 35%. For **3g**: 36%. Compounds **3b–g** are also colorless oils.

§ *Selected data* for **4a**: 44%, pale yellow oil, bp 90–100 °C (2 mmHg); δ_H(400 MHz, $CDCl_3$) 1.43 (9 H, s, Bu^t), 6.75 (1 H, dd, *J* 8.4 and 11.0, 4-H), 7.25 (1 H, d, *J* 8.4, 5-H), 7.49 (1 H, d, *J* 11.0, 3-H), 7.40–7.60 and 8.30–8.40 (3 H, m and 1 H, m, Ar–H); HRMS: Calc. for $C_{14}H_{16}BCl$ (M^+) 230.1034, 232.1004. Found 230.1031, 232.1011. For **5a**: 54%, colorless oil, bp 80–100 °C (4×10^{-6} mmHg); δ_H(400 MHz, $CDCl_3$) 1.19 (9 H, s, Bu^t), 6.50 (1 H, dd, *J* 7.0 and 11.7, 4-H), 6.75 (1 H, d, *J* 7.0, 3-H), 6.88 (1 H, d, *J* 11.7, 5-H), 7.17–7.52 and 7.71–7.80 (6 H, m and 3 H, m, Ar-H); HRMS: Calc. for $C_{20}H_{21}B$ (M^+) 272.1736. Found 272.1734.

¶ The reaction of **3a** with $SbCl_3$ was carried out in $CDCl_3$, and the formation of **6a** was characterized by ^{1}H NMR spectroscopy. *Selected data* for **6a**: δ_H(400 MHz, $CDCl_3$) 1.25 (9 H, s, Bu^t), 6.41 (1 H, dd, *J* 5.5 and 13.0, 4-H), 6.68 (1 H, d, *J* 5.5, 3-H), 7.07 (1 H, d, *J* 13.0, 5-H), 7.25–7.54 and 7.92 (3 H, m and 1 H, d, *J* 6.4, Ar–H).

‖ *Selected data* for **7a**: 57% from **3a**, colorless oil; δ_H(400 MHz, $CDCl_3$) 0.95 (3 H, s, Sb–Me), 1.18 (9 H, s, Bu^t), 6.28 (1 H, dd, *J* 6.0 and 13.2, 4-H), 6.69 (1 H, d, *J* 6.0, 3-H), 6.82 (1 H, d, *J* 13.2, 5-H), 7.29–7.49 and 7.61–7.71 (3 H, m and 1 H, m, Ar-H); δ_C(100 MHz, $CDCl_3$) −6.18 (q), 30.59 (q), 39.36 (s), 127.43 (d), 127.86 (d), 128.14 (d), 129.43 (d), 129.57 (d), 132.62 (d), 133.81 (s), 137.05 (d), 142.80 (s), 157.20 (s); HRMS: Calc. for $C_{15}H_{19}Sb$ (M^+) 320.0525. Found 320.0533. For **7b**: 41% from **3b**, colorless oil. For **8a**: 36% from **3a**, colorless oil. For **8b**: 41% from **3b**, colorless oil.

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Received in Cambridge, UK, 4th December 1997; 7/08739J