SYNTHESES OF NOVEL GROUP 15 AND 16 THIENO[2,3-*b*]-, THIENO[3,4-*b*]-, AND THIENO [3,2-*b*]-HETEROLES

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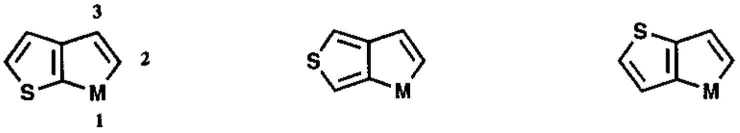
Abstract - Group 15 (P, As and Sb) and group 16 (S, Se, and Te) thieno[2,3-*b*]- (**1**), thieno[3,4-*b*]- (**2**), and thieno[3,2-*b*]heteroles (**3**) were prepared from the corresponding 1,4-dilithium intermediates, derived from (*Z*)-(ß-bromo-ß-trimethylsilylvinyl)thiophenes (**6**), (**10**), and (**13**) by treatment with *tert*-butyllithium, respectively. These thienoheteroles obtained are novel fused heterocyclic ring systems, except for thienothiophenes and thienoselenophenes.

Although a variety of new five-five fused aromatic heterocyclic ring systems containing one heteroatom in each ring have been prepared, most of these systems so far reported consist of the well-known simple heteroles such as furan, pyrrole, and thiophene rings.[1] With regard to thienoheteroles represented by the structures (**1**)-(**3**), thienopyrroles,[2] thienothiophenes, [3,4] and thienoselenophenes [3,5] have been prepared. However, their synthetic routes are not always versatile and thienoheteroles containing an element other than the above elements (N, S, and Se) are little known. Therefore, we are interested in the synthesis of these fused systems containing Main Group heavier elements and report here versatile synthetic routes to group 15 (P, As, Sb) and group 16 (S, Se, Te) thieno[2,3-*b*]- (**1**), thieno[3,4-*b*]- (**2**), and thieno[3,2-*b*]-heteroles (**3**), each of which can be obtained from a corresponding common starting material.



1 **2** **3**

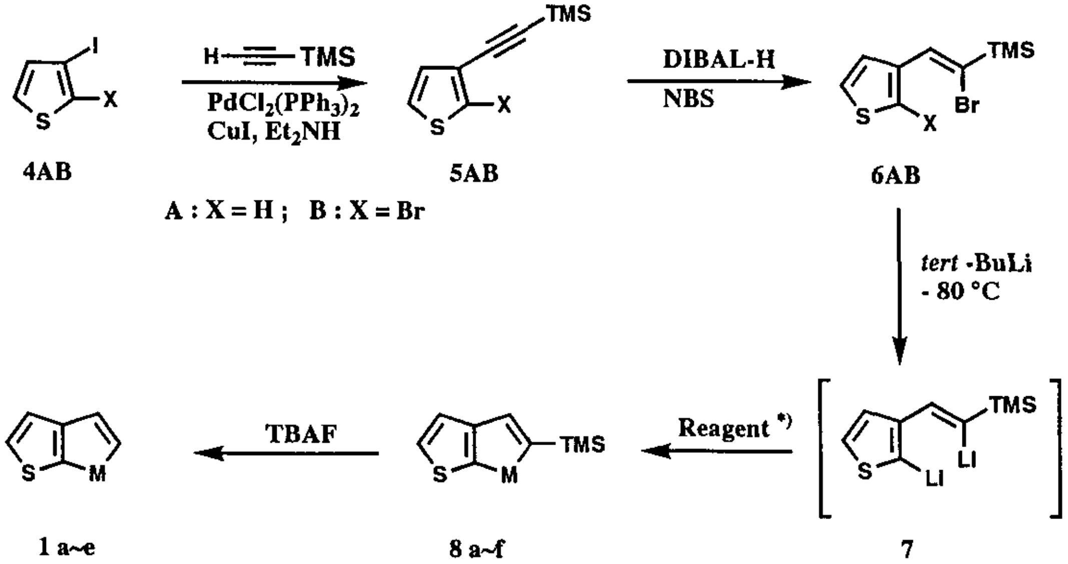
	a	b	c	d	e	f
M	S	Se	Te	PPh	AsPh	SbPh

Scheme 1

The thienoheteroles (**1**)-(**3**) obtained are novel heterocyclic ring systems except for thienothiophenes and thienoselenophenes.

We have previously reported that the 1,4-dilithium intermediate, derived from (*Z*)-ß-bromo-ß-trimethylsilylstyrene, reacted with dihalogeno metal reagents to give the corresponding 1-benzoheteroles [6] and the 1-benzoheteroepines could be prepared from 1-bromo-1-trimethylsilyl-4-(*o*-bromophenyl)buta-1,3-diene *via* the 1,6-dilithium intermediate.[7] These results led us to examine the present synthetic routes.

3-Iodothiophene (**4 A**) was coupled with trimethylsilyl(TMS)acetylene in the presence of a catalytic amount of a mixture of bis(triphenylphosphine)palladium dichloride and copper (I) iodide[8] to give the 3-(trimethylsilylethynyl)thiophene (**5 A**) in *ca.* 80% yield. The ethynyl compound (**5 A**) was hydraluminated with diisobutylaluminium hydride (DIBALH) followed by bromination with *N*-bromosuccinimide (NBS) to give the (*Z*)-3-(ß-bromo-ß-trimethylsilylvinyl)thiophene (**6 A**) regio- and stereo-selectively in 75% yield. The vinyl compound (**6 A**) was treated with *tert*-butyllithium in dry ether at -80 °C, then with a reagent [$(PhSO_2)_2S$, $(PhSO_2)_2Se$, $TeCl_4$, $PhPCl_2$, $PhAsCl_2$ or $PhSbCl_2$], resulting in ring closure forming the 2-trimethylsilylthieno[2,3-*b*]heteroles (**8a-f**)[9] in 45-65% yields, presumably *via* the key 1,4-dilithium intermediate (**7**). The trimethylsilyl group in **8a-e** was removed by treatment with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran containing water to give the desired C-unsubstituted thieno[2,3-*b*]-



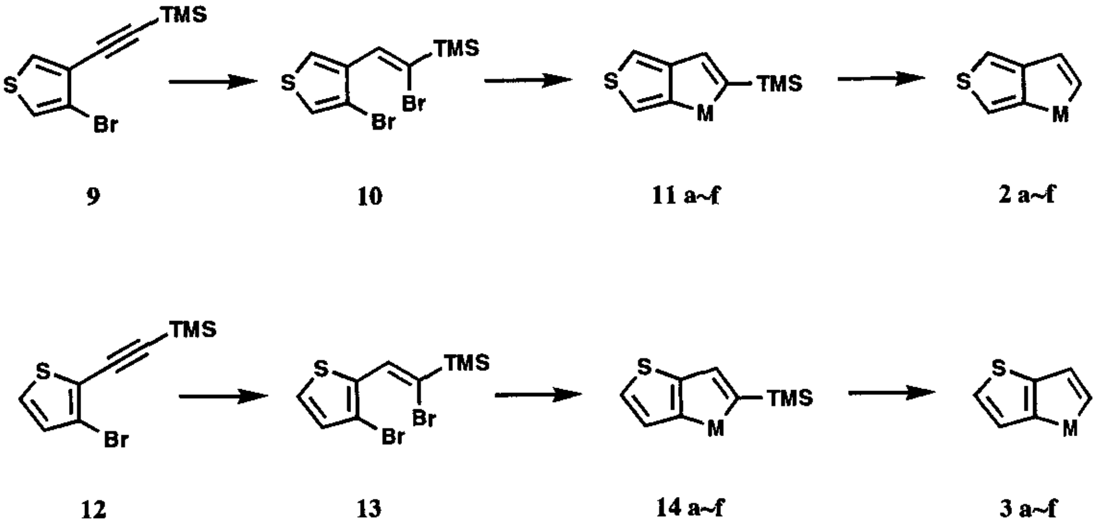
*) Reagent; $(PhSO_2)_2S$, $(PhSO_2)_2Se$, $TeCl_4$, $PhPCl_2$, $PhAsCl_2$ or $PhSbCl_2$

Scheme 2

heteroles (**1a-e**)[10] in 50-60% yields, however, the stibole (**8f**) was gradually decomposed under the reaction condition to afford no detrimethylsilylation product (**1f**).

The 2-bromothiophene derivative (**6B**), prepared similarly from 2-bromo-3-iodothiophene (**4B**)[11] through **5B**, also afforded **8** *via* the same dilithium intermediate (**7**), but in lower yields (20-40%).

Similarly, thieno[3,4-*b*]heteroles (**2a-f**) and thieno[3,2-*b*]heteroles (**3a-f**) could be synthesized. The starting dibromo compounds (**10**) and (**13**) were obtained in *ca.* 90% yields from 3-bromo-4-(trimethylsilyl)ethynyl- (**9**) and 3-bromo-2-(trimethylsilyl)ethynyl-thiophene (**12**),which were prepared from 3-bromo-4-iodothiophene[12] and 3-bromo-2-iodothiophene,[11] respectively. Treatment of the dibromo compounds (**10**) and (**13**) with the reagents resulted in the formation of 2-trimethylsilylthieno[3,4-*b*]heteroles (**11a-f**) and 2-trimethylsilylthieno[3,2-*b*]heteroles (**14a-f**), which afforded the corresponding C-unsubstituted thienoheteroles (**2a-f**)[13] and (**3a-f**),[14] respectively, by treatment with TBAF.



Scheme 3

In all cases of the ring-closure reactions *via* dilithium intermediates, the formation of other possible thienoheteroles, such as thieno[3,4-*b*]heteroles (**11**) from **6A** and 3-bromothieno[2,3-*b*]heteroles from **10**, was not observed.These results show that the lithiation of the α-position of the thiophene ring proceeds smoothly as well as bromo-lithium exchange reactions, but the lithiation of the ß-position dose not occur, and the exchange reaction occurs predominantly over the α-lithiation.The trimethylsilyl group is also essential for the present synthetic routes, by analogy with the syntheses of 1-benzoheteroles[6] starting from phenylacetylene and of 1-benzoheteroepines[7] from 1-phenylbut-1-en-3-ynes.

As stated in the introductory paragraphs, although the thienothiophenes (**1a**, **2a**, and **3a**) and thienoselenophenes (**1b**, **2b**, and **3b**) are known, the other thienoheteroles reported are new ring systems, whose structures were elucidated mainly by ^{1}H-NMR spectral comparison with known thienoheteroles. Further studies on the reactivities of these novel ring systems are now under investigation.

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9. Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. **8a-8c**: oil; **8d**: mp 73-74 °C; **8e**: mp 57-58 °C; **8f**: mp 40-41 °C.
10. **1a**: Colorless oil; **1b**: pale yellow oil; **1c**: pale yellow oil; **1d**: mp 55.5-57 °C; **1e**: mp 45.5-46.5 °C.
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13. **2a**: Colorless oil; **2b**: pale yellow oil; **2c**: pale yellow oil; **2d**: mp 69-71 °C; **2e**: mp 53-54 °C; **2f**: mp 51-53 °C.
14. **3a**: mp 52-53.5 °C; **3b**: mp 89-90 °C; **3c**: mp 95-96 °C; **3d**: mp 50-52 °C; **3e**: mp 36-38 °C; **3f**: colorless oil.

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