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TIN–TELLURIUM EXCHANGE REACTION IN TIN-CONTAINING HETEROCYCLES: A NEW ENTRY FOR THE PREPARATION OF TELLURIUM HETEROCYCLES¹

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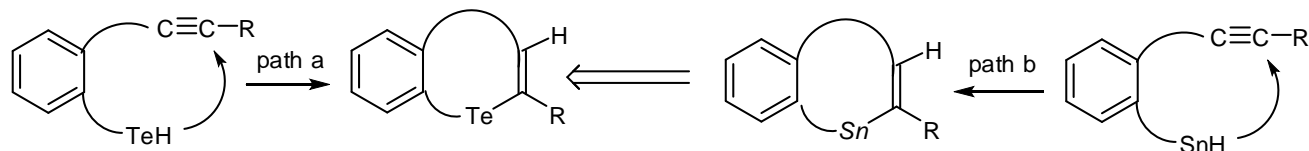
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Abstract – An alternative, simple and practical preparation of benzo[*b*]-tellurophene, 1*H*-isotellurochromene, and 1-benzo- and 3-benzotellurepines by taking advantage of the tin-tellurium replacement reaction from the corresponding five-, six- and seven-membered tin-containing heterocycles was achieved.

Much attention has focused on the chemistry of not only aromatic, but also non-aromatic heterocycles containing a heavier element, and many results about their syntheses, chemical properties and applications have been reported. It is well known that five-,² six-³ and seven-membered⁴ tin-containing vinyl compounds are excellent precursors of tin-metal exchange reactions⁵ for the preparation of the corresponding heterocycles containing a heavier element, *i.e.*, boron,^{2a-d,3a,3b,3p,4a-h} phosphorus,^{2e,3d,3g,3i,3l} arsenic,^{2e,3c,3d,3g,3i,3j,3l,3m} antimony^{3e,3h,3i,3l,3n,3o,4i} and bismuth^{3f,3i,3k,3l,3o} elements. Thus, the synthesis of the parent tin containing heterocycles seemed extremely desirable.

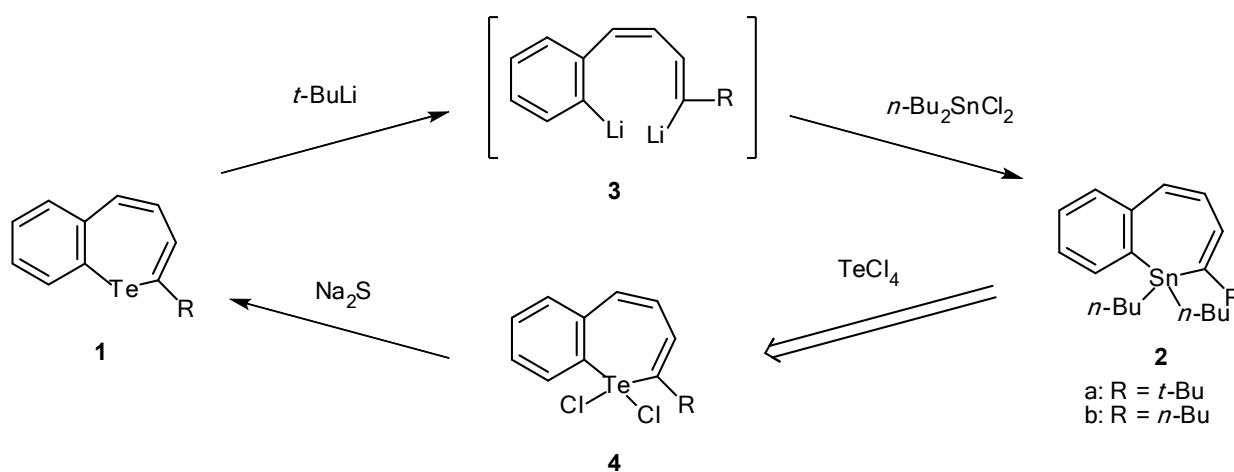
Previously, we succeeded in the preparation of the 1-benzotellurepines (1),⁶ which are novel seven-membered conjugated heterocycles containing a tellurium element, *via* the successive intramolecular cyclization of tellurols into an acetylene moiety (Scheme 1, path a).⁷ Moreover, we have focused on the

Synthesis of various tellurium-containing heterocyclic ring systems using efficient similar intramolecular cyclization reactions involving an acetylene group. The 1-benzostannepine skeleton (**2**)⁸ has also been constructed by this intramolecular cyclization methodology (path b).



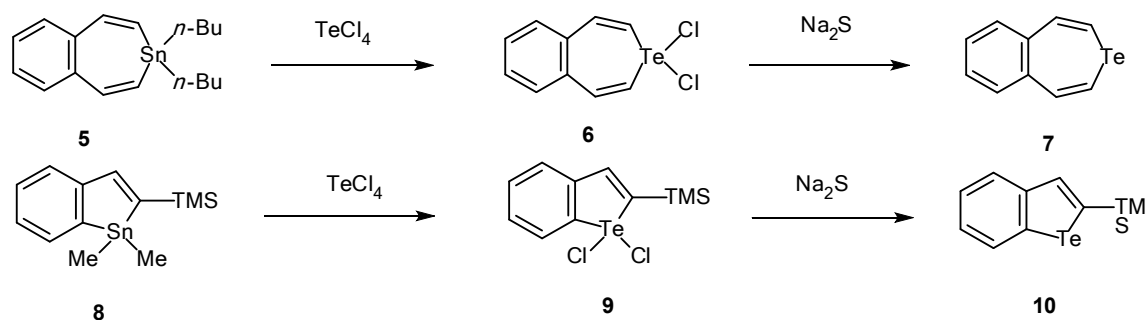
Scheme 1

Furthermore, the 1-benzostannepines (**2**) have previously been prepared through dilithium intermediates (**3**)⁹ which were generated by the treatment of the 1-benzotellurepines (**1**) with *tert*-BuLi in the presence of TMEDA. In this paper, we describe an alternative route for the preparation of the several heterocycles containing of a tellurium element by the novel replacement reaction of the tin-tellurium element.¹⁰



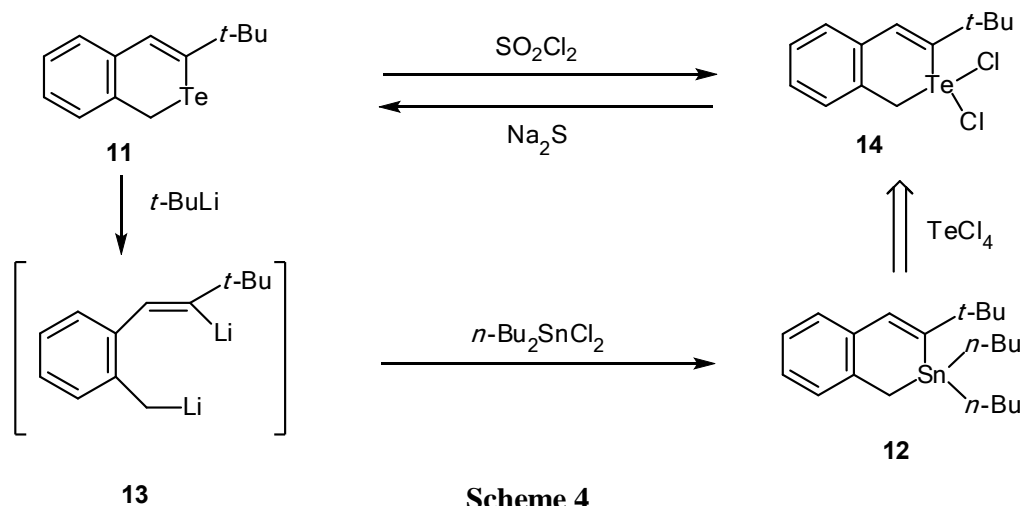
Scheme 2

The treatment of the 2-*tert*-butyl and 2-*n*-butyl-1-benzostannepines (**2a, b**)⁸ with 1.0 equivalent of TeCl₄ in CHCl₃ at 0 °C resulted in the tin-tellurium exchange reaction to give the corresponding 1,1-dichlorotellurepines (**4a, b**) in 82 and 77% yields, respectively. Compounds **4a** and **b** were obtained as thermally stable yellow and pale yellow crystals at room temperature under an inert atmosphere. The 1,1-dichlorotellurepines (**4a, b**) were dechlorinated upon treatment with a 2% aqueous Na₂S solution reverting to the tellurepines (**1**)⁶ in almost quantitative yield.



3,3-Dichloro-3-benzotellurepine (**6**) was also synthesized by the reaction of the 3-benzostannepine (**5**)¹¹ with TeCl_4 in 78% yield. A five-membered tin heterocycle, the stannaindole (**8**),¹² can be readily transformed into the benzo[*b*]tellurophene (**9**) based on this telluration in 80% yield. Compounds **6** and **9** were also treated with Na_2S to give the known parent tellurium heterocycles (**7**, **10**).^{13,14}

In addition, the six-membered 2-stannanaphthalene (**12**)¹⁵ similarly reacted with TeCl_4 to afford the dichloroisotellurochromene (**14**, 80% yield), which was quantitatively dechlorinated upon treatment with Na_2S , reverting to **11**.¹⁶ (*E*)-*o*-(2'-Lithiovinyl)benzyl lithium (**13**), generated by the tellurium-lithium exchange of 3-*tert*-butyl-1*H*-isotellurochromene (**11**) with BuLi , reacted with an electrophile and a metal reagent to afford the styrene derivatives and 1,2-dihydro-2-metalanaphthalenes involving the 1,2-dihydro-2-stannanaphthalene (**12**) in good yields, respectively. Very recently, we reported¹⁷ that the 2,2-dichloroisotellurochromene (**14**) was obtained by the treatment of **11** with SO_2Cl_2 in high yield and has the tellurane structure of the hypervalent tellurium compound. Thus, the mutual transformation between the 1*H*-isotellurochromene (**11**) and 1,2-dihydro-2-stannanaphthalene (**12**) has been accomplished.



In conclusion, the tin-tellurium exchange reaction was found to be a unique and useful tool for the preparation of tellurium-containing heterocycles from the vinylic tin heterocycles. Thus, the 1-benzotellurepines, 3-benzotellurepine, isotellurochromene and benzo[*b*]tellurophene were obtained from the tin-containing heterocycles in high yields.

EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Horiba FT-720 spectrometer. Mass spectra (MS) and HRMS were recorded on a JEOL JMS-DX300 instrument. NMR spectra were determined with a JEOL EX-90A (90 MHz) or a JEOL JNM-GSX 400 (400 MHz) spectrometer in CDCl₃ using tetramethylsilane as internal standard and *J* values are given in Hz. Microanalyses were performed in the Microanalytical Laboratory in this Faculty.

Starting Tin-Containing Heterocycles

1-Benzostannepines (**2**),⁸ 3-benzostannepine (**5**),¹¹ 1-stannaindole (**8**)¹² and 1,2-dihydro-2-stannanaphthalenes (**12**)¹⁵ were prepared by the reported methods.

General Procedure for the Sn-Te Exchange Reaction

TeCl₄ (135 mg, 0.5 mmol) was added in one portion to a solution of tin heterocycle **2** (0.5 mmol) in benzene (5 mL) under an argon at 5 °C. The reaction mixture was vigorously stirred at r.t. for 30 min. Hexane (ca. 15 mL) was added to the mixture, the resulting precipitate was filtered off, and washed with hexane. The crude products were recrystallized from CH₂Cl₂-hexane or benzene-hexane.

2-*tert*-Butyl-1,1-dichloro-1-benzotellurepine (**4a**)

82% yield, pale yellow prisms, mp 156-158 °C (decomp.), (lit.,^{6b} mp 155-158 °C).

2-*n*-Butyl-1,1-dichloro-1-benzotellurepine (**4b**)

77% yield, yellow needles, mp 113-116 °C (decomp.). MS (EI) *m/z* (%): 384(M⁺, 1), 349 (1), 314 (7), 184 (40), 141 (100). ¹H-NMR (400 MHz, CDCl₃) 1.00, 1.48-1.53, 1.73-1.80, 3.00 (3H, t, *J* = 7.3 Hz, 2H, m, 2H, m, 2H, t, *J* = 7.5 Hz, *n*-Bu), 6.30 (1H, dd, *J* = 7.7 and 13.6 Hz, 4-H), 6.68 (1H, d, *J* = 13.6 Hz, 5-H), 6.97 (1H, d, *J* = 7.7 Hz, 3-H), 7.46-7.55, 8.05 (3H, m, 1H, dd, *J* = 6.6 and 2.6 Hz, Ph-H). ¹³C-NMR (100 MHz, CDCl₃) 13.8 (q), 21.9 (t), 31.4 (t), 38.5 (t), 125.1 (d), 128.7 (s), 130.2 (d), 131.8 (d), 133.7 (d), 133.9 (d), 134.5 (d), 136.1 (d), 139.6 (s), 140.3 (s). HRMS *m/z*: C₁₄H₁₆ ³⁵Cl₂ ¹³⁰Te: 383.9691. Found: 383.9749.

3,3-Dichloro-3-benzotellurepine (6)

77% yield, colorless prisms, mp 45-47 °C (decomp), (lit.,¹³ mp 45-48 °C).

1,1-Dichloro-2-(trimethylsilyl)benzo[*b*]tellurophene (9)

88% yield, pale yellow prisms, mp 197-200 °C. MS (EI) *m/z* (%): 376, 374, 372 (M^+ , 2, 4, 3), 339 (15), 337 (13), 304 (80), 289 (90), 159 (100). ¹H-NMR (400 MHz, CDCl₃) 0.46 (9H, s, SiMe₃), 7.44, 7.50-7.64, 7.84 (1H, ddd, *J* = 7.7, 7.4 and 1.8 Hz, 2H, m, 1H, d, *J* = 7.7 Hz, Ph-H), 7.96 (1H, s, 3-H). ¹³C-NMR (100 MHz, CDCl₃) -0.03 (q), 129.4 (d), 129.5 (d), 130.2 (d), 132.3 (d), 148.9 (s), 151.0 (s), 152.5 (d), 159.8 (s). HRMS *m/z*: C₁₁H₁₄³⁵Cl₂Si¹³⁰Te: 373.9304. Found: 373.9276.

3-*tert*-Butyl-2,2-dichloroisotellurochlomene (14)

80% yield, colorless prisms, mp 188-189 °C, (lit.,¹⁷ mp 188-190 °C).

General Procedure for the Dechlorination with Sodium Sulfide

A 2% aqueous Na₂S solution (5 mL) was added to a solution of **4a** (0.2 mmol) in hexane (5 mL) with vigorous stirring in ice-bath for 10 min. Water (10 mL) was added to the reaction mixture, and the whole was extracted with CH₂Cl₂ (20 mL x 3). The combined extract was dried (MgSO₄) and evaporated *in vacuo*. The residue was chromatographed on silica gel with hexane to give the tellurium heterocycles. The obtained compounds were identical with the authentic samples prepared in our previous paper.

2-*tert*-Butyl-1-benzotellurepine (1a): 92%.⁶

2-*n*-Butyl-1-benzotellurepine (1b): 89%.⁶

3-Benzotellurepine (7): 91%.¹³

2-(Trimethylsilyl)benzo[*b*]tellurophene (10): 95%.¹⁴

3-*tert*-Butylisotellurochlomene (11): 88%.¹⁶

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