

A Versatile Synthetic Route to 1-Benzometalloles Involving the First Examples of Several C-Unsubstituted Benzometalloles

Jyoji Kurita, Makoto Ishii, Shuji Yasuie and Takashi Tsuchiya*

Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-11, Japan

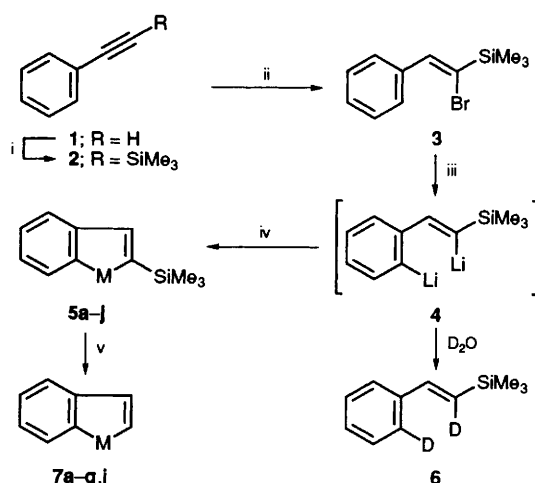
The group 14 (Si, Ge, Sn), group 15 (P, As, Sb, Bi) and group 16 (S, Se, Te) (2-trimethylsilyl)-1-benzometalloles **5** have been prepared from phenylacetylene *via* three steps and converted into the corresponding C-unsubstituted benzometalloles **7** by detrimethylsilylation.

A variety of fully unsaturated monocyclic and fused five-membered heterocyclic rings containing an element other than nitrogen, oxygen or sulfur (metalloles) have been prepared.¹ However, their synthetic routes are not always versatile, in addition, most of known metalloles are highly substituted and only few examples of C-unsubstituted metalloles have been reported. We report here a versatile synthetic route to group 14 (Si, Ge, Sn), group 15 (P, As, Sb, Bi) and group 16 (S, Se, Te), 1-benzometalloles, all of which can be obtained easily from a common starting material, and the synthesis of the first examples of several C-unsubstituted benzometalloles.

Phenyl(trimethylsilyl)acetylene **2** prepared from phenylacetylene **1** was hydraluminated² with diisobutylaluminium hydride (DIBAL-H) in hexane followed by bromination with *N*-bromosuccinimide (NBS) to give (*Z*)-β-bromo-β-(trimethylsilyl)styrene **3** in *ca.* 80% yield from **1**. The key starting compound **3** was treated with *n*-butyllithium in dry diethyl ether under argon atmosphere, then with a metal reagent to result in ring closure giving rise to the desired 2-trimethylsilyl-1-benzometalloles **5a-j** in 60–90% yields (Table 1),[†] *via* the dilithium intermediate **4**.³ When deuterium oxide was used instead of the metal reagents, the dideuteriostyrene **6** was

formed. This result clearly gives evidence for the intermediacy of the 1,4-dianion species **4** in the reaction process.

It is to be emphasized that the trimethylsilyl (TMS) group is essential for the present synthetic route since it plays an important role in the route. Namely, the presence of the TMS group in **2** causes the regio- and stereo-selective formation of the (*Z*)-β-bromostyrene **3** in a high yield. Replacement of the TMS group by an alkyl or aryl group did not lead to such selective bromination affording a mixture of four olefinic isomers, and (*Z*)-β-bromostyrene having no other substituent on the vinyl function, on treatment with *n*-butyllithium, underwent only elimination to give phenylacetylene **1**. Finally, the TMS group in **5** can be readily removed forming the C-unsubstituted benzometalloles **7** in high yields. The group 16 metalloles **7a-c** were obtained almost quantitatively by treatment of **5a-c** with aqueous potassium hydroxide in methanol. However, similar alkaline treatment of the other group metalloles **5d-j** resulted mainly in decomposition to



Scheme 1 Reagents and conditions: i, BuⁿLi, diethyl ether, Me₃SiCl, -78 °C, 1.5 h, 85%; ii, DIBAL-H, hexane, room temp., 20 h, NBS, -20 °C to room temp., 3 h, 92%; iii, BuⁿLi, diethyl ether, argon, reflux, 2 h; iv, reagents (see Table 1), diethyl ether, 0 °C to room temp., 1–2 h, 60–90%; v, 30% KOH, MeOH, 65–75 °C, 2–3 h, quant., for **7a-c**; CsF, THF-H₂O (5%), 65 °C, 2 h, 90%, for **7d**; TBAF, THF-H₂O(5%), 60 °C, 2 h, 85–97%, for **7e-g,i**

Table 1 2-(Trimethylsilyl)benzometalloles **5**

Compound	M	Reagent	Yield (%)
5a	S	(PhSO ₂) ₂ S	62 ^b
5b	Se	Red Se	67 ^b
5c	Te	Te powder	90 ^b
5d^a	POPh	PhPCl ₂	83 ^c
5e	AsPh	PhAsCl ₂	90 ^d
5f	SbPh	PhSbCl ₂	82 ^e
5g	BiPh	PhBiBr ₂	78 ^f
5h	SiMe ₂	Me ₂ SiCl ₂	80 ^b
5i	GeMe ₂	Me ₂ GeCl ₂	85 ^b
5j	SnMe ₂	Me ₂ SnCl ₂	87 ^b

^a 1-Phenyl-2-(trimethylsilyl)benzophosphole was initially formed, but it was readily oxidised to be isolated as **5d**. ^b Oil. ^c M.p. 146–147 °C. ^d M.p. 66–67 °C. ^e M.p. 59–60 °C. ^f M.p. 73–75 °C.

[†] Satisfactory elemental analyses and spectroscopic (¹H NMR and mass) data were obtained for all new benzometalloles **5a-j** and **7e-g, i**.

give **7** in very poor yields, but treatment with a fluoride reagent such as caesium fluoride and tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) containing water afforded the corresponding C-unsubstituted benzometalloles **7** in high yields, except for the benzosilole **5h** and benzostannole **5j**, which decomposed to give no products.

Although the benzoselenole **7b**,⁴ benzotellulole **7c**⁵ and benzophosphole **7d**[‡] are known, the other C-unsubstituted benzometalloles **7e–g**,ⁱ are new compounds. § It should be noted in the ¹H NMR spectra of new group 15 benzometalloles **7e–g** that the 3-protons (δ **7e**, 7.49; **7f**, 7.89; **7g**, 9.93) resonate at lower field than the 2-protons (δ **7e**, 7.16; **7f**, 7.42; **7g**, 9.30) by analogy with 1-phenylbenzophosphole⁶ (δ 3-H, 7.36; 2-H, 6.82), but in contrast to 1-phenylindole⁷ and group 16 (O, S, Se, Te) benzoheteroles,⁸ of which 3-protons resonate at higher field than the 2-protons. The values of the chemical shifts of the olefinic protons are in the order **7d** (P) > **7e** (As)

> **7f** (Sb) > **7g** (Bi); this tendency is similar to that observed for the group 16 benzometalloles **7a–c**.⁸

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‡ The benzophosphole 1-oxide **7d** was readily deoxygenated by treatment with trichlorosilane in benzene to give 1-phenyl-1-benzophosphole.

§ Selected data (m.p. and ¹H NMR) for new N-unsubstituted benzometalloles **7**: **7e**: m.p. 61–63°C; δ 7.16 (1H, d, 2-H), 7.49 (1H, d, 3H), 7.1–7.7 (9H, m, Ar-H) and $J_{2,3}$ 7.7 Hz; **7f**: m.p. 28–29°C; δ 7.42 (1H, d, 2-H), 7.89 (1H, d, 3-H), 7.0–7.6 (9H, m, Ar-H) and $J_{2,3}$ 9.3 Hz; **7g**: m.p. 55–58°C; δ 9.30 (1H, d, 2-H), 9.93 (1H, d, 3-H), 7.1–7.7 (9H, m, Ar-H) and $J_{2,3}$ 8.8 Hz; **7i**: b.p. 93–95°C (20 mmHg); δ 0.52 (6H, s, GeMe₂), 6.54 (1H, d, 2-H), 7.34 (1H, d, 3-H), 7.2–7.6 (4H, m, Ar-H) and $J_{2,3}$ 9.5 Hz. The assignment of the olefinic protons of these compounds was based on the chemical shifts of 3-protons of the corresponding 2-deuterio-1-benzometalloles prepared from **5** by treatment with TBAF in THF containing D₂O.