Pergamon

Tetrahedron 56 (2000) 3255–3260

TETRAHEDRON

Electrophilic 2-Thienylselenenylation of Thiophene. Preparation of Oligo(seleno-2,5-thienylenes)

Marcello Tiecco,* Lorenzo Testaferri, Luana Bagnoli, Francesca Marini, Andrea Temperini, Cristina Tomassini and Claudio Santi

Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, I-06100 Perugia, Italy

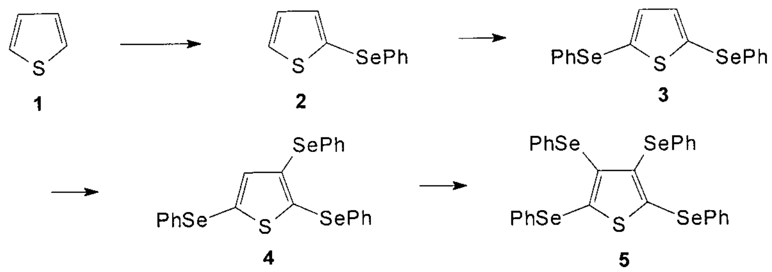
Received 28 December 1999; revised 28 February 2000; accepted 16 March 2000

Abstract—The substitution reactions of thiophene and 2-methylthiophene with the electrophilic selenenylating agent produced from the 2,2′-dithienyl diselenide by oxidation with iodobenzene diacetate involve only the α-positions and give rise to the formation of oligo(seleno-2,5-thienylenes). Products deriving from the attack at the α-positions of thiophene and 2-methylthiophene were also observed starting from the 5,5′-dimethyl-2,2′-dithienyl diselenide. The same electrophilic reagents reacted with furan and 2-methylfuran to afford a mixture of the mono- and di-substituted compounds. © 2000 Elsevier Science Ltd. All rights reserved.

We have recently reported that the strongly electrophilic phenylselenenyl sulfate, which is easily produced from the oxidation of diphenyl diselenide with ammonium persulfate,[1,2] can be conveniently employed to effect electrophilic aromatic phenylselenenylation reactions on activated substrates. Once introduced, the PhSe group activates the aromatic substrate to further substitution. Thus, for instance, in the case of thiophene **1**, substitution can take place at the β-positions also. Under controlled experimental conditions, it was thus possible to introduce the desired number of PhSe groups and to produce mono **2**, bis **3**, tris **4** or tetrakis(phenylseleno)thiophene **5** (Scheme 1).[3] Similar results were also obtained by Engman and coworkers, who found that the same reactions can be effected with alkylselenenyl sulfates also.[4] Tetrasubstituted thiophenes were obtained in good yields with methyl, 1-butyl and 1-octylselenenyl sulfates.

We now report that when thiophene and 2-methylthiophene are treated with the electrophilic selenenylating agent derived from the 2,2′-dithienyl diselenide the substitution reaction involves only the α-positions and gives rise to the formation of oligo(seleno-2,5-thienylenes). Products deriving from the attack at the α-positions of thiophene and 2-methylthiophene were also observed starting from the 5,5′-dimethyl-2,2′-dithienyl diselenide. Small amounts of products in which substitution occurred at the β-position also were obtained only in the case of the reaction of this latter reagent with equimolecular amounts of 2-methylthiophene. The same electrophilic reagents reacted with furan and 2-methylfuran to afford a mixture of the mono- and di-substituted compounds.

2,2′-Dithienyl diselenide **6** was prepared, as reported in the literature,[5] from 2-thienyllithium[6] and selenium metal (Scheme 2). 5,5′-Dimethyl-2,2′-dithienyl diselenide **7** was similarly obtained from 2-methylthiophene. The electrophilic selenenylating agents were prepared by oxidation of

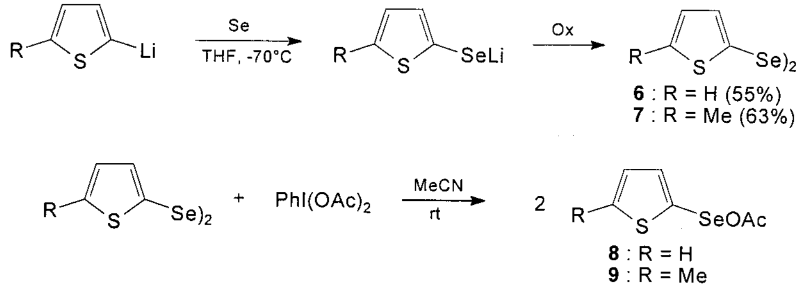


Scheme 1.

Keywords: dithienyl diselenides; electrophilic 2-thienylselenenylation; oligo(seleno-2,5-thienylenes).

* Corresponding author. Tel.: +39-075-5855100; fax: +39-075-5855116; e-mail: tiecco@unipg.it

PII: S0040-4020(00)00245-3



Scheme 2.

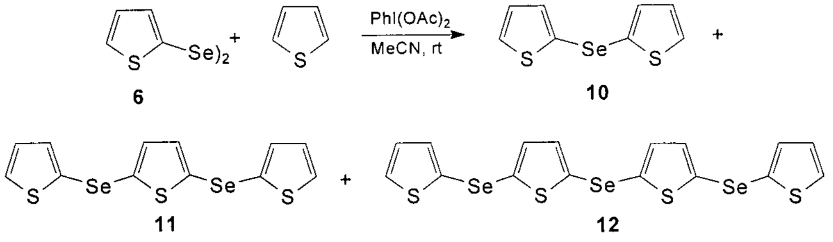
these diselenides. Preliminary experiments showed that in the present case ammonium persulfate gave rise to several secondary products. Oxidation was therefore effected under milder conditions using iodobenzene diacetate, according to the procedure recently proposed by us for the oxidation of diphenyl diselenide.[7] Under these conditions the electrophilic reagents are suggested to be the 2-thienylselenenyl acetates **8** and **9** (Scheme 2).

The first experiments were carried out with **6** and thiophene in equimolecular amounts (1 mmol). These were treated with iodobenzene diacetate (2 mmol) in acetonitrile (6 ml) at room temperature for 24 h. Under these conditions only polymeric material was obtained which was not further investigated. A further experiment in which 10 mmol of thiophene were employed gave similar results. The reaction was therefore repeated using a larger amount of thiophene (50 mmol). A clean reaction mixture was obtained in this case. This was composed of the 2-(2-thienylseleno)thiophene **10**, the 2,5-di(2-thienylseleno)thiophene **11** and the 2-(2-thienylseleno)-5-{[5-(2-thienylseleno)-2-thienyl]seleno}thiophene **12** which could be easily separated by column chromatography (Scheme 3). Under these conditions the oligomer containing four thiophene rings **12** was the major reaction product, the three products being formed in 8, 10 and 52% yield, respectively. Reaction yields were calculated on the amount of the diselenide **6** employed. As expected, using a larger amount of thiophene (100 mmol) the formation of compound **10** was favored (50%). The amount of **11** was also increased to 30% and compound **12** was still present, although in low yield (8%).

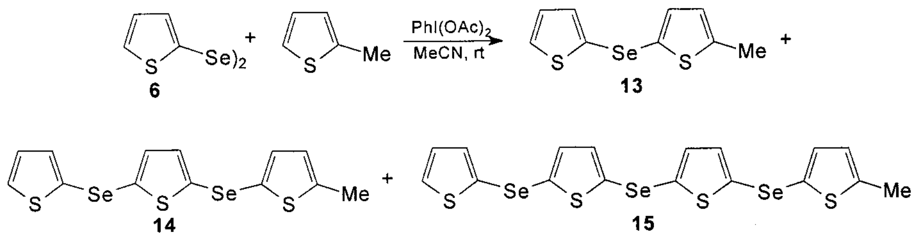
The formation of compounds **11** and **12** even in the presence of a large excess of thiophene indicates that the introduction of the 2-thienylseleno groups activate the thiophene ring to further electrophilic substitution.

Some interesting differences were observed when **6** was allowed to react with the 2-methylthiophene under reaction conditions identical to those reported above in the case of thiophene.

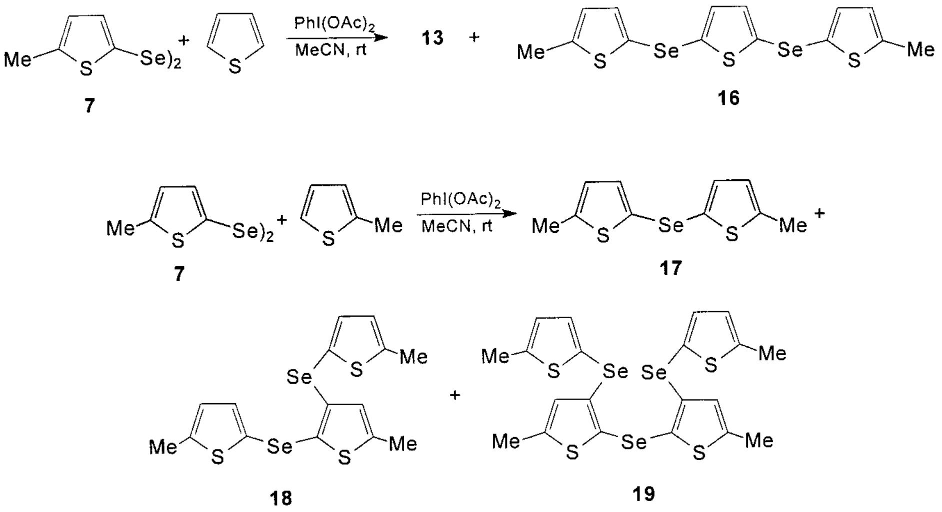
An experiment carried out with 1 mmol of **6** and 100 mmol of 2-methylthiophene afforded a mixture of the two selenides **13** (78%) and **14** (15%) (Scheme 4). The yields of these products changed to 62 and 31%, respectively, when the amount of 2-methylthiophene was reduced to 50 mmol. It can be observed that the yield of the monosubstituted product **13** was considerably greater than that of the corresponding product **10** isolated from the reaction in thiophene. Moreover the oligomer containing four thiophene rings **15**, analogous to **12**, was not formed at all in either case. These results indicate that 2-methylthiophene is



Scheme 3.



Scheme 4.

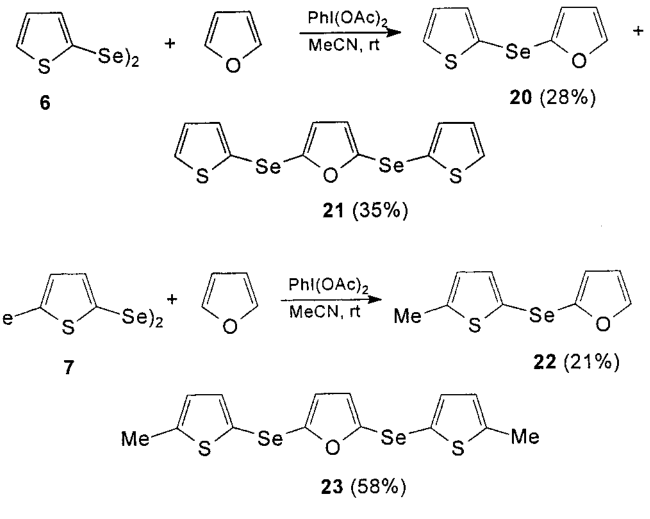


Scheme 5.

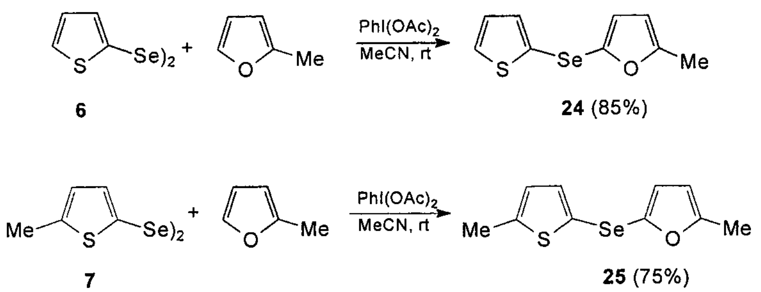
considerably more reactive than thiophene and therefore in this case the reaction stops at the first stages and affords compound **13** together with small amounts of **14**.[8] Thus, in order to obtain the product of further substitution the amount of 2-methylthiophene must be greatly reduced. Indeed, from an experiment in which 1 mmol only of 2-methylthiophene was employed, leaving the amounts of all the other reagents unchanged, a 27% yield of the selenide **15** was isolated together with a 42% yield of **14**. Compound **15** could also be obtained as the sole reaction product, in 78% yield, from the reaction of **11** with an equimolecular amount of the 5,5′-dimethyl-2,2′-dithienyl diselenide **7**, under experimental conditions identical to those reported above for the reactions of **6** with thiophene and 2-methylthiophene.

The results reported in Schemes 3 and 4 indicate that the attack of the electrophilic 2-thienylselenenylating agent exclusively occurs at the very reactive α-positions. Thus, for instance, in compounds **11** and **14**, although the β-positions of the central thiophene rings are activated by the presence of two thienylseleno groups,[3] the available α-positions are still more reactive and the substitution selectively affords the oligo(seleno-2,5-thienylene) compounds **12** and **15**, respectively.

Starting from the diselenide **7**, i.e. using the 2-methyl-2-thienylselenenyl acetate **9** as the electrophilic reagent, the formation of the oligo(seleno-2,5-thienylenes) should be avoided and the reaction could give rise to polysubstituted thiophenes as observed in the reactions of thiophene with phenylselenenyl sulfate.[3] In the presence of iodobenzene diacetate (2 mmol), the 5,5′-dimethyl-2,2′-dithienyl diselenide **7** (1 mmol) reacted with thiophene (50 mmol) or with 2-methylthiophene (50 mmol), at room temperature for 24 h, to give exclusively the products deriving from the substitution at the α-positions. Thus, as indicated in Scheme 5 compound **13** (5%) and **16** (72%) were isolated from the reaction of thiophene and compound **17** (78%) was obtained from the reaction with 2-methylthiophene. The formation of small amounts of the products deriving from substitution at the β-position was observed only in the reaction carried out with 1 mmol of 2-methylthiophene and 1 mmol of the diselenide **7**. In this case, in the initially formed selenide



Scheme 6.



Scheme 7.

17 no α-positions are available and the attack of the selenenylating agent occurred at the β-positions to afford two further products which were identified as **18** (15%) and **19** (15%) (Scheme 5).

Finally, the electrophilic selenenylation of furan and 2-methylfuran was also examined. These experiments were all carried out using 50 mmol of furan or 2-methylfuran and 1 mmol of diselenides **6** or **7** at room temperature. The results obtained are summarised in the Schemes 6 and 7. In every case the reactions afforded good yields of the substitution products deriving from attack at the available α-positions of furan. Mixtures of compounds **20** and **21** and **22** and **23** were obtained from the reactions of furan with **6** and **7**, respectively. These products were easily separated by column chromatography and reaction yields are indicated in parentheses in the Scheme.

As indicated in Scheme 7, the reactions of the two diselenides with 2-methylfuran gave rise to the formation of the single products **24** and **25**, respectively, which were isolated in very good yields.

The results described in this paper demonstrate that the diselenides **6** and **7** can be conveniently employed to produce electrophilic 2-thienylselenenylating agents which easily effect substitution reactions on thiophene and furan derivatives. Of particular interest are the reactions of **6** with thiophene and 2-methylthiophene since they represent a very simple method to effect the syntheses of oligo(seleno-2,5-thienylenes) which can have some practical interest as a selenium rich donors from which ion radical salts could be prepared.[9]

Experimental

Starting materials were commercially available and were used without further purification. New compounds were characterized by MS, ^{1}H, and ^{13}C NMR spectroscopy. GLC analyses and MS spectra were carried out with an HP 5890 gas chromatograph (dimethyl silicone column, 12.5 m) equipped with an HP 5971 Mass Selective Detector. In the cases of the ions containing one or more selenium atoms only the most prominent peaks are reported. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and TMS as standard. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer. Mps were determined on a Kofler melting point apparatus and are uncorrected.

Synthesis of 2,2′-dithienyl diselenide (6) and of 5,5′-dimethyl-2,2′-dithienyl diselenide (7)

22 ml (35 mmol) of 1.6 M *n*-butyllithium in hexane was added to a solution of 3 g (35 mmol) of thiophene or 3.4 g (35 mmol) of 2-methylthiophene in 25 ml of anhydrous tetrahydrofuran under nitrogen at −40°C. After 1 h at −30°C the temperature of the reaction mixture was lowered to −70°C and 2.8 g (35 mg atom) of powdered selenium was added. After 30 min at −70°C the mixture was stirred for 1 h at −10°C. The reaction was quenched with 20 ml of 10% aqueous NH_4Cl solution and 2 g of potassium ferricyanide were added. Stirring was continued overnight at room temperature. The mixture was extracted with ether, dried over Na_2SO_4 and evaporated. The dithienyl diselenides were isolated in pure form after column chromatography on silica gel using light petroleum as eluant. Physical and spectroscopic data of the two diselenides are reported below.

2,2′-Dithienyl diselenide (6). Mp 60–62°C; ^{1}H NMR δ 7.40 (dd, 2H, J=1.2, 5.3 Hz), 7.18 (dd, 2H, J=1.2, 3.5 Hz), 6.94 (dd, 2H, J=3.5, 5.3 Hz); ^{13}C NMR δ 136.7 (two carbons), 132.7 (two carbons), 127.9 (two carbons), 125.5 (two carbons). MS *m*/*z* (relative intensity) 326 (22), 324 (19), 246 (20), 166 (100), 163 (65), 161 (32), 159 (12), 121 (15), 119 (19), 117 (13), 92 (11). Anal. Calcd for $C_8H_6S_2Se_2$: C, 29.65; H, 1.87. Found: C, 29.51; H, 1.21.

5,5′-Dimethyl-2,2′-dithienyl diselenide (7). Mp 49–51°C; ^{1}H NMR δ 6.98 (d, 2H, J=3.5 Hz), 6.59 (dq, 2H, J=0.9, 3.5 Hz), 2.47 (d, 6H, J=0.9 Hz); ^{13}C NMR δ 147.7 (two carbons), 137.1 (two carbons), 126.3 (two carbons), 122.9 (two carbons), 15.5 (two carbons). MS *m*/*z* (relative intensity) 354 (2), 274 (16), 194 (100), 193 (39), 177 (12), 161 (19), 97 (26), 53 (8). Anal. Calcd for $C_{10}H_{10}S_2Se_2$: C, 34.11; H, 2.86. Found: C, 34.01, H; 2.75.

Electrophilic thienylselenenylation of thiophene derivatives

A mixture of dithienyl diselenide (**6** or **7**) (1 mmol), $PhI(OAc)_2$ (2 mmol) and thiophene derivatives was stirred in acetonitrile (6 ml) at room temperature. As indicated previously, the experiments with the diselenide **6** were effected using 1, 50 or 100 mmol of thiophene or 2-methylthiophene. The reactions of the diselenide **7** were carried out using 50 mmol of thiophene and 50 or 1 mmol of 2-methylthiophene. The progress of the reactions was monitored by TLC and GC–MS. The reaction mixture was poured into a 10% aqueous Na_2CO_3 solution and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. The reaction products were isolated in pure form after column chromatography on silica gel using light petroleum as eluant. Reaction times and yields are reported in the discussion section. Physical and spectroscopic data of the reaction products, **10–19**, are reported below.

2-(2-Thienylseleno)thiophene (10). Oil; ^{1}H NMR δ 7.36 (dd, 2H, J=1.2, 5.3 Hz), 7.27 (dd, 2H, J=1.2, 3.5 Hz), 6.95 (dd, 2H, J=3.5, 5.3 Hz); ^{13}C NMR δ 134.6 (two carbons), 130.8 (two carbons), 127.8 (two carbons), 126.3 (two carbons). MS *m/z* (relative intensity) 246 (28), 244 (13), 167 (11), 166 (100), 121 (12), 82 (6), 45 (4). Anal. Calcd for $C_8H_6S_2Se$: C, 39.19; H, 2.47. Found: C, 39.02, H; 2.30.

2,5-Di(2-thienylseleno)thiophene (11). Mp 62–63°C; ^{1}H NMR δ 7.37 (dd, 2H, J=1.2, 5.2 Hz), 7.26 (dd, 2H, J=1.2, 3.5 Hz), 7.06 (s, 2H), 6.95 (dd, 2H, J=3.5, 5.2 Hz); ^{13}C NMR δ 135.2 (two carbons), 134.6 (two carbons), 131.3 (two carbons),128.0 (two carbons), 125.3 (four carbons). MS *m/z* (relative intensity) 408 (13), 406 (13), 328 (3), 249 (18), 248 (100), 243 (34), 241 (16), 166 (16), 164 (21), 162 (16), 124 (25), 121 (16), 82 (14). Anal. Calcd for $C_{12}H_8S_3Se_2$: C, 35.47; H, 1.98. Found: C, 35.65; H, 2.10.

2-(2-Thienylseleno)-5-{[5-(2-thienylseleno)-2-thienyl]-seleno}thiophene (12). Mp 122–123°C; ^{1}H NMR δ 7.38 (dd, 2H, J=1.1, 5.3 Hz), 7.27 (dd, 2H, J=1.1, 3.5 Hz), 7.05 (s, 4H), 6.96 (dd, 2H, J=3.5, 5.3 Hz); ^{13}C NMR δ 135.4 (two carbons), 135.3 (two carbons), 134.5 (two carbons), 132.1 (four carbons), 131.4 (two carbons), 130.4 (two carbons), 128.0 (two carbons). Anal. Calcd for $C_{16}H_{10}S_4Se_3$: C, 33.87, H, 1.78. Found: C, 33.52; H, 1.73.

2-Methyl-5-(2-thienylseleno)thiophene (13). Oil; ^{1}H NMR δ 7.33 (dd, 1H, J=1.2, 5.2 Hz), 7.21 (dd, 1H, J=1.2, 3.5 Hz), 7.08 (d, 1H, J=3.4 Hz), 6.92 (dd, 1H, J=3.5, 5.2 Hz), 6.59 (dq, 1H, J=1.0, 3.4 Hz), 2.44 (d, 3H, J=1.0 Hz); ^{13}C NMR δ 145.7, 135.1, 134.0, 130.4, 127.7, 126.8, 126.0, 123.1, 15.3. MS *m/z* (relative intensity) 260 (25), 257 (12), 180 (100), 147 (18), 97 (7), 45 (7). Anal. Calcd for $C_9H_8S_2Se$: C, 41.71; H; 3.11. Found: C, 41.65; H, 3.02.

2-[(5-Methyl-2-thienyl)seleno]-5-(2-thienylseleno)thiophene (14). Mp 55–57°C; ^{1}H NMR δ 7.37 (dd, 1H, J=1.2, 5.3 Hz), 7.26 (dd, 1H, J=1.2, 3.5 Hz), 7.07 (d, 1H, J=3.5 Hz), 7.06 (d, 1H, J=3.5 Hz), 7.03 (d, 1H, J=3.5 Hz), 6.94 (dd, 1H, J=3.5, 5.3 Hz), 6.61 (dq, 1H, 1.0, 3.5 Hz), 2.45 (d, 3H, J=1.0 Hz); ^{13}C NMR δ 146.4, 135.8, 135.1, 134.7, 134.0, 132.2, 131.2, 130.9, 127.9, 126.2, 125.5, 122.1, 15.4. MS *m/z* (relative intensity) 422 (1), 262 (100), 261 (33), 259 (54), 257 (27), 245 (28), 243 (16), 229 (13), 179 (17), 178 (14), 162 (14), 131 (41), 97 (14), 82 (14), 45 (8). Anal. Calcd for $C_{13}H_{10}S_3Se_2$: C; 37.16; H, 2.40. Found: C 37.01, H, 2.20.

2-({5-[(5-Methyl-2-thienyl)seleno]-2-thienyl}seleno)-5-(2-thienylseleno)thiophene (15). Mp 103–105°C; ^{1}H NMR δ 7.38 (dd, 1H, J=1.2, 5.3 Hz), 7.27 (dd, 1H, J=1.2, 3.5 Hz), 7.08 (d, 1H, J=3.5 Hz), 7.05–7.01 (m, 4H), 6.95 (dd, 1H, J=3.5, 5.3 Hz), 6.61 (dq, 1H, J=1.0, 3.5 Hz), 2.46 (d, 3H, J=1.0 Hz); ^{13}C NMR δ 146.5, 136.0, 135.3 (two carbons), 135.2, 134.5, 133.9, 132.8, 131.9, 131.3, 130.5, 129.8, 128.0, 126.2, 125.2, 121.9, 15.4. Anal. Calcd for $C_{17}H_{12}S_4Se_3$: C, 35.15; H, 2.08. Found: C, 35.28; H, 2.09.

2-Methyl-5-({5-[(5-methyl-2-thienyl)seleno]-2-thienyl}-seleno)thiophene (16). Mp 74–75°C; ^{1}H NMR δ 7.05 (d, 2H, J=3.5 Hz), 7.01 (s, 2H), 6.59 (dq, 2H, J=1.0, 3.5 Hz), 2.44 (d, 6H, J=1.0 Hz); ^{13}C NMR δ 146.3 (two carbons), 135.7 (two carbons), 134.2 (two carbons), 131.7 (four carbons), 126.2 (two carbons), 15.4 (two carbons). MS *m/z* (relative intensity) 436 (30), 431 (26), 356 (4), 276 (98), 261 (26), 259 (100), 257 (49), 194 (15), 178 (22), 138 (38), 97 (19), 35 (13). Anal. Calcd for $C_{14}H_{12}S_3Se_2$: C, 38.72; H, 2.79. Found: C, 38.65; H, 2.63.

2-Methyl-5-[(5-methyl-2-thienyl)seleno]thiophene (17). Oil; ^{1}H NMR δ 7.06 (d, 2H, J=3.5 Hz), 6.59 (dq, 2H, J=1.0, 3.5 Hz), 2.49 (d, 6H, J=1.0 Hz); ^{13}C NMR δ 145.5 (two carbons), 134.6 (two carbons), 125.9 (two carbons), 123.7 (two carbons), 15.3 (two carbons). MS *m/z* (relative intensity) 274 (19), 194 (100), 193 (35), 161 (18), 97 (18), 45 (5). Anal. Calcd for $C_{10}H_{10}S_2Se$: C, 43.96; H, 3.69. Found: C, 43.80, H, 3.15.

5-Methyl-2,3-di[(5-methyl-2-thienyl)seleno]thiophene (18). Oil; ^{1}H NMR δ 7.05 (d, 1H, J=3.5 Hz), 7.04 (d, 1H, J=3.5 Hz), 6.62 (dq, 1H, J=1.0, 3.5 Hz), 6.55 (dq, 1H, J=1.0, 3.5 Hz), 6.30 (q, 1H, J=1.0 Hz), 2.44 (d, 3H, J=1.0 Hz), 2.40 (d, 3H, J=1.0 Hz), 2.27 (d, 3H, J=1.0 Hz); ^{13}C NMR δ 146.5, 145.9, 144.7, 136.7, 135.6, 134.1 (two carbons), 128.7, 126.3, 126.0, 122.5, 120.7, 15.5, 15.3 (two carbons). MS *m/z* (relative intensity) 450 (32), 447 (28), 290 (14), 273 (100), 269 (26), 257 (45), 256 (24), 240 (13), 192 (24), 177 (12), 97 (14), 59 (10). Anal. Calcd for $C_{15}H_{14}S_3Se_2$: C, 40.19; H, 3.15. Found: C, 39.95, H, 3.01.

5-Methyl-2-({5-methyl-3-[(5-methyl-2-thienyl)seleno]-2-thienyl}seleno-3-[(5-methyl-2-thienyl)seleno]thiophene (19). Oil; ^{1}H NMR δ 6.94 (d, 2H, J=3.5 Hz), 6.61(q, 2H J=1.0 Hz), 6.51 (dq, 2H, J=1.0, 3.5 Hz), 2.45 (d, 12H, J=1.0 Hz); ^{13}C NMR δ 145.6 (two carbons), 144.2 (two carbons), 134.7 (two carbons), 132.1 (two carbons), 128.8 (two carbons), 126.7 (two carbons), 126.0 (two carbons), 123.7 (two carbons), 15.5 (two carbons), 15.3 (two carbons). Anal. Calcd for $C_{20}H_{18}S_4Se_3$: C, 38.54; H, 2.91. Found: C 38.15; H, 2.70.

Electrophilic thienylselenenylation of furan derivatives

These experiments were carried out under reaction conditions identical to those described above for the reactions of the thiophene derivatives. Physical and spectroscopic data of the reaction products, **20–25**, are reported below.

2-(2-Thienylseleno)furan (20). Oil; ^{1}H NMR δ 7.50 (dd, 1H, *J*=1.0, 1.9 Hz), 7.36 (dd, 1H, *J*=1.1, 5.2 Hz), 7.26 (dd, 1H, *J*=1.1, 3.3 Hz), 6.96 (dd, 1H, *J*=3.3, 5.2 Hz), 6.64 (dd, 1H, *J*=1.0, 3.2 Hz), 6.36 (dd, 1H, *J*=1.9, 3.2 Hz); ^{13}C NMR δ 146.3, 143.1, 134.5, 130.7, 127.8, 123.9, 118.5, 111.6. MS *m*/*z* (relative intensity) 230 (38), 228 (18), 202 (20), 163 (6), 150 (100), 122 (30), 121 (72), 116 (16), 93 (13), 45 (6). Anal. Calcd for C_8H_6OSSe: C, 41.94; H, 2.64. Found: C, 41.65; H, 2.38.

2,5-Di(2-thienylseleno)furan (21). Mp 99–101°C; ^{1}H NMR δ 7.35 (dd, 2H, *J*=1.2, 5.3 Hz), 7.25 (dd, 2H, *J*=1.2, 3.6 Hz), 6.91 (dd, 2H, *J*=3.6, 5.3 Hz), 6.51 (s, 2H); ^{13}C NMR δ 143.5 (two carbons), 134.9 (two carbons), 130.9 (two carbons), 127.8 (two carbons), 123.3 (two carbons), 119.8 (two carbons). MS *m*/*z* (relative intensity) 392 (10), 229 (81), 227 (39), 203 (18), 201 (74), 199 (37), 197 (14), 163 (17), 121 (100), 117 (23), 116 (43), 71 (17). Anal. Calcd for $C_{12}H_8OS_2Se_2$: C, 36.95; H, 2.07. Found: C, 36.68; H, 1.89.

2-[(5-Methyl-2-thienyl)seleno]furan (22). Oil; ^{1}H NMR δ 7.42 (dd, 1H, *J*=0.8, 1.9 Hz), 7.09 (d, 1H, *J*=3.5 Hz), 6.58-6.60 (m, 2H), 6.28 (dd, 1H, *J*=1.9, 3.2 Hz), 2.47 (d, 3H, *J*=1.1 Hz); ^{13}C NMR δ 146.2, 145.8, 144.5, 135.7, 135.1, 126.1, 118.1, 111.6, 15.4. MS *m*/*z* (relative intensity) 244 (23), 242 (13), 215 (7), 164 (100), 163 (21), 135 (44), 117 (6), 97 (9), 45 (6). Anal. Calcd for C_9H_8OSSe: C, 44.46, H, 3.32. Found: C, 44.30; H, 3.11.

2,5-Di[(5-methyl-2-thienyl)seleno]furan (23). Mp 72–74°C; ^{1}H NMR δ 7.06 (d, 2H, *J*=3.4 Hz), 6.60 (dq, 2H, *J*=0.9, 3.4 Hz), 6.48 (s, 2H), 2.48 (d, 6H, *J*=0.9 Hz); ^{13}C NMR δ 145.9 (two carbons), 143.8 (two carbons), 135.4 (two carbons), 126.1 (two carbons), 120.2 (two carbons), 119.4 (two carbons), 15.3 (two carbons). MS *m*/*z* (relative intensity) 420 (11), 418 (11), 340 (2), 260 (61), 244 (10), 243 (100), 217 (15), 215 (67), 213 (29), 177 (16), 135 (69), 134 (19), 97 (21), 91 (7), 53 (9). Anal. Calcd for $C_{14}H_{12}OS_2Se_2$: C, 40.21, H, 2.89. Found: C, 40.01; H, 2.55.

2-Methyl-5-(2-thienylseleno)furan (24). Oil; ^{1}H NMR δ 7.32 (dd, 1H, *J*=1.1, 5.3 Hz), 7.22 (dd, 1H, *J*=1.1, 3.5 Hz), 6.92 (dd, 1H, *J*=3.5, 5.3 Hz), 6.55 (d, 1H, *J*=3.1 Hz), 5.94 (dq, 1H, *J*=0.9, 3.1 Hz), 2.29 (d, 3H, *J*=0.9 Hz); ^{13}C NMR δ 156.6, 137.1, 134.0, 130.3, 127.8, 125.1, 120.3, 107.8, 13.8. MS *m*/*z* (relative intensity) 244 (19), 201 (7), 164 (100), 135 (12), 121 (19), 117 (4), 82 (4), 43 (7). Anal. Calcd for C_9H_8OSSe: C, 44.46; H, 3.32. Found: C, 44.21; H, 3.15.

2-Methyl-5-[(5-methyl-2-thienyl)seleno]furan (25). Oil; ^{1}H NMR δ 7.03 (d, 1H, *J*=3.4 Hz), 6.58 (dq, 1H, *J*=1.1, 3.4 Hz), 6.52 (d, 1H, *J*=3.1 Hz), 5.93 (dq, 1H, *J*=1.0, 3.1 Hz), 2.43 (d, 3H, *J*=1.1 Hz), 2.29 (d, 3H, *J*=1.0 Hz); ^{13}C NMR δ 156.2, 145.2, 137.4, 134.5, 125.9, 121.6, 119.8, 107.7, 15.2, 13.4. MS *m*/*z* (relative intensity) 258 (16), 179 (16), 178 (100), 177 (30), 135 (25), 89 (9), 53 (10). Anal. Calcd for $C_{10}H_{10}OSSe$: C, 46.71; H, 3.92. Found C, 46.51; H, 3.81.

Acknowledgements

Financial support from *Ministero dell'Università e della Ricerca Scientifica e Tecnologica, Italy*, National Project Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni, *University of Perugia*, Progetti di Ateneo, and *CNR, Rome*, is gratefully acknowledged.

References

1. Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron Lett.* **1989**, *30*, 1417–1420.
2. Tiecco, M.; Testaferri, L.; Tingoli, M.; Bagnoli, L.; Marini, F. *J. Chem. Soc. Perkin Trans. 1* **1993**, 1989–1993 and references cited therein.
3. Tiecco, M.; Testaferri, L.; Tingoli, M.; Marini, F.; Mariggiò, S. *Tetrahedron* **1994**, *50*, 10549–10554.
4. Engman, L.; Erikson, P. *Heterocycles* **1996**, *43*, 861–871.
5. Jen, K.-Y.; Benfaremo, N.; Cava, M. P.; Huang, W.-S.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 633–634.
6. Jones, E.; Moodie, I. M. In *Org. Synth.*, Breslow, R., Ed.; Wiley: New York, 1970; Vol. 50, pp 104–106.
7. Tingoli, M.; Tiecco, M.; Testaferri, L.; Temperini, A. *Synth. Commun.* **1998**, *28*, 1769–1778.
8. A competitive experiment carried out with the 5,5′-dimethyl-2,2′-dithienyl diselenide and iodobenzene diacetate showed that 2-methylthiophene is about 150 times more reactive than thiophene.
9. Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355–390.