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

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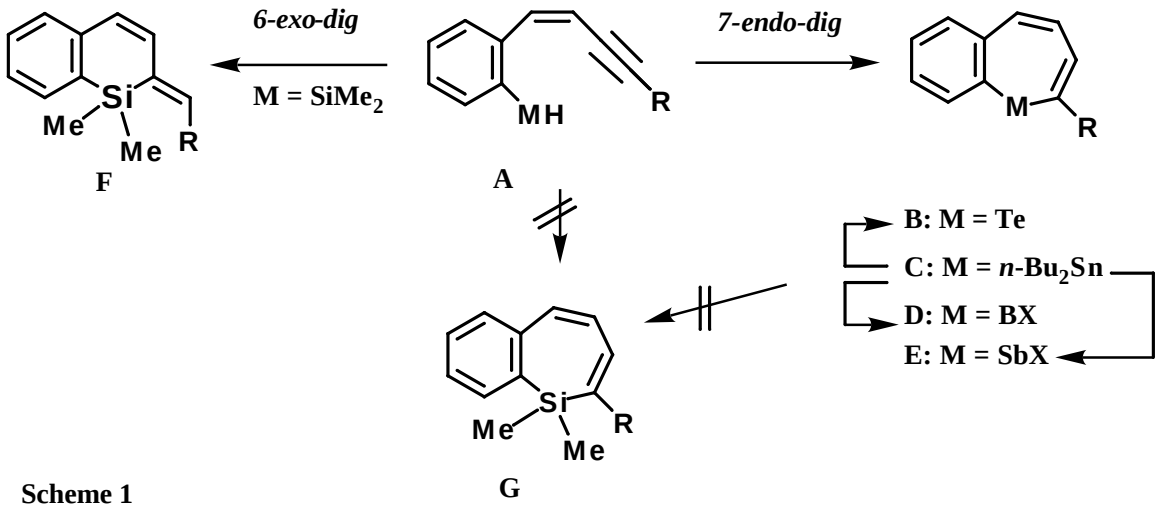
Abstract- Treatment of 1-benzotellurepines (**1**) with *t*-BuLi in the presence of TMEDA in ether followed by addition of a metal reagent (Cl_2SnBu_2, Cl_2SbPh and Cl_2SiMe_2) afforded the corresponding 1-benzostannepines (**4**), 1-benzostibepines (**5**) and 1-benzosilepines (**6**), respectively, 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.[2] However, compared with the synthetic methods for the preparation of five- and six-membered heterocycles, those of the fully unsaturated seven-membered heterocycles (heteroepines)[3] have been investigated to a limited extent. In particular, 1-benzoheteroepines have been only rarely reported.[4,5] 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.

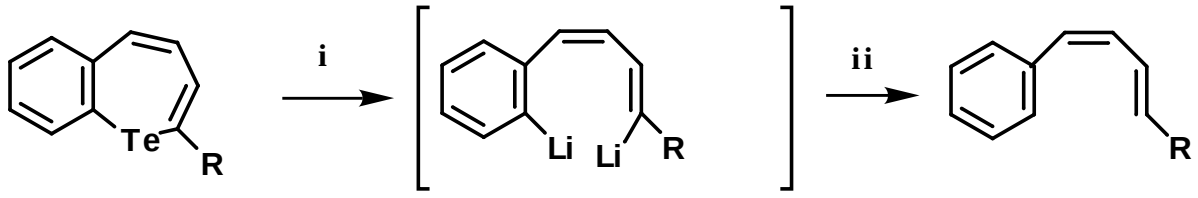


Scheme 1

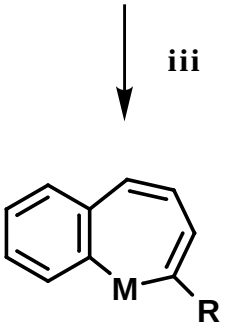
Previously, we reported the synthesis of 1-benzotellurepines (**B**),[6,7] novel fully unsaturated seven-membered tellurium-containing heterocycles, and also succeeded in the preparation of 1-benzostannepines (**C**).[8] The method for the preparation of these seven-membered heterocyclic compounds is 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) benzyllithuim, 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*-Bu_2SnCl_2) 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



1 **3** **2**



	M	Yields (%)	
		R = *t*-Bu	R = *n*-Bu
4	*n*-Bu_2Sn	35	35
5	SbPh	37	39
	$SiMe_2$		

Scheme 2 ***Reagents and Conditions*****:** i**,** *t*-BuLi, TMEDA, ether, -80 ° C to rt; ii, H_2O, rt; iii, MCl_2, 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_2SbPh) or dichlorodimethylsilane (Cl_2SiMe_2) instead of *n*-Bu_2Sn Cl_2 after the lithiation of **1**, while the yields were not good since they are thermally labile. Although the C-unsubstituted 1-benzostibepine[5] and 1-benzosilepine[4] 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 ^{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 *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_2O (20 mL) at -80 ℃ 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_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 ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel using *n*- hexane : CH_2Cl_2 (20:1) as an eluent to give the metalepines (**4-6**).

2-*tert*-Butyl-1,1-di*n*-butyl-1-benzostannepine (4a): 35 % yield, pale yellow oil. This compound was identical with the authentic sample prepared in our previous paper.[8]

2-*n*-Butyl-1,1-di*n*-butyl-1-benzostannepine (4b): 35 % yield, pale yellow oil. ^{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, *J* = 5.9 and 13.6 Hz, 4-H), 6.50 (1H, d, *J* = 5.9 Hz, 3-H), 6.71 1H, d, *J* = 13.6 Hz, 5-H), 7.26-7.32 and 7.42-7.44 (3H, m, and 1H, m, Ph-H). HRMS *m/z*: $C_{22}H_{34}Sn$ (M^+): 418.1682. Found: 418.1757.

2-*tert*-Butyl-1-phenyl-1-benzostibepine (5a): 37 % yield, colorless oil. ^{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. ^{1}H-NMR (400 MHz): 0.87, 1.20-1.52 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. ^{1}H-NMR (400 MHz): 0.40 (6H, s, $SiMe_2$), 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. ^{1}H-NMR (400 MHz): 0.35 (6H, s, $SiMe_2$), 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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