TETRA-2-THIENYL- AND TETRAKIS(5,2'-BITHIOPHENE-2-YL)-THIOPHENES AND SELENOPHENES

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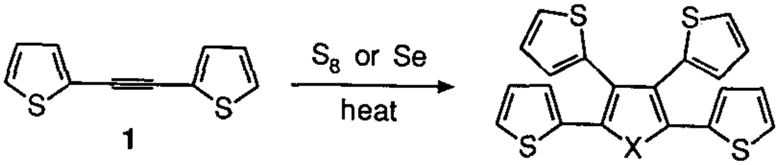
Abstract-Heating a mixture of di-2-thienylacetylene (**1**) and elemental selenium in benzene at 220-225 °C for 9 h in a stainless steel autoclave affords tetra-2-thienylselenophene (**2b**) in 65% yield. In similar ways, heating a mixture of bis(5,2'-bithiophene-2-yl)acetylene (**3**) and elemental sulfur or selenium gives tetrakis-(5,2'-bithiophene-2-yl)thiophene (**4a**) or selenophene (**4b**), respectively, in satisfactory yields.

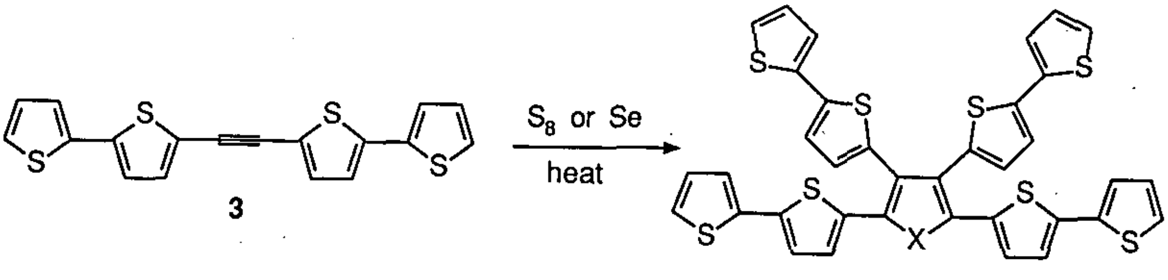
α-Oligothiophenes have been attracting much attention as building blocks for electronic molecular devices.[1] We recently reported the preparation of a series of α-oligothiophenes[2] and their positional isomers[3] and have been investigating the physico-chemical properties of these compounds to find their applications as molecular elctronic devices.[4] We have also reported the preparation of tetra-2-thienylthiophene (**2a**) by reaction of elemental sulfur with di-2-thienylacetylene (**1**).[5] In this connection, we have become interested in the preparation of the selenophene analog of **2a** and its higher thiophene and selenophene analogs.

A mixture of 382 mg (2 mmol) of **1** and 80 mg (1 mmol) of elemental selenium in 50 ml of benzene was heated at 220-225 °C for 9 h in a stainless steel autoclave. Column chromatographic work-up of the mixture gave 300 mg (65%) of tetra-2-thienylselenophene (**2b**).[6] Heating a mixture of 356 mg (1 mmol) of bis(5,2'-bithiophene-2-yl)acetylene (**3**) and 32 mg (1 mmol) of sulfur in 50 ml of benzene at 205-210 °C for 14 h in an autoclave affords 205 mg (57%) of tetrakis(5,2'-bithiophene-2-yl)thiophene (**4a**)[6] with about 10% recovery of **3**. Similarly, heating an equivalent mixture of **3** and elemental selenium in benzene for 9 h at 230 °C gives tetrakis(5,2'-bithiophene-2-yl)selenophene (**4b**)[6] in 64% yield.

Since acetylenes (**1**) and (**3**) are readily obtainable by application of the recently developed procedure,[7] the present reaction provides an easy access to structurally and functionally interesting heterocycles such as (**2**) and (**4**). The present method is also applicable to the preparation of a wide variety of tetraarylthiophenes and selenophenes.[8] Cv oxidation potential data of **2a,b** and **4a,b**, determined in CH_2Cl_2 with 0.1 M elcetrolyte (tetrabutylammonium perchlorate), are summarized in Table 1 along with uv-vis data. Every compound shows irreversible oxidation peaks because the radical cations formed are very reactive and undergo polymerization as many thiophenes do electrochemical polymerization.[9]



2a: X=S
2b: X=Se



4a: X=S **4b**: X=Se

Table 1 Cv Oxidation Potential and Uv-vis Data of Compounds **2a,b** and **4a,b**

Compounds	λ_{max} (CH_2Cl_2) nm (ε)	E^{ox} (V *vs.* Ag/Ag$^+$)
2a	230 (19900), 358 (24200)	0.95
2b	232 (23100), 369 (15900)	0.90
4a	250 (26800), 344 (42500), 406 (30700)	0.75
4b	250 (24400), 344 (36800), 430 (32300)	0.74

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6. **2b**: mp 194-195 °C (from cyclohexane); ^{1}H-nmr ($CDCl_3$, 400 MHz) δ 6.67 (2H, dd, *J*=3.4, 1.0 Hz), 6.70-6.94 (4H, m), 7.04 (2H, dd, *J*=3.4, 1.0 Hz), 7.17 (2H, dd, *J*=5.2, 1.0 Hz), 7.28 (2H, dd, *J*=5.2, 1.0 Hz); ^{13}C-nmr ($CDCl_3$, 100 MHz) δ 126.65, 126.71, 126.79, 126.81, 127.06, 129.40, 134.27, 137.32, 137.60, 138.13. Anal. Calcd for $C_{20}H_{12}S_4Se$: C, 52.27; H, 2.63. Found: C, 52.26; H, 2.79. **4a**: mp 214-215 °C (from C_6H_6/hexane); ^{1}H-nmr ($CDCl_3$, 400 MHz) δ 6.85 (2H, d, *J*=3.7 Hz), 6.94 (2H, d, *J*=3.7 Hz), 6.96(2H, d, *J*=3.7 Hz), 7.00 (2H, d, *J*=3.9 Hz), 7.01 (2H, d, *J*=3.9 Hz), 7.05 (2H, d, *J*=3.7 Hz), 7.07 (2H, dd, *J*=3.7, 0.9 Hz), 7.10 (2H, dd, *J*=3.7, 0.9 Hz), 7.14-7.17 (4H, m); ^{13}C-nnr ($CDCl_3$, 100 MHz) δ 123.62, 123.80, 123.83, 124.02, 124.33, 124.70, 127.17, 127.74, 127.85, 130.36, 131.99, 133.49, 133.90, 134.08, 136.90, 137.37, 138.35, 139.42. Anal. Calcd for $C_{36}H_{20}S_9$: C, 58.34; H, 2.72. Found: C, 58.44; H, 2.92. **4b**; mp 226-228 °C (from

C_6H_6/hexane); ^{1}H-nmr ($CDCl_3$, 400 MHz) δ 6.82 (2H, d, *J*=3.6 Hz), 6.94-6.99 (m, 8H), 7.04-7.06 (4H, m), 7.10-7.17 (6H, m); ^{13}C-nmr ($CDCl_3$, 100 MHz) δ 123.57, 123.72, 123.78, 123.98, 124.28, 124.72, 127.61, 127.74, 127.86, 130.39, 133.80, 135.75, 136.14, 136.89, 137.40, 138.25, 138.57, 139.35. Anal. Calcd for $C_{36}H_{20}S_8Se$: C, 54.87; H, 2.56. Found: C, 54.94; H. 2.71.

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