HETEROCYCLES, Vol. 82, No. 1, 2010, pp. 441 - 447. © The Japan Institute of Heterocyclic Chemistry
Received, 17th March, 2010, Accepted, 23rd April, 2010, Published online, 27th April, 2010
DOI: 10.3987/COM-10-S(E)15

TIN–TELLURIUM EXCHANGE REACTION IN TIN-CONTAINING HETEROCYCLES: A NEW ENTRY FOR THE PREPARATION OF TELLURIUM HETEROCYCLES[1]

Haruki Sashida,[a],* Mamoru Kaname,[a] and Kazuo Ohyanagi [b]

[a] Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan; [b] Faculty of Pharmacy, Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan
h-sashida@hokuriku-u.ac.jp

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.

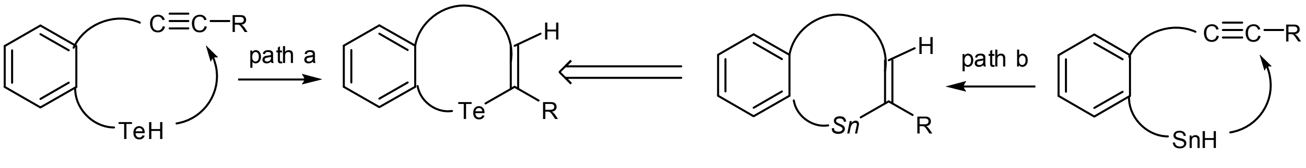
Much attention has focused on the chemistry of not only aromatic, but also non-aromatic heterocycles containing a heavier element, and many results about their syntheses, chemical properties and applications have been reported. It is well known that five-,[2] six-[3] and seven-membered[4] tin-containing vinyl compounds are excellent precursors of tin-metal exchange reactions[5] 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

---

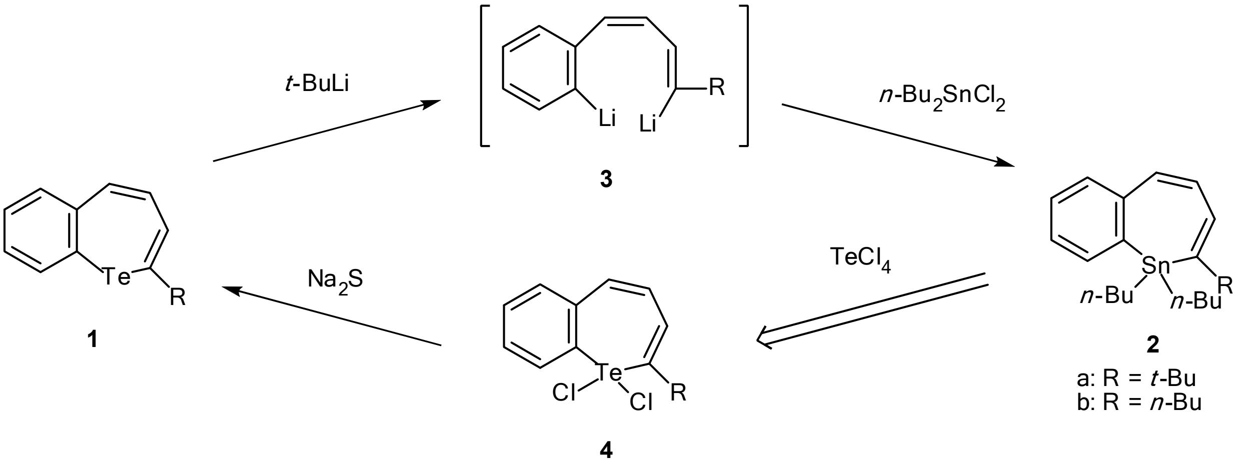
Dedicated to Professor Dr. Albert Eschenmoser, ETH Zürich, on his 85th birthday.

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).



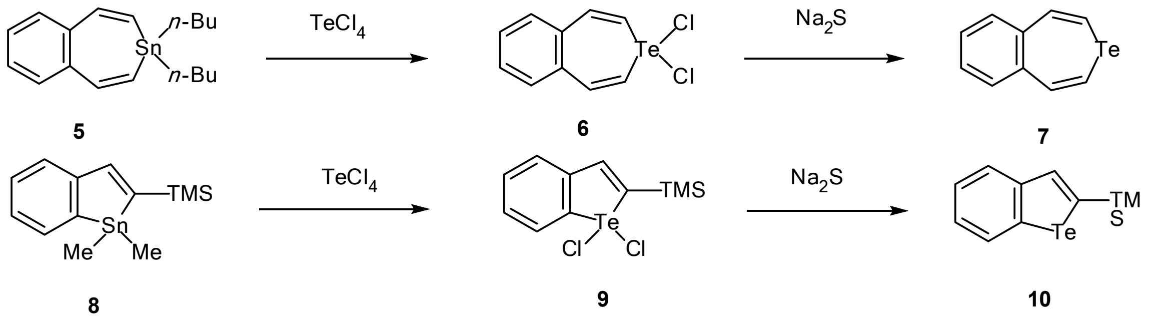
Scheme 1

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

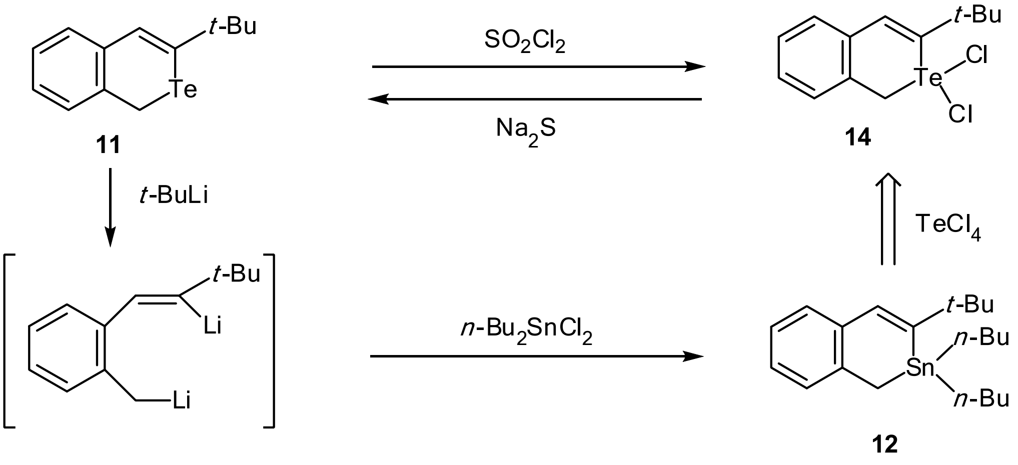
The treatment of the 2-*tert*-butyl and 2-*n*-butyl-1-benzostannepines (**2a**, **b**)[8] with 1.0 equivalent of $TeCl_4$ in $CHCl_3$ at 0 ˚C resulted in the tin-tellurium exchange reaction to give the corresponding 1,1-dichlorotellurepines (**4a**, **b**) in 82 and 77% yields, respectively. Compounds **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 Na_2S solution reverting to the tellurepines (**1**)[6] in almost quantitative yield.



Scheme 3

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)benzyllithium (**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 stylene derivatives and 1,2-dihydro-2-metalanaphthalenes involving the 1,2-dihydro-2-stannanaphthalene (**12**) in good yields, respectively. Very recently, we reported[17] 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 tellulium compound. Thus, the mutual transformation between the 1*H*-isotellurochromene (**11**) and 1,2-dihydro-2-stannanaphthalene (**12**) has been accomplished.



Scheme 4

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 $CDCl_3$ 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

$TeCl_4$ (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 CH_2Cl_2-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). ^{1}H-NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (100 MHz, $CDCl_3$) 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*: $C_{14}H_{16}\,{}^{35}Cl_2{}^{130}Te$: 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). ^{1}H-NMR (400 MHz, $CDCl_3$) 0.46 (9H, s, $SiMe_3$), 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). ^{13}C-NMR (100 MHz, $CDCl_3$) -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*: $C_{11}H_{14}\,^{35}Cl_2Si^{130}Te$: 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 Na_2S 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 CH_2Cl_2 (20 mL x 3). The combined extract was dried ($MgSO_4$) 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]

ACKNOWLEDGEMENT

This work was supported in part by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (19590022). The authors wish to express to Mrs. Koichi Itoh and Atsuhiro Kuroda (Hokuriku University) for their technical assistances.

REFERENCES AND NOTES

1. Studies on tellurium-containing heterocycles. Part 29. Part 28: see H. Sashida, H. Satoh, K. Ohyanagi, and M. Kaname, *Molecules*, 2010, **15**, 1466.
2. (a) J. J. Eisch, N. K. Hota, and S. Kozima, *J. Am. Chem. Soc.*, 1969, **91**, 4575; (b) G. E. Herberich, B. Buller, B. Hessner, and W. Oschmann, *J. Organometal. Chem.*, 1980, **195**, 253; (c) J. J. Eisch, J.

E. Galle, and S. Kozima, *J. Am. Chem. Soc.*, 1986, **108,** 379; (d) J. Ashe, III, X. Fang, and J. W. Kampf, *Organometallics*, 1999, **18**, 1821; (e) A. J. Ashe, III and X. Fang, *Chem. Commun.*, 1999, 1283.

3. (a) P. Jutzi, *J. Organometal. Chem.*, 1969, **19**, 1; (b) A. J. Ashe, III and P. Shu, *J. Am. Chem. Soc.*, 1971, **93**, 1804; (c) P. Jutzi and K. Deuchert, *Angew. Chem.*, *Int. Ed.*, 1969, **8**, 991; (d) A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, **93**, 3293; (e) A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, **93**, 6690; (f) A. J. Ashe, III and M. D. Gordon, *J. Am. Chem. Soc.*, 1972, **94**, 7596; (g) G. Märkl and F. Kneidl, *Angew. Chem.*, *Int. Ed.*, 1973, **11**, 931; (h) A. Meinema, C. J. R. Crispim Romão, and J. G. Noltes, *J. Organometal. Chem.*, 1973, **55**, 139; (i) P. Jutzi, *Angew. Chem., Int. Ed.*, 1975, **14**, 232; (j) G. Märkl, H. Kellerer, and F. Kneidl, *Tetrahedron Lett.*, 1975, 2411; (k) A. J. Ashe, III, *Tetrahedron Lett.*, 1976, 415; (l) A. J. Ashe, III, *Acc. Chem. Res.*, 1978, **11**, 153; (m) A. J. Ashe, III, D. J. Bellville, and H. S. Freidman, *J. Chem. Soc., Chem. Commun.*, 1979, 880; (n) F. Bickelhaupt, R. Lourens, H. Vermeer, and R. J. M. Weustink, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 3; (o) A. J. Ashe, III, T. R. Diephouse, and M. Y. El-Sheikh, *J. Am. Chem. Soc.*, 1982, **104**, 5693; (p) A. J. Ashe, III, X. Fang, and J. W. Kampf, *Organometallics*, 1999, **18**, 466.
4. (a) J. Leusink, W. Drenth, J. G. Noltes, and G. J. M. van der Kerk, *Tetrahedron Lett.*, 1967, 1263; (b) G. Axelrad and D. Halpern, *Chem. Commun.*, 1971, 291; (c) A. J. Ashe, III, J. W. Kampf, C. M. Kausch, H. Konishi, M. O. Kristen, and J. Kroker, *Organometallics*, 1990, **9**, 2944; (d) A. J. Ashe, III, J. W. Kampf, Y. Nakadaira, and J. M. Pace, *Angew. Chem.*, *Int. Ed.*, 1992, **31**, 1255; (e) Y. Sugihara, T. Yagi, I. Murata, and A. Imamura, *J. Am. Chem. Soc.*, 1992, **114**, 1479; (f) Y. Sugihara, R. Miyatake, and T. Yagi, *Chem. Lett.*, 1993, 933; (g) Y. Sugihara, R. Miyatake, T. Yagi, and I. Murata, *Tetrahedron*, 1994, **50**, 6495; (h) Y. Sugihara, R. Miyatake, I. Murata, and A. Imamura, *J. Chem. Soc., Chem. Commun.*, 1995, 1249; (i) A. J. Ashe III, L. Goossen, J. W. Kampf, and H. Konishi, *Angew. Chem., Int. Ed.*, 1992, **31**, 1642.
5. L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *J. Am. Chem. Soc.*, 1957, **79**, 5884.
6. (a) H. Sashida, K. Ito, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1493; (b) H. Sashida, K. Ito, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1995, **43**, 19.
7. (a) H. Sashida, *Rev. on Heteroatom Chemistry*, 2001, **22**, 59; (b) H. Sashida, *J. Synth. Org. Chem. Jpn.*, 2001, **59**, 355.
8. H. Sashida and A. Kuroda, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1965.
9. H. Sashida, *Heterocycles*, 2000, **53**, 49.
10. A part of this work has been appeared in a preliminary communication: H. Sashida, A. Kuroda, and T. Tsuchiya, *Chem. Commun.*, 1998, 767.

11. A. J. Leusink, J. G. Noltes, H. A. Budding, and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 1036.
12. J. Kurita, M. Ishii, S. Yasuike, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun*., 1993, 1309.
13. H. Sashida, H. Kurahashi, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun*., 1991, 802.
14. H. Sashida, K. Sadamori, and T. Tsuchiya, *Synth. Commun*., 1998, **28**, 713.
15. H. Sashida, *Synthesis*, 1999, 1866.
16. (a) H. Sashida and K. Ohyanagi, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2123; (b) H. Sashida, K. Ohyanagi, M. Minoura, and K.-y. Akiba, *J. Chem. Soc., Perkin Trans. 1*, 2002, 606.
17. H. Sashida, S. Nakabayashi, M. Kaname, and M. Minoura, *Heterocycles*, 2010, **80**, 1339.