Synthesis of 1-Stibaphenalenes, the First Example of Group 15 Phenalenes, via a 1, 5-Dilithium Intermediate

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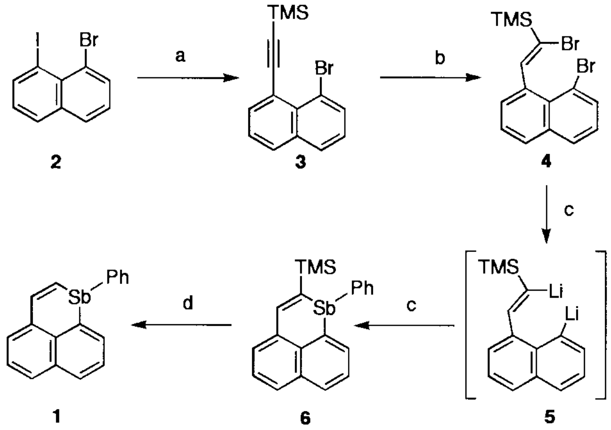
The first examples of 1-stibaphenalenes **1** and **6** have been prepared by the condensation of dibromophenylstibane with 1,5-dilithium intermediate **5**, generated in situ from (*Z*)-1-bromo-2-[1-(8-bromonaphthyl)]-1-trimethylsilylethene (**4**). Single crystal X-ray analysis of **1** revealed that the naphthalene and the fused stibinine ring are almost coplanar (mean deviation 0.0264 Å), and the phenyl group on the antimony is oriented perpendicular with the phenalene ring.

The synthesis of new heterocyclic rings containing main group heavier elements other than nitrogen, oxygen or sulfur has recently received increasingly intensive study, and a variety of monocyclic and fused heterocyclic compounds containing group 14 (Si, Ge, and Sn), group 15 (P, As, and Sb), and group 16 (S, Se, and Te) heavier elements have been prepared.[1] With regards to 1-heterophenalenes, however, only a few examples such as 1-silaphenalenes[2] and 1-thiaphenalene[3] have been reported. On the other hand, we have recently reported that the condensation of 1,4-, 1,6- and 1,9-dilithium compounds, generated from the appropriate dihalides by treatment with alkyllithium reagents, with group 14, 15, and 16 dihalides (MX_2, M=SiR_2, GeR_2, SnR_2, AsR, SbR, BiR, Se, and Te), afforded the corresponding hetroles,[4] heteroepines,[5] and heteroecines,[6] respectively. In the course of our continuing studies on the synthesis of new heterocyclic compounds, we were interested in the synthesis of new 1-heterophenalens. Here we report the synthesis of 1-stibaphenalenes which are the novel herterocyclic ring systems, by the condensation of dibromophenylstibane with the key 1,5-dilithium intermediate **5**, and the X-ray crystal structure of *C*-unsubstituted 1-stibaphenalene **1** obtained from the desilylation of **6** with TBAF.

The present synthetic routes to 1-stibaphenalenes **6** and **1** are shown in Scheme 1. 1-Bromo-8-iodonaphthalene (**2**),[7] prepared from 1,8-naphthalic anhydride via 3 steps, was coupled with trimethylsilylacetylene in diethylamine in the presence of a catalytic amount of a mixture of bis(triphenylphosphine)palladium dichloride and copper(I) iodide to afford 1-[(8-bromonaphthyl)]-2-trimethylsilylacetylene (**3**) in 69% yield.[8] The alkyne **3** was hydraluminated with DIBAL-H followed by bromination with NBS, giving rise to the (*Z*)-1-bromo-2-[1-(8-bromonaphthyl)]-1-trimethylsilylethene (**4**) in 59% yield. The stereochemistry of the olefine function on **4** was elucidated by ^{1}H NMR spectral analysis; an NOE was observed between 2-H and the TMS protons, indicating that the C1–C2 bond has (*Z*)–stereochemistry. The dibromo compound **4** was treated with a large excess (5–6 mol equiv) of *tert*-butyllithium in dry ether under an argon atmosphere at –80 °C, and followed with dibromophenylstibane, resulting in ring closure to form the expected 2-trimethylsilyl-1-stibaphenalene **6**. When a monobromo compound, (*Z*)-1-bromo-2-(1-naphthyl)-1-trimethylsilylethene, prepared from 1-iodonaphthalene by the same procedure, was used instead of the dibromo compound **4** in the above reaction, no ring-closure products were formed. This result indicates that the presence of the bromine moiety in the 8 position on the naphthalene ring is essential for the formation of 1,5-dilithium intermediate **5** under the present conditions. The TMS group in **6** was readily removed by treatment with TBAF in THF containing water to give the desired *C*-unsubstituted 1-phenalene **1** in 61% yield.[9] The stibaphenalenes **6** and **1** obtained here were isolated as stable crystalline compounds, and no change was observed even when heated at 110 °C for 24 h in toluene in the presence or in the absence of AIBN. Treatment of stibaphenalene **1** with SO_2Cl_2 resulted in oxidation of antimony atom to afford 1,1-dichloro-1-phenyl-λ^5-stibaphenalene (mp 224–228 °C), which reverted to **1** by treatment with aqueous Na_2S.



a) 2-TMS-Phenylacetylene, $PdCl_2(PPh_3)_2$,CuI in Et_2NH, rt, 5 h, 69%;
b) DIBAL-H in hexane, rt, 12 h, and then NBS, 0 °C→ rt, 5 h, 59%;
c) ^{t}BuLi in ether, –80 °C,1 h, and then $PhSbBr_2$, –80 °C→ rt, 4 h, 57%;
d) H_2O-TBAF(95%) in THF, 0 °C, 1 h, 61%.

Scheme 1.

The structures of 1-stibaphenalenes **6** and **1** were elucidated mainly by their HRMS, NMR spectral and combustion analyses. In the ^{1}H NMR spectrum of **6**, the signals for TMS protons and 2-H appeared at δ 0.15 (s) and δ 7.76 (s), respectively, while in **1**, two vinyl protons appeared at δ 6.79 for 2-H and δ 7.36 for 3-H (each d, J=12.8 Hz).

The ORTEP drawing (a) and its side view (b) of the *C*-unsubstituted 1-stibaphenalene **1** obtained from the single crystal X-ray analysis are illustrated in Figure 1.[10] The results revealed that the naphthalene and the fused stibinine rings are almost planar (mean deviation 0.0264 Å) to each other. The phenyl group on the antimony atom is oriented nearly perpendicular to the phenalene ring; the dihedral angles for C(3)–C(2)–Sb–C(1'), C(9)–C(9a)–Sb–C(1'), and C(9b)–C(9a)–Sb–C(1') are –98.3(10)°, –82.1(8)°, and 100.1(7)°, respectively. The three Sb–C distances, Sb–C(2) (2.125 Å), Sb–C(9a) (2.174 Å), and Sb–C(1') (2.135 Å), are close to the typical range of Sb–C (sp^2) bonds (2.1–2.25 Å),[5b,11] and no noticeable difference in the C–C bond lengths is seen, except for the C(1)–C(2) bond (1.30 Å) which is relatively shorter than that of a standard double bond. The bond angles surrounding of the antimony atom are slightly undistributed (91.6°, 95.4°, and 98.4°), in that the inner angle of the stibinine ring (C2)–Sb–C(9a) (91.6°) is increased owing to an influence of the ring closing to a 6-membered ring; the corresponding angles for 5-membered 4,7-dimethoxy-2,3-dimethyl-1-phenylstibindole[11] and 7-membered 1-phenyl-1-benzostibepine[5b] have been reported to be 79.9° and 85.8°, respectively.

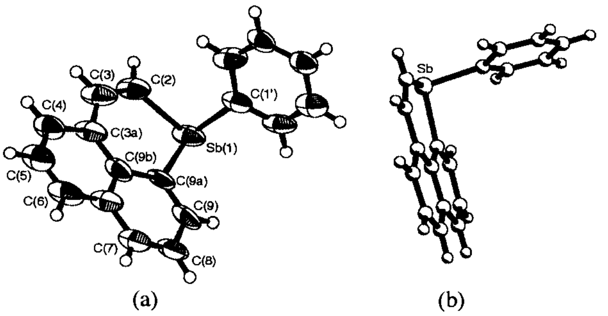


Figure 1. Molecular structure of 1-phenyl-1-stibaphenarene (**1**). (a) Front view. (b) Side view.

It is clear from the above results that the condensation of 1,5-dilithium intermediate **5**, readily accessible from 1-bromo-8-iodonaphthalene, with the dibromostibane gave the novel ring system 1-stibaphenalene **6** which can be easily derived to the *C*-unsubstituted 1-stibaphenalenes **1**. To the best of our knowledge, these are the first examples of 1-heterophenalens having group 15 heavier elements. Further studies in this area, including the chemical behavior of 1-stibaphenalenes and the preparation of 1-heterophenalenes comprising other heavier elements, are in progress.

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9 Satisfactory analytical (combustion and/or high-resolution mass) and spectral (IR, NMR, and MS) data were obtained for all new compounds reported. **3**: yellow oil; **4**: pale yellow oil; **6**: mp 129–130 °C, pale red prisms (hexane), ^{1}H NMR (400 MHz, *J* Hz, $CDCl_3$, Std., CH_2Cl_2, δ 5.30); δ 0.15 (9H, s, TMS), 7.1–7.2 (3H, m, Ar-H), 7.36 (1H, dd, J = 8.2 and 7.2, Ar-H), 7.4–7.5 (4H, m, Ar-H), δ 7.76 (1H, s, 3-H), δ 7.78 (1H, dd, J = 5.1 and 1.5, Ar-H), 7.8–7.85 (2H, m, Ar-H); HR-MS; *m/z*: 422.0458 (Calcd. for $C_{21}H_{21}SbSi$, 422.0451); **1**: mp 77–78 °C, colorless needles (MeOH), ^{1}H NMR (400 MHz, *J* Hz, $CDCl_3$, Std., CH_2Cl_2, δ 5.30); δ 6.79 (1H, d, J = 12.8, 2-H), 7.15–7.2 (3H, m, Ar-H), 7.39 (1H, dd, J = 8.5 and 7.0, Ar-H), 7.4–7.5 (4H, m, Ar-H), 7.56 (1H, d, J = 12.8, 3-H), 7.75–7.85 (3H, m, Ar-H); UV λ_{max} nm(log ε) (EtOH) 228(4.32), 235(4.32), 267sh (3.75), 319sh (3.81), 325sh (3.88), 336(4.00), 341sh (3.99), 325 (3.96); HR-MS; *m/z*: 350.0054 (calcd for $C_{18}H_{13}Sb$, 350.0055).

10 Crystal data for **1**: $C_{18}H_{13}Sb$, fw =351.05, monoclinic, a = 11.043(3), b = 5.330(6), c = 23.22(2) Å, β = 98.68 (6)°, V = 1350(1) Å^3, T = 100±1 K, space group $P2_1/c$(no. 14), Z = 4, μ(Mo Kα) = 20.21 cm^{-1}, 1948 reflections measured, 1776 reflections {I>2.40 σ(I)} were used in all calculations, R = 0.068, R_w = 0.092. The data were collected on a Rigaku RAXIS-II imaging plate area detector with graphite-monochromated Mo Kα (λ = 0.71070 Å). All of the structures were solved by direct method (program SIR92) and expanded using Fourier technique (program DIRDIF94)

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