AN ALTERNATIVE ROUTE FOR THE PREPARATION OF
1-BENZOSTANNEPINES, 1-BENZOSTIBEPINES AND
1-BENZOSILEPINES VIA Te-Li EXCHANGE OF
1-BENZOTELLUREPINES

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Abstract - Treatment of 1-benzotellurepines (1) with t-BuLi in the presence of
TMEDA in ether followed by addition of a metal reagent (Cl₂SnBu₂, Cl₂SbPh and
Cl₂SiMe₂) afforded the corresponding 1-benzostannepines (4), 1-benzostibepines
(5) and 1-benzosilepines (6), respectively, in one pot via the tellurium - lithium
exchange.

Recently, the synthesis of heterocyclic rings containing an element heavier than nitrogen, oxygen, or surfur
has received increasing attention. However, compared with the synthetic methods for the preparation of five-
and six-membered heterocycles, those of the fully unsaturated seven-membered heterocycles (heteroepines) have
been investigated to a limited extent. In particular, 1-benzoheteroepines have been only rarely reported.
This deficit is due on the one hand, to the instability of the heteroepines, and on the other hand, to
the absence of suitable access for their preparation.

Scheme 1
Previously, we reported the synthesis of 1-benzotellurepines (B), 6,7 novel fully unsaturated seven-membered tellurium-containing heterocycles, and also succeeded in the preparation of 1-benzostannepines (C).8 The method for the preparation of these seven-membered heterocyclic compounds is based on the 7-endo-dig cyclization to an acetylenic moiety of the o-(1-buten-3-ynyl)phenylmetalols (A). In addition, the stannepines (C) were found to be converted into the corresponding 1-benzo-borepines (D), -stibepines (E) and -tellurepines (B) by a tin-metal exchange reaction. However, 1-benzosilepines (G) could not be prepared by the above two methods; the intramolecular hydrosilylation of the Si-H group to an acetylene moiety gave the six-membered 6-exo-dig products (F),9 and the tin-silicon exchange reaction of the stannepines did not proceed (Scheme 1).

In our previous paper,7 we reported that 2-tert-butyl-1-benzotellurepine (1a) reacted with 2.2 equiv. of n-BuLi in the presence of TMEDA in ether, and followed by quenching with aqueous ammonium chloride to give the diene compound (2) in 70-86 % yields. This result clearly indicates the generation of the 1,6-dilithio compound (3) as an intermediate for producing the diene (2). More recently, we described that the treatment of isotellurochromene, a six-membered tellurium-containing heterocycle, with n-BuLi resulted in a tellurium-lithium exchange to give (E)-o-(2’-lithiovinyl) benzyllithium, the 1,5-dilithiated synthetic building block.10 These findings suggest that 1-benzosilepines may be prepared from the tellurepines (1). This paper describes the conversion of the 1-benzotellurepines (1) into the seven-membered heterocycles containing Sn, Sb or Si via the Te-Li exchange.

The tellurepines (1) were lithiated with 2.2 equiv. of t-BuLi in the presence of TMEDA in ether followed by addition of dibutyltin dichloride (n-Bu₂SnCl₂) to give the desired 1,1-dibutyl-1-benzostannepines (4) as the sole characterized products in ca. 35 % yields. The lithiation of 1 with 1.0 equiv. of t-BuLi followed by the addition of 1.0 equiv. of tin reagent gave a 1:1 mixture of the starting tellurepine (1) and the stannepine (4). The use of a 2.0 equiv. of lithiating reagent was necessary in order to completely generate the essential

![Scheme 2](image-url)

**Scheme 2 Reagents and Conditions:** i, t-BuLi, TMEDA, ether, -80 °C to rt; ii, H₂O, rt; iii, MCl₂, rt.
intermediate (3). Compounds (4) may probably be formed by the successive coupling of 3 with the tin reagent. Similarly, the 1-benzostibepines (5) and the 1-benzosilepines (6) were also obtained by the treatment of dichlorophenylstibine (Cl\textsubscript{2}SbPh) or dichlorodimethylsilane (Cl\textsubscript{2}SiMe\textsubscript{2}) instead of n-Bu\textsubscript{2}SnCl\textsubscript{2} after the lithiation of 1, while the yields were not good since they are thermally labile. Although the C-unsubstituted 1-benzostibepine\textsuperscript{5} and 1-benzosilepine\textsuperscript{6} have been prepared, the 2-tert-butyl (6a) and 2-n-butyl derivatives (6b) are hitherto unknown compounds. These results are summarized in Scheme 2.

In conclusion, an alternative synthetic route for 1-benzostannepines, 1-benzostibepines and 1-benzosilepines from 1-benzotellurepines as sole key starting materials was achieved. Further studies on the details of the reactivities of not only the 1-benzotellurepines but also the tellurium - lithium exchange of the heterocycles containing a tellurium atom are now under investigation.

EXPERIMENTAL

General Methods.
The MS spectra and HRMS spectra were recorded on a JEOL JMS-DX300 instrument. The \textsuperscript{1}H-NMR spectra were determined with a JEOL PMX-60SI (60 MHz), JEOL EX-90A (90 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in deuteriochloroform using tetramethylsilane as the internal standard and the \textit{J} values are given in Hz.

**General procedure for the metalepines (4-6):**
To a stirring solution of 2-tert-butyl-1-benzotellurepine (1, 314 mg, 1.00 mmol) and TMEDA (350 mg, 3.00 mmol) in Et\textsubscript{2}O (20 mL) at -80 °C under an argon atmosphere was slowly added t-BuLi (1.50 mol in pentane solution, 1.46 mL, 2.20 mmol). The reaction mixture was stirred under these conditions for 30 min. The metal reagent (MCl\textsubscript{2}, 1.20 mmol) was added to the reaction mixture in one portion, the cooling bath was removed, and the temperature of the mixture was gradually allowed to rise to rt during 3-4 h. The resulting mixture was further stirred for 1 h, poured into ice-water, and then extracted with ethyl acetate (50 mL x 3). The organic extracts were washed with brine (50 mL x 2), dried (MgSO\textsubscript{4}), and evaporated. The residue was chromatographed on silica gel using \textit{n}-hexane : CH\textsubscript{2}Cl\textsubscript{2} (20:1) as an eluent to give the metalepines (4-6).

**2-tert-Butyl-1,1-din-butyl-1-benzostannepine (4a):** 35 % yield, pale yellow oil. This compound was identical with the authentic sample prepared in our previous paper.\textsuperscript{8}

**2-n-Butyl-1,1-din-butyl-1-benzostannepine (4b):** 35 % yield, pale yellow oil. \textsuperscript{1}H-NMR (400 MHz): 0.87-0.91, 1.13-1.17, 1.30-1.38, 1.53-1.59 and 2.24-2.34 (9H, m, 4H, m, 8H, m, 4H, m and 2H, m, n-Bu x 3), 6.13 (1H, dd, \textit{J} = 5.9 and 13.6 Hz, 4-H), 6.50 (1H, d, \textit{J} = 5.9 Hz, 3-H), 6.71 1H, d, \textit{J} = 13.6 Hz, 5-H), 7.26-7.32 and 7.42-7.44 (3H, m, and 1H, m, Ph-H). HRMS \textit{m/z}: C\textsubscript{22}H\textsubscript{34}Sn (M\textsuperscript{+}): 418.1682. Found: 418.1757.

**2-tert-Butyl-1-phenyl-1-benzostibepine (5a):** 37 % yield, colorless oil. \textsuperscript{1}H-NMR (400 MHz): 1.31
(9H, s, t-Bu), 5.93 (1H, dd, J = 6.2 and 13.0 Hz, 4-H), 6.42 (1H, d, J = 13.0 Hz, 5-H), 6.85 (1H, d, J = 6.2 Hz, 3-H), 7.12 (5H, br s, Sb-Ph-H), 7.33-7.67 and 7.79-7.98 (3H, m and 1H, m, Ph-H). HRMS m/z: C_{20}H_{21}Sb (M⁺): 382.0682. Found: 382.0681.

2-n-Butyl-1-phenyl-1-benzostibepine (5b): 39 % yield, colorless oil. ¹H-NMR (400 MHz): 0.87, 1.00-1.52 and 2.20-2.30 (3H, t, J = 7.3 Hz, 4H, m and 2H, m, n-Bu), 6.23 (1H, dd, J = 5.5 and 13.0 Hz, 4-H), 6.61 (1H, dt, J = 1.3 and 5.5 Hz, 3-H), 6.84 (1H, J = 13.0 Hz, 5-H), 7.25 (5H, br s, Sb-Ph-H), 7.28-7.54 and 7.58-7.72 (3H, m, 1H and m, Ph-H). HRMS m/z: C_{20}H_{21}Sb (M⁺): 382.0682. Found: 382.0688.

2-tert-Butyl-1,1-dimethyl-1-benzosilepine (6a): 19 % yield, pale yellow oil. ¹H-NMR (400 MHz): 0.40 (6H, s, SiMe₂), 1.16, (9H, s, t-Bu), 6.38 (1H, dd, J = 6.2 and 12.5 Hz, 4-H), 6.58 (1H, d, J = 6.2 Hz, 3-H), 6.95 (1H, d, J = 12.5 Hz, 5-H), 7.25-7.59 (4H, m, Ph-H). HRMS m/z: C_{20}H_{21}Si (M⁺): 242.1491. Found: 242.1490.

2-n-Butyl-1,1-dimethyl-1-benzosilepine (6b): 15 % yield, pale yellow oil. ¹H-NMR (400 MHz): 0.35 (6H, s, SiMe₂), 0.90, 1.15-1.40 and 2.20-2.35 (3H, t, J = 7.0, 4H, m and 2H, m, n-Bu), 6.34 (1H, dd, J = 6.0 and 12.8 Hz, 4-H), 6.68 (1H, d, J = 6.0 Hz, 3-H), 6.93 (1H, d, J = 12.8 Hz, 5-H), 7.25-7.55 (4H, m, Ph-H). HRMS m/z: C_{20}H_{21}Si (M⁺): 242.1491. Found: 242.1489.

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REFERENCES AND NOTES
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