# SYNTHESES OF NOVEL DITHIENO[2,3-*b*; 3',2'-*f*]- AND DITHIENO[3,4-*b*; 3',4'-*f*]HETEROEPINES CONTAINING GROUP 14, 15 AND 16 HEAVIER ELEMENTS

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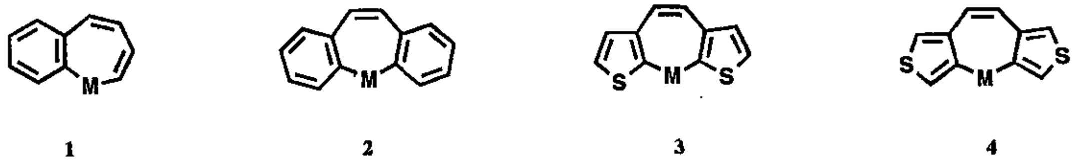
**Abstract** - The dithieno[2,3-*b*;3',2'-*f*]- (**3**) and dithieno[3,4-*b*;3',4'-*f*]-heteroepines (**4**) containing Group 14 (Si, Ge, and Sn), Group 15 (P, As, Sb, and Bi) and Group 16 (S, Se, and Te) elements were prepared from 2-bromo-3-iodothiophene and 3-bromo-4-iodothiophene *via* four steps, respectively, and thermal stabilities of these novel heterocyclic ring systems were examined.

The synthesis of fully unsaturated seven-membered heterocyclic rings (heteroepines) containing a heavier element other than nitrogen, oxygen or sulfur has received increasingly intensive study in recent years and we have reported on the syntheses of the 1-benzoheteroepines (**1**)[1-3] and dibenzo[*b*,*f*]heteroepines (**2**),[1] as well as 3-benzoheteroepines,[4] containing Group 14, 15, and 16 heavier elements, and on the thermal stabilities of these novel fused heterocyclic rings. These results prompted us to prepare fused heteroepines condensed with aromatic heterocyclic rings. We report here the syntheses of Group 14 (Si, Ge, and Sn), Group 15 (P, As, Sb, and Bi) and Group 16 (S, Se, and Te) dithieno[2,3-*b*; 3',2'-*f*]- (**3a-j**) and dithieno[3,4-*b*; 3',4'-*f*]heteroepines (**4a-j**), all of which are novel heterocyclic ring systems, although some dithienoborepines,[5] dihydrodithieno-oxepines and -thiepines[6] are known.

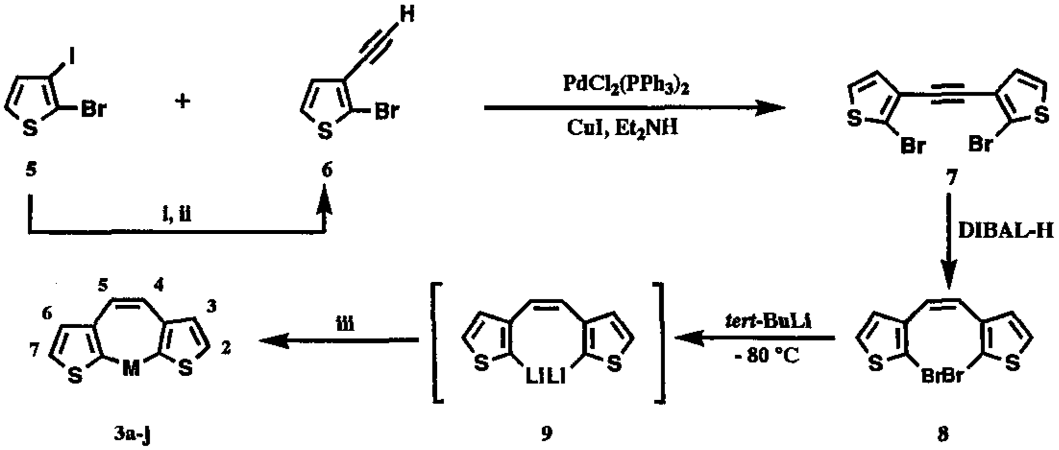


| No | a | b | c | d | e | f | g | h | i | j |
|---|---|---|---|---|---|---|---|---|---|---|
| M | S | Se | Te | PPh | AsPh | SbPh | BiPh | $SiMe_2$ | $GeMe_2$ | $SnMe_2$ |

Scheme 1

2-Bromo-3-iodothiophene (**5**)[7] was coupled with 2-bromo-3-ethynylthiophene (**6**), prepared in 65% yield from **5** by treatment with trimethylsilylacetylene followed by detrimethylsilylation using sodium hydroxide, in the presence of a catalytic amount of a mixture of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in diethylamine to give the dithienylacetylene (**7**) in 91% yield.[8] The acetylene (**7**) was treated with diisobutylaluminium hydride (DIBAL-H) to afford stereoselectively *cis*-1,2-bis(2-bromo-3-thienyl)ethene (**8**) in *ca*. 70% yield.[9]

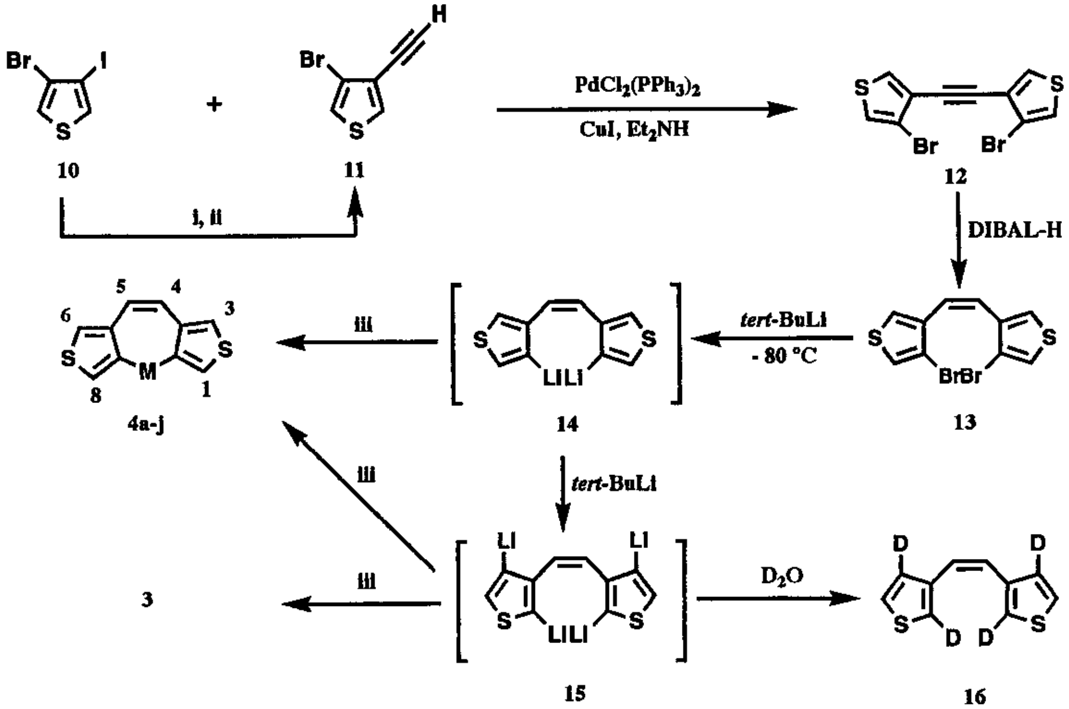
The ethene (**8**) was treated with *tert*-butyllithium (2.2 mol eq) in dry ether at -80 °C, then with a metal reagent (see Scheme 2, iii) to result in ring closure giving the desired dithieno[2,3-*b*; 3',2'-*f*]heteroepines (**3a-j**)[10] in 30-65% yields, presumably *via* the dilithium intermediate (**9**). When deuterium oxide was used instead of the metal reagents, *cis*-1,2-bis(2-deuterio-3-thienyl)ethene was isolated in 90% yield, giving evidence for the intermediacy of the key 1,6-dianion species (**9**) for the reaction process and indicating that the amount (2.2 mol eq) of the alkyllithium is sufficient to form **9**.



i) H—≡—TMS, PdCl$_2$(PPh$_3$)$_2$, CuI, Et$_2$NH
ii) 12N NaOH, MeCN, triethylbenzylammonium bromide
iii) a: (PhSO$_2$)$_2$S; b: (PhSO$_2$)$_2$Se; c: TeCl$_4$; d: PhPCl$_2$; e: PhAsCl$_2$; f: PhSbCl$_2$; g: PhBiBr$_2$
h: Me$_2$SiCl$_2$; i: Me$_2$GeCl$_2$; j: Me$_2$SnCl$_2$

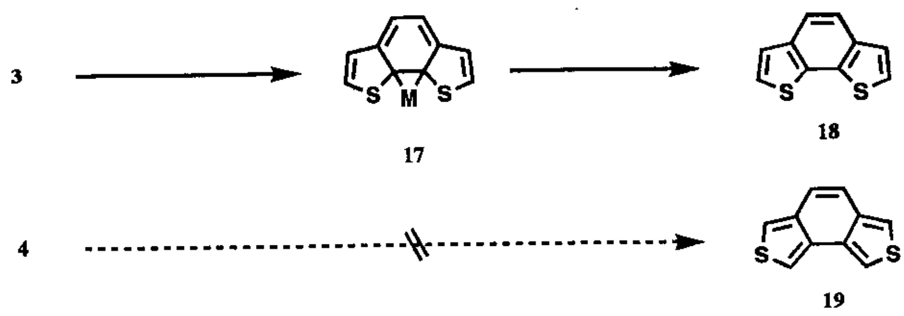
Scheme 2

Next, the another dithienoheteroepines (**4**) were similarly obtained (Scheme 3). Treatment of 3-bromo-4-iodothiophene (**10**)[11] with 3-bromo-4-ethynylthiophene (**11**), prepared from **10**, gave the bis(3-thienyl)acetylene (**12**),[12] which was reduced with DIBAL-H to form the key starting *cis*-dibromodithienylethene (**13**).[12] The ethene (**13**) afforded the desired dithieno[3,4-*b*; 3',4'-*f*]heteroepines (**4a-j**)[13] in 20-40% yields, by treatment with *tert*-butyllithium (2.5 mol eq) followed by the metal reagents, *via* the dilithium intermediate (**14**). When an excess (4-5 mol eq) of the alkyllithium was used, small amounts of the isomers (**3**) were also formed together with **4**, indicating that the α-lithiation of the thiophene ring in **13** was also occurred as well as the bromine-lithium exchange to form the tetralithium intermediate (**15**), which may cyclize to either **3** or **4** by the metal reagents. The formation of **15** was confirmed by the fact that the tetradeuterio product (**16**) was proved to be formed by $^1$H-NMR spectral analysis when deuterium oxide was used instead of the metal reagents. It is known that the α-lithiation competes with the β-bromine-lithium exchange in the reaction of β-bromothiophenes with alkyllithiums.[14]



Scheme 3

All of the dithienoheteroepines (**3**) and (**4**) are hitherto unknown heterocyclic rings, and were characterized mainly on the basis of their $^1$H-NMR spectra, in which only three kinds of vinyl proton signals were observed, *e.g.*, **3f**: δ 6.67 (2H, s), 7.14 and 7.49 (each 2H, d, *J*=4.8 Hz); **4f**: δ 6.47 (2H, s), 7.28 and 7.42 (each 2H, d, *J*=2.9 Hz), indicating that **3** and **4** have symmetrical structures.



Scheme 4

Benzoheteroepines are thermally labile towards heteroatom extrusion and gradually decomposed to naphthalene *via* the norcaradiene intermediates (*e.g.*, half-lives of **1b** (Se) and **1c** (Te) at 50 °C are 110 and 133 min, respectively).[4] The dithienoheteroepines (**3**) are far more stable than **1**, but somewhat less stable than **2**,[4] and **3b** and **3c** decomposed completely to the dithienobenzene (**18**) at 110 °C for 5 h and 180 °C for 1 h, respectively *via* the intermediates (**17**). However, the thienoheteroepines (**4**) are very stable and remained unchanged even when heated at 180 °C for 24 h, probably because any norcaradiene intermediates can not be formed from **4**, thus giving no dithienobenzene (**19**). Further investigation on the properties of the new rings is in progress.

## REFERENCES AND NOTES

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5. A. T. Jeffries III and S. Granowitz, *Chem. Scripta*, 1973, **4**, 183.
6. A. Almqvist and R. Hakansson, Chem. Scripta, 1976, **10**, 117; P. Meunier, *J. Heterocycl. Chem.*, 1978, **15**, 593.
7. S. Gronowitz and B. Holm, *Acta Chem. Scand., B*, 1976, **30**, 423.
8. Satisfactory elemental analyses and spectral data were obtained for all new compounds reported. **6**: 72% yield from **5**; bp 53-57 °C (3 mmHg); $^1$H-NMR δ: 3.30 (1H, s), 6.98 and 7.22 (each 1H, d, *J*=5.6 Hz). **7**: 91% yield; mp 41-42 °C; $^1$H-NMR δ: 7.04 and 7.23 (each 2H, d, *J*=5.7 Hz).
9. This compound (**8**: 65% yield; mp 48-50 °C) has been prepared from (2-bromo-3-thienyl)methyltriphenylphosphonium bromide or 2-bromo-3-formylthiophene, but was obtained as a *cis-trans* (2:1) mixture (W. J. Archer, R. Cook, and R. Taylor, *J. Chem. Soc., Perkin Trans.* 2, 1983, 813). Therefore, we prepared it by the new route reported.
10. **3a**: 28% yield, mp 93-94 °C; **3b**: 33% yield, mp 110-111 °C; **3c**: 21% yield, mp 135-136 °C; **3d**: 52% yield, mp 144-145 °C; **3e**: 67% yield, mp 85-86 °C; **3f**: 64% yield, mp 113-114 °C; **3g**:unstable and decomposed during purification; **3h**: 31% yield, oil; **3i**: 40% yield, oil; **3j**: 61% yield, oil.
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12. **12**: 55% yield; mp 58-59 °C; $^1$H-NMR δ: 7.26 and 7.54 (each 2H, d, *J*=3.5 Hz). **13**: 61% yield; mp 32-33 °C; $^1$H-NMR δ: 7.03 and 7.23 (each 2H, d, *J*=3.3 Hz).
13. **4a**: 18% yield, mp 122-123 °C; **4b**: 28% yield, mp 147-148 °C; **4c**: 15% yield, mp 171-173 °C; **4d**: 40% yield, mp 144-145 °C; **4e**: 36% yield, mp 100-104 °C; **4f**: 29% yield, mp 98-99 °C; **4h**: 27% yield, oil; **4i**: 38% yield, oil; **4j**: 16% yield, oil.
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