Synthesis of 6,7,9,10-tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine and 4,7,8,10-tetrahydro-5*H*-thieno[2,3-*f*][1,4]oxathionine by *S*-ylide rearrangement

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6,7,9,10-Tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine 7 and 4,7,8,10-tetrahydro-5*H*-thieno[2,3-*f*][1,4]-oxathionine 17 have been synthesized by a [2,3] sigmatropic rearrangement of *S*-methylides 6 and 16 which are generated by the fluoride ion-induced desilylation of 3-(2-thienyl)-4-[(trimethylsilyl)methyl]-1,4-oxathianium triflate 4 and the 3-(3-thienyl)- analogue 14.

Although the bioactivities of eight- to ten-membered heterocyclic compounds are interesting with regard to the development of new medicines, studies in this field are limited because convenient synthetic routes have not been fully investigated.[1] Sommelet–Hauser rearrangement of five- to seven-membered cyclic ammonium *N*-ylides and cyclic sulfonium *S*-ylides are useful for three-carbon-ring enlargement.[2] We previously reported that the fluoride ion-induced desilylation of [(trimethylsilyl)methyl]onium salts is suitable for the syntheses of eight- to ten-membered cyclic amines and sulfides.[3,4] We report here the synthesis of new nine-membered heterocyclic compounds, 6,7,9,10-tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine **7** and 4,7,8,10-tetrahydro-5*H*-thieno[2,3-*f*][1,4]oxathionine **17**, by *S*-ylide rearrangement.

Results and discussion

The starting sulfides, 3-(2-thienyl)-1,4-oxathiane **3** and the 3-thienyl analogue **13** were prepared from 2-thienylmagnesium bromide **1** or lithium di(3-thienyl)cuprate **12** with 3-chloro-1,4-oxathiane **2** (Schemes 1 and 3). They were then treated with (trimethylsilyl)methyl triflate to give mixtures of *cis*- and *trans*-3-(2-thienyl)-4-[(trimethylsilyl)methyl]-1,4-oxathianium triflate *cis*-**4**, *trans*-**4** (*cis*:*trans* = 37:63) and 3-(3-thienyl)- analogues *cis*-**14**, *trans*-**14** (*cis*:*trans* = 14:86). Although we initially tried to isolate each stereoisomer, isolation was difficult because a mixture of *cis*-**4** and *trans*-**4** did not crystallize, and a mixture of *cis*-**14** and *trans*-**14** decomposed in the solvents at room temp. The configurations of both of the major isomers were estimated to be *trans* by comparison of the chemical shifts of protons of the CH_2Si groups (*cis* > *trans*) and at position 3 (*cis* < *trans*) in the ^1H NMR spectra of the mixtures, according to determination of the stereochemistry of *cis*- and *trans*-3-phenyl-4-[(trimethylsilyl)methyl]-1,4-oxathianium perchlorate.[4b]

Reaction of a mixture of salts *cis*-**4** and *trans*-**4** (37:63) with caesium fluoride in 1,2-dimethoxyethane (DME) gave (*E*)- and (*Z*)-3a,4,6,7-tetrahydro-9*H*-thieno-[3,2-*f*][1,4]oxathionine (*E*)-**5**, (*Z*)-**5** and 3-[(2-hydroxyethyl)sulfanylmethyl]-2-vinylthiophene **8** after 1 h at room temp. (Table 1, entry 1), and no significant difference was observed after 24 h (entry 2). When the reaction was carried out in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[5] the products changed to 6,7,9,10-tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine **7** (entry 3). The configuration of compound (*Z*)-**5** was confirmed by observation of nuclear Overhauser effect (NOE) enhancement (7.7%) of the proton at position 10 upon irradiation of a proton at position 4.

Thus, (*E*)-**5** and (*Z*)-**5**, which are [2,3] sigmatropic rearrangement products of ylide **6**, are stable at room temp. and can be aromatized by the aid of a strong base. When these compounds were kept for 4 days at room temp. in air, (*E*)-**5** changed to a mixture of products **7**, **8** and 10-hydroxy-6,7,9,10-tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine **11** in the proportions 18:68:14, and (*Z*)-**5** changed to a mixture of the same products in the proportion 91:3:6. Thus, alcohol **8** is formed mainly from isomer (*E*)-**5** by an intramolecular [1,5] proton transfer from position 3a to position 8.

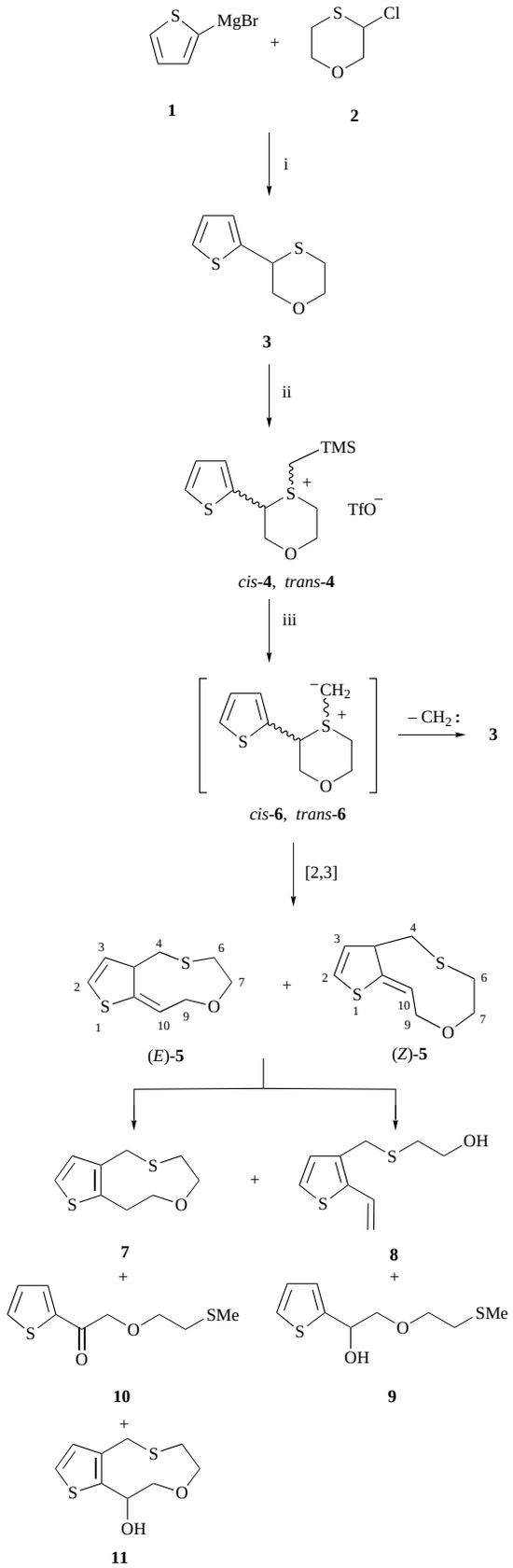
The conformation of the starting onium salts is retained in the product ylides in the desilylation.[3i] Ylide *cis*-**6** may exist in either an axial–equatorial or equatorial–axial form (Scheme 2). One of these is converted into isomer (*E*)-**5** and the other is converted into isomer (*Z*)-**5**. Ylide *trans*-**6** exists as an equatorial–equatorial conformation and is isomerized to isomer (*Z*)-**5**. The ratio of (*E*)-**5** to (*Z*)-**5** products (15:67) is consistent with the ratio of salts *cis*-**4** to *trans*-**4** (37:63).

Although many [2,3] sigmatropic rearrangement products ('isotoluene' compounds) have been isolated in *N*-ylide reactions,[3] sigmatropic rearrangement products from 1-phenyl-3,4-dihydro-1*H*-2-benzothiopyranium 2-methylides[4a] and 3-phenyl-1,4-oxathianium 4-ylides,[4b] could not be isolated because of their instability in aqueous media. However, compounds (*E*)-**5** and (*Z*)-**5** are stable in aqueous media.

In our previous works concerning desilylation,[3–5] we commonly used dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) as the solvent. The use of DMF in this reaction, however, resulted in the competitive formation of a new product 2-{1-hydroxy-2-[2-(methylsulfanyl)ethoxy]ethyl}thiophene **9**, and the yields of compounds (*E*)-**5**, (*Z*)-**5** and **8** were decreased (entries 4 and 5). The products of the reaction in DMSO were further complicated by the formation of 2-{2-[2-(methylsulfanyl)ethoxy]acetyl}thiophene **10** and **3** (entries 7–9).

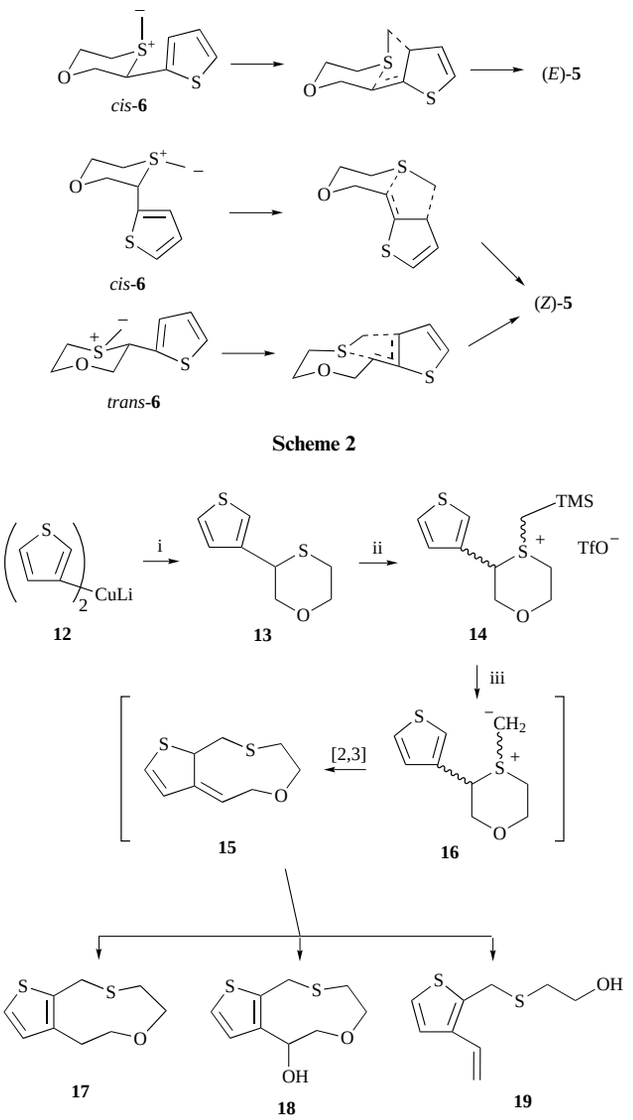
Compounds **9** and **10** should be formed *via* bicycles (*E*)-**5** or (*Z*)-**5**, because the main product was compound **7** when the reactions were carried out in the presence of DBU (entries 6 and 10). Oxygen atoms of the hydroxy group of the alcohol **9** and the carbonyl group of ketone **10** would be transferred from the solvent molecules, although the mechanism is still unclear. Compound **3** may be formed from bicycle **5** by the elimination of carbene.

The reaction of salts *cis*-**14** and *trans*-**14** (ratio 14:86) with caesium fluoride gave a mixture of many products in DME, DMF or DMSO, contrary to the case of salts *cis*-**4** and *trans*-**4** (Scheme 3). While 4-hydroxy-4,7,8,10-tetrahydro-5*H*-thieno[2,3-*f*][1,4]oxathionine **18** (37%) was isolated from the reaction mixture in DMSO, and compound **18** (19%) and 2-[(2-hydroxyethyl)sulfanylmethyl]-3-vinylthiophene **19** (8%)



Scheme 1 *Reagents and conditions*: i, Et_2O, benzene, RT, 24 h; ii, Me_3SiCH_2OTf, CH_2Cl_2, RT, 3 h; iii, CsF, DME, DMF or DMSO, RT, 24 h

were isolated from the reaction in the presence of DBU, the expected 4,7,8,10-tetrahydro-5*H*-thieno[2,3-*f*][1,4]oxathionine **17** was not obtained. Although 7,8,10,10a-tetrahydro-5*H*-thieno[2,3-*f*][1,4]oxathionine **15** is initially formed, *via* the ylide **16**, it is quickly converted into the alcohols **18** and **19**. The



Scheme 3 *Reagents and conditions*: i, **2**, THF, hexane, benzene, −45 °C to RT, 12 h; ii, Me_3SiCH_2OTf, CH_2Cl_2, RT, 2 h; iii, CsF, (DBU), DMSO, RT, 24 h

addition of DBU shortly after the addition of caesium fluoride, contrary to the normal order, gave compound **17** in 46% yield. Reaction of the salt **14** with DBU may be preferable to that with caesium fluoride in this case.

Experimental

All reactions were carried out in N_2. Diethyl ether was distilled from sodium benzophenone ketyl. Benzene was distilled from sodium. Tetrahydrofuran (THF) was distilled from $LiA1H_4$. DMSO and DBU were dried by distillation under reduced pressure from CaH_2. DMF was dried by distillation under reduced pressure from BaO. DME was dried by distillation from CaH_2. CsF was dried over P_2O_5 at 180 °C. Distillation was performed on a Büchi Kugelrohr distillation apparatus. NMR spectra were recorded on a JEOL JNM-EX270, JNM-LA400 or JNM-A500 spectrometer. IR spectra were recorded on a Jasco FT/IR-5300 spectrometer. Mass spectra were measured on a JEOL JMS-SX102A system. All mps (Yanaco micro melting point apparatus) and bps (oven temperature) are uncorrected. *J*-Values are given in Hz.

3-(2-Thienyl)-1,4-oxathiane 3

3-Chloro-1,4-oxathiane **2** was prepared from 1,4-oxathiane (3.1 g, 30 mmol) and *N*-chlorosuccinimide (4.0 g, 30 mmol) in

Table 1 Reaction of *cis*- and *trans*-3-(2-thienyl)-4-[(trimethylsilyl)methyl]-1,4-oxathianium triflate *cis*-**4**, *trans*-**4** with CsF at room temp.

Entry	Solvent	Additive	Reaction time (*t*/h)	Total yield (%)	Product proportions[a]						
					(*E*)-**5**	(*Z*)-**5**	**7**	**8**	**9**	**10**	**3**
1	DME		1	78	8	72	0	20	0	0	0
2	DME		24	93	15	67	0	18	0	0	0
3	DME	DBU	24	92	0	0	100	0	0	0	0
4	DMF		1	71	7	43	0	0	50	0	0
5	DMF		24	95	9	51	0	0	40	0	0
6	DMF	DBU	24	88	0	0	95	5	0	0	0
7	DMSO		2	96	19	72	*b*	0	6	3	*b*
8	DMSO		24	91	13	44	*b*	0	12	31	*b*
9	DMSO		48	93	0	0	23	0	34	28	15
10	DMSO	DBU	24	90	0	0	85	9	0	0	6

[a] Proportions of the products were determined by integration of the ^{1}H NMR signals at 500 MHz. [b] The proportions were not determined due to overlapping of the signal with others.

benzene (50 cm^3) according to the reported method.[6] The benzene solution of chloride **2** was added to a solution of 2-thienylmagnesium bromide **1**, prepared from 2-bromothiophene (4.9 g, 30 mmol) and magnesium turnings (0.73 g, 30 mmol) in Et_2O (50 cm^3). The mixture was stirred for 24 h at room temp. (RT) and quenched with 20% aq. H_2SO_4 (50 cm^3). The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined extracts were washed successively with 10% aq. NaOH and water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (hexane–Et_2O, 20:1), and the eluent was distilled to give the *title compound* **3** (2.8 g, 49%), as a non-distillable oil [decomposed at 108 °C (1.2 mmHg)] (Found: C, 51.4; H, 5.4. $C_8H_{10}OS_2$ requires C, 51.6; H, 5.4%); ν_{max}(film)/cm^{-1} 1450, 1285 and 1105; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.57 (1 H, ddd, *J* 2.6, 3.3 and 13.5, 5-H), 2.98 (1 H, ddd, *J* 3.3, 10.3 and 13.5, 5-H), 3.77 (1 H, ddd, *J* 2.6, 10.3 and 11.7, 6-H), 3.81 (1 H, dd, *J* 9.2 and 11.4, 2-H), 4.13 (1 H, ddd, *J* 3.3, 3.3 and 11.7, 6-H), 4.22 (1 H, dd, *J* 3.3 and 11.4, 2-H), 4.31 (1 H, dd, *J* 3.3 and 9.2, 3-H), 6.94 (1 H, dd, *J* 3.7 and 5.1, ArH), 7.01 (1 H, dd, *J* 1.1 and 3.7, ArH) and 7.21 (1 H, dd, *J* 1.1 and 5.1, ArH); δ_C(100.5 MHz; $CDCl_3$) 27.9, 39.1, 68.1, 74.6, 124.8, 125.6, 126.7 and 141.4; *m*/*z* (EI) 186.0170 (M^+. $C_8H_{10}OS_2$ requires *M*, 186.0173), 186 (36%), 128 (100), 126 (82) and 97 (30).

Since compound **3** is unstable at RT, it was dissolved in CH_2Cl_2 (60 cm^3) (0.5 M solution) and stored at −10 °C over 4 Å molecular sieves under N_2.

cis- and *trans*-3-(2-Thienyl)-4-[(trimethylsilyl)methyl]-1,4-oxathianium triflate *cis*-4, *trans*-4

To an aliquot of a 0.5 M solution of compound **3** (2 cm^3, 1 mmol) was added (trimethylsilyl)methyl triflate (260 mg, 1.1 mmol), and the mixture was stirred at RT for 3 h and concentrated under reduced pressure to give a mixture of the title salts *cis*-**4** and *trans*-**4** (37:63, the mixture was subsequently used for the following reaction with CsF) as an oil; δ_H(400 MHz; $CDCl_3$) *cis*-**4**: 0.17 (9 H, s), 1.59 (1 H, d, *J* 13.9, CH_2), 2.33 (1 H, d, *J* 13.9, CH_2), 3.53–3.60 (1 H, m, 5-H), 4.23–4.30 (1 H, m, 2-H), 5.45–5.50 (1 H, br s, 3-H), 7.13 (1 H, dd, *J* 3.7 and 5.1, ArH) and 7.52 (1 H, dd, *J* 1.1 and 5.1, ArH); *trans*-**4**: 0.14 (9 H, s, $SiCH_3$), 2.35 (1 H, d, *J* 13.9, CH_2), 3.14 (1 H, d, *J* 13.9, CH_2), 3.60–3.78 (2 H, m, 5-H_2), 5.29 (1 H, dd, *J* 3.3 and 9.9, 3-H), 7.70 (1 H, dd, *J* 3.7 and 5.1, ArH) and 7.42 (1 H, dd, *J* 1.1 and 3.7, ArH); other signals overlapped 3.05–3.13 (1 H), 4.00–4.16 (1 H, 2 H), 4.32–4.49 (2 H, 2 H) and 7.43–7.48 (1 H, 1 H).

Reaction of salts 4 with CsF in DME

To a solution of salts *cis*-**4** and *trans*-**4** (37:63) in DME (5 cm^3) was added CsF (0.30 g, 2 mmol). The mixture was stirred at RT and poured into water (50 cm^3) after either 1 h or 24 h. The ethereal extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give a mixture (1 h: 156 mg; 24 h: 189 mg) of (*E*)- and (*Z*)-3a,4,6,7-tetrahydro-9*H*-thieno[3,2-*f*][1,4]oxathionines (*E*)-**5**, (*Z*)-**5** and 3-[(2-hydroxyethyl)sulfanylmethyl]-2-vinylthiophene **8**. The products were isolated on a silica gel column (Et_2O–hexane, 10:90 to 50:50) and their proportions were determined from the integrated values of the proton signals in the ^{1}H NMR spectrum of the mixture. The results are shown in Table 1.

Compound (*E*)-**5**: an oil; ν_{max}(film)/cm^{-1} 2900, 1640 and 1130; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.56 (1 H, dd, *J* 9.2 and 14.5, 4-H), 2.69 (1 H, ddd, *J* 4.0, 10.6 and 14.5, 6-H), 2.77–2.90 (2 H, m, 4- and 6-H), 3.54 (1 H, ddd, *J* 2.6, 10.6 and 12.5, 7-H), 4.11 (1 H, ddd, *J* 3.6, 4.0 and 12.5, 7-H), 4.30–4.40 (2 H, m, 9- and 3a-H), 4.85 (1 H, dd, *J* 6.6 and 14.2, 9-H), 5.58 (1 H, ddd, *J* 1.3, 3.0 and 6.3, 3-H), 5.66–5.73 (1 H, m, 10-H) and 6.44 (1 H, dd, *J* 1.3 and 6.3, 2-H); δ_C(67.8 MHz; $CDCl_3$) 34.4, 37.7, 51.4, 70.6, 72.2, 120.1, 123.8, 126.0 and 144.2.

Compound (Z)-**5**: an oil (Found: C, 53.8; H, 6.0. $C_9H_{12}OS_2$ requires C, 54.0; H, 6.0%); ν_{max}(film)/cm^{-1} 2910, 1640 and 1055; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.60–2.73 (2 H, m, 4- and 6-H), 2.89 (1 H, ddd, *J* 2.6, 7.3 and 16.5, 6-H), 3.00 (1 H, dd, *J* 5.0 and 14.0, 4-H), 3.65 (1 H, ddd, *J* 2.6, 5.9 and 13.9, 7-H), 3.84–3.95 (2 H, m, 7- and 3a-H), 4.00 (1 H, dd, *J* 10.6 and 11.5, 9-H), 4.29 (1 H, ddd, *J* 1.0, 4.6 and 11.5, 9-H), 5.69 (1 H, dd, *J* 3.3 and 6.3, 3-H), 5.92 (1 H, dddd, *J* 1.3, 2.0, 4.6 and 10.6, 10-H) and 6.36 (1 H, ddd, *J* 0.9, 1.3 and 6.3, 2-H); δ_C(67.9 MHz; $CDCl_3$) 40.3, 42.9, 55.1, 69.9, 71.2, 117.3, 124.9, 125.2 and 148.00. NOE enhancement was observed: 7.7% at δ 5.92 (10-H), 12.5% at δ 3.85 (3a-H) and 11.2% at δ 2.65 (4- and 6-H) under irradiation at δ 3.00 (4-H).

Compound **8**: an oil; ν_{max}(film)/cm^{-1} 3410, 1620 and 900; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.10–2.30 (1 H, br s, OH), 2.55 (2 H, t, *J* 5.9, SCH_2), 3.59 (2 H, t, *J* 5.9, OCH_2), 3.67 (2 H, s, ArCH_2), 5.07 (1 H, d, *J* 10.9, CH=CH_2), 5.50 (1 H, d, *J* 17.2, CH=CH_2), 6.79 (1 H, dd, *J* 10.9 and 17.2, C*H*=CH_2), 6.88 (1 H, d, *J* 5.3, ArH) and 7.03 (1 H, d, *J* 5.3, ArH); δ_C(125.4 MHz; $CDCl_3$; Me_4Si) 28.1, 34.6, 60.5, 114.5, 123.7, 127.4, 129.6, 135.2 and 138.8; *m*/*z* (EI) 200.0311 (M^+. $C_9H_{12}OS_2$ requires *M*, 200.0329), 200 (40%), 123 (100) and 79 (22).

Reaction of salts 4 with CsF in the presence of DBU in DME

To a solution of salts *cis*-**4** and *trans*-**4** (37:63) in DME (5 cm^3) were added DBU (0.30 g, 2 mmol) and CsF (0.30 g, 2 mmol). The mixture was stirred for 24 h and worked up in a manner similar to that described above. The ethereal extract was concentrated to give 6,7,9,10-*tetrahydro*-4H-*thieno*[3,2-f][1,4]*oxathionine* **7** (185 mg, 92%), bp 120 °C (1.5 mmHg) (Found: C, 53.7; H, 6.0. $C_9H_{12}OS_2$ requires C, 54.0; H, 6.0%); ν_{max}(film)/cm^{-1} 1465, 1115 and 705; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.06 (2 H, t, *J* 4.8, 6-H_2), 2.88 (2 H, t, *J* 4.5, 10-H_2), 3.65 (2 H, t, *J* 4.5, 9-H_2), 3.82 (2 H, t, *J* 4.8, 7-H_2), 4.00 (2 H, s, 4-H_2), 6.98 (1 H, d, *J* 5.1, ArH) and 7.09 (1 H, d, *J* 5.1, ArH); δ_C(100.5 MHz; $CDCl_3$; Me_4Si) 26.9, 29.8, 29.9, 72.8, 75.4, 122.3, 129.7,

133.9 and 139.1; *m*/*z* (EI) 200.0323 (M^+. $C_9H_{12}OS_2$ requires *M*, 200.0329), 200 (100%), 123 (30) and 110 (69).

Reaction of salts 4 with CsF in DMF

To a solution of salts *cis*-**4** and *trans*-**4** (37 : 63) in DMF (5 cm^3) was added CsF (0.30 g, 2 mmol). The mixture was stirred for either 1 h or 24 h and worked up in a manner similar to that described above. The ethereal extract was concentrated to give a mixture (1 h: 148 mg; 24 h: 198 mg) of compounds (*E*)-**5**, (*Z*)-**5** and 2-{1-hydroxy-2-[2-(methylsulfanyl)ethoxy]ethyl}thiophene **9**. Samples of the products were isolated on a silica gel column (hexane–Et_2O, 90 : 10 to 50 : 50).

Compound **9**: an oil (Found: C, 49.7; H, 6.3. $C_9H_{14}O_2S_2$ requires C, 49.5; H, 6.5%); ν_{max}(film)/cm^{-1} 3420, 1115 and 705; δ_H(500 MHz; $CDCl_3$; Me_4Si) 2.15 (3 H, s, CH_3), 2.74 (2 H, t, *J* 2.7), 3.15 (1 H, d, *J* 3.1, OH), 3.61 (1 H, dd, *J* 7.9 and 8.8), 3.72–3.75 (3 H, m), 5.14 (1 H, ddd, *J* 3.1, 6.7 and 8.8), 6.98 (1 H, dd, *J* 3.7 and 4.8, ArH), 7.02 (1 H, dd, *J* 1.2 and 3.7, ArH) and 7.26 (1 H, dd, *J* 1.2 and 4.8, ArH); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 15.9, 33.7, 69.0, 70.3, 77.3, 124.3, 124.9, 126.6 and 143.5; *m*/*z* (EI) 126 (95%, M − $HOCH_2CH_2SMe$), 113 (99), 85 (43) and 75 (100).

Reaction of salts 4 with CsF in DMSO

To a solution of salts *cis*-**4** and *trans*-**4** (37 : 63) in DMSO (5 cm^3) was added CsF (0.30 g, 2 mmol). The mixture was stirred for either 2 h, 24 h or 48 h and then was worked up in a manner similar to that described above. The ethereal extract was concentrated (2 h: 190 mg; 24 h: 189 mg; 48 h: 192 mg) and chromatographed on a silica gel column (hexane–Et_2O, 90 : 10 to 50 : 50) to give compound (*E*)-**5**, (*Z*)-**5**, **7**, **9** and 2-{2-[2-(methylsulfanyl)ethoxy]acetyl}thiophene **10** (entries 7–9).

Compound **10**: an oil (Found: C, 49.9; H, 5.65. $C_9H_{12}O_2S_2$ requires C, 50.0; H, 5.6%); ν_{max}(film)/cm^{-1} 1675, 1415 and 1135; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.16 (3 H, s, CH_3), 2.78 (2 H, t, *J* 6.6), 3.79 (2 H, t, *J* 6.6), 4.62 (2 H, s), 7.16 (1 H, dd, *J* 4.0 and 4.8, ArH), 7.69 (1 H, dd, *J* 1.1 and 4.8, ArH) and 7.89 (1 H, dd, *J* 1.1 and 4.0, ArH); δ_C(100.5 MHz; $CDCl_3$; Me_4Si) 16.0, 33.5, 70.9, 74.4, 128.2, 132.7, 134.1, 140.9 and 189.8; *m*/*z* (EI) 216 (M^+, 0.1%), 111 (82), 97 (27) and 74 (100).

Reaction of salts 4 with CsF in the presence of DBU in DMF or DMSO

To a DMF or DMSO (5 cm^3) solution of salts *cis*-**4** and *trans*-**4** described above were added DBU (0.30 g, 2 mmol) and CsF (0.30 g, 2 mmol). The mixture was worked up to give a mixture (176 mg) of compounds **7** and **8** from the reaction in DMF, or a mixture (180 mg) of products **7**, **8**, and **3** from the reaction in DMSO.

Change in isomers (*E*)-5 and (*Z*)-5 at RT

Compound (*E*)-**5** or (*Z*)-**5** (15 mg, 0.08 mmol) was kept for 4 days at RT in air and then was dissolved in $CDCl_3$ (0.6 cm^3) to determine its ^1H NMR spectrum. The spectrum from isomer (*E*)-**5** showed the presence of compounds **7**, **8** and 10-hydroxy-6,7,9,10-tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine **11** in the proportions 18 : 68 : 14, and that from isomer (*Z*)-**5** was a mixture of proportions 91 : 3 : 6. The $CDCl_3$ solution was concentrated and the residue was chromatographed on a silica gel column (hexane–Et_2O, 1 : 1).

Compound **11**: bp 110 °C (1.5 mmHg); ν_{max}(film)/cm^{-1} 3410, 1235 and 1065; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.07–2.11 (2 H, m, 6-H_2), 2.30 (1 H, d, *J* 4.4, OH), 3.48 (1 H, dd, *J* 8.3 and 10.5, 9-H), 3.81 (1 H, ddd, *J* 3.2, 4.1 and 12.7, 7-H), 3.87–3.93 (2 H, m, 4- and 7-H), 3.96 (1 H, dd, *J* 2.4 and 10.5, 9-H), 4.14 (1 H, d, *J* 12.4, 4-H), 5.01 (1 H, ddd, *J* 2.4, 4.4 and 8.37, 10-H), 7.00 (1 H, d, *J* 5.1, ArH) and 7.21 (1 H, d, *J* 5.1, ArH); δ_C(125.7 MHz; $CDCl_3$) 27.3, 30.0, 69.3, 75.7, 76.1, 123.6, 130.2, 133.3 and 144.0; *m*/*z* (EI) 216.0282 (M^+. $C_9H_{12}O_2S_2$ requires *M*, 216.0279), 216 (42%), 156 (14), 126 (100) and 97 (13).

3-(3-Thienyl)-1,4-oxathiane 13

A suspension of 3-lithiothiophene was prepared from 3-bromothiophene (8.2 g, 50 mmol) and butyllithium (1.6 M in hexane; 30 cm^3, 48 mmol) in a mixture of hexane (60 cm^3) and THF (6 cm^3) according to the reported method.[7] This suspension was added to a suspension of copper(I) iodide (4.8 g, 25 mmol) in THF (90 cm^3) for 25 min at −40 °C and the mixture was stirred for 1 h to give a suspension of lithium di-(3-thienyl)cuprate **12**. A benzene solution of compound **2** (26 mmol) was added to the suspension of cuprate **12** at −40 °C, and stirred at RT for 12 h. Saturated aq. $(NH_4)_2SO_4$ was added to the mixture, which was then filtered. The filtrate was extracted with Et_2O (200 cm^3). The extract was washed successively with water and saturated aq. NaCl, dried ($MgSO_4$), and concentrated. The residue was chromatographed on a silica gel column (hexane–Et_2O, 97 : 3), and the eluent was concentrated under reduced pressure to give the *title compound* **13** (2.2 g, 47%) as a non-distillable oil (Found: C, 51.4; H, 5.4. $C_8H_{10}OS_2$ requires C, 51.6; H, 5.4%); ν_{max}(KBr)/cm^{-1} 1450, 1285 and 1105; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.52 (1 H, ddd, *J* 2.2, 2.9 and 13.6, 5-H), 2.98 (1 H, ddd, *J* 3.3, 10.6 and 13.6, 5-H), 3.76 (1 H, ddd, *J* 2.2, 10.6 and 11.7, 6-H), 3.79 (1 H, dd, *J* 9.2 and 11.3, 2-H), 4.12–4.17 (2 H, m, 3- and 6-H), 4.19 (1 H, dd, *J* 2.9 and 11.3, 2-H), 7.07 (1 H, dd, *J* 1.5 and 5.1, ArH), 7.22 (1 H, m, ArH) and 7.28 (1 H, dd, *J* 2.9 and 5.1, ArH); δ_C(100.5 MHz; $CDCl_3$) 27.9, 39.2, 68.1, 73.8, 122.3, 125.9, 127.0 and 139.0; *m*/*z* (EI) 186.0167 (M^+. $C_8H_{10}OS_2$ requires *M*, 186.0173), 186 (75%), 128 (100), 126 (70) and 97 (27).

3-(3-Thienyl)-4-[(trimethylsilyl)methyl]-1,4-oxathianium triflate 14

(Trimethylsilyl)methyl triflate (2.4 g, 10 mmol) was added to a solution of compound **13** (1.5 g, 8 mmol) in CH_2Cl_2 (20 cm^3) at RT and the mixture was stirred for 2 h. The solvent was evaporated off under reduced pressure. The residue was washed with Et_2O and concentrated to give the *title salt* **14** (*cis* : *trans*, 14 : 86) (3.1 g, 93%), mp 84–86 °C (from Et_2O) (Found: C, 36.7; H, 5.0. $C_{13}H_{21}F_3O_4S_3Si$ requires C, 36.95; H, 5.0%); ν_{max}(KBr)/cm^{-1} 1270, 1160 and 860; δ_H(500 MHz; $CDCl_3$; Me_4Si) *cis*-**14**: 0.20 (9 H, s), 1.86 (1 H, d, *J* 14.0), 2.98–3.04 (1 H, m), 4.15–4.19 (1 H, m), 4.28–4.33 (1 H, m), 4.37–4.44 (1 H, m), 4.53–4.58 (1 H, m), 5.26–5.29 (1 H, m), 7.37–7.39 (1 H, m) and 7.83–7.85 (1 H, m) (other signals overlapped with those of *trans*-**14**); *trans*-**14**: 0.18 (9 H, s, $SiCH_3$), 2.30 (1 H, d, *J* 14.0, CH_2), 3.14 (1 H, d, *J* 14.0, CH_2), 3.61 (1 H, d, *J* 12.2, 5-H), 3.78 (1 H, ddd, *J* 3.1, 12.2 and 15.3, 5-H), 4.06–4.13 (2 H, m, 2- and 6-H), 4.34 (1 H, dd, *J* 3.1 and 13.4, 2-H), 4.49 (1 H, ddd, *J* 3.1, 3.1 and 14.0, 6-H), 5.14 (1 H, dd, *J* 3.1 and 10.4, 3-H), 7.20 (1 H, dd, *J* 1.2 and 4.6, ArH), 7.48 (1 H, dd, *J* 3.1 and 4.6, ArH) and 7.76 (1 H, dd, *J* 1.2 and 3.1, ArH); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) *trans*-**14**: −1.6 (3 C), 24.4, 39.0, 53.7, 64.1, 69.7, 126.1, 128.4, 128.7 and 129.0.

Reaction of salt 14 with CsF

To a solution of salt **14** (422 mg, 1 mmol) in DMSO (5 cm^3) was added CsF (0.30 g, 2 mmol) at RT. The mixture was stirred for 24 h, poured into water (50 cm^3) and extracted with Et_2O. The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue (170 mg) from the extract was chromatographed on a silica gel column (Et_2O–hexane, 30 : 70) to give 4-*hydroxy*-4,7,8,10-*tetrahydro*-5H-*thieno*-[2,3-f][1,4]*oxathionine* **18** (80 mg, 37%), mp 77–79 °C (Found: C, 50.0; H, 5.6. $C_9H_{12}O_2S_2$ requires C, 50.0; H, 5.6%); ν_{max}(film)/cm^{-1} 3395, 1235, 1115 and 1065; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.12–2.18 (2 H, m, 8-H), 2.46 (1 H, br s, OH), 3.55 (1 H, dd, *J* 7.6 and 10.6, 5-H), 3.75–3.86 (3 H, m, 5-H, and 7-H_2), 4.26 (2 H, s, 10-H_2), 4.83 (1 H, br d, *J* 7.6, 4-H), 6.95 (1 H, d, *J* 5.3, ArH) and 7.24 (1 H, d, *J* 5.3, ArH); δ_C(67.9 MHz; $CDCl_3$) 27.6, 29.5, 69.6, 75.3, 75.8, 124.7, 125.5, 136.4 and 142.9; *m*/*z* (EI) 216.0275 (M^+. $C_9H_{12}O_2S_2$ requires *M*, 216.0279), 216 (57%), 156 (17), 126 (100) and 97 (24).

Reaction of salt 14 with CsF in the presence of DBU

(**A**) To a solution of salt **14** in DMSO were added DBU (0.30 g, 2 mmol) and CsF (0.30 g, 2 mmol) in a manner similar to that described above. The mixture was stirred for 24 h at RT and worked up. The residue (185 mg) from the ethereal extract was chromatographed on a silica gel column (hexane–Et_2O, 70 : 30 to 50 : 50) to give alcohol **18** (40 mg, 19%) and 2-[(2-*hydroxyethyl*)*sulfanylmethyl*]-3-*vinylthiophene* **19** (15 mg, 8%) as an oil; ν_{max}(film)/cm^{-1} 3400, 1625 and 1050; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.02 (1 H, t, *J* 5.9, OH), 2.72 (2 H, t, *J* 5.9, SCH_2), 3.70 (2 H, q, *J* 5.9, OCH_2), 3.96 (2 H, s, $ArCH_2$), 5.28 (1 H, dd, *J* 1.0 and 11.2, $CH{-}CH_2$), 5.58 (1 H, dd, *J* 1.0 and 17.5, $CH{=}CH_2$), 6.74 (1 H, dd, *J* 11.2 and 17.5, $CH{=}CH_2$) and 7.05–7.20 (2 H, m, ArH); δ_C(125.4 MHz; $CDCl_3$) 27.8, 34.8, 60.5, 114.8, 123.9, 125.3, 128.6, 136.9 and 137.1; *m*/*z* (EI) 200.0328 (M^+. $C_9H_{12}OS_2$ requires *M*, 200.0329), 200 (91%), 123 (100) and 79 (66).

(**B**) CsF (0.30 g, 2 mmol) was added to a solution of salt **14** in DMSO and 5 min after DBU (0.30 g, 2 mmol) was added. The reaction mixture was treated as described above. The residue (184 mg) from the ethereal extract was chromatographed on a silica gel column (hexane–Et_2O, 70 : 30 to 50 : 50) to give 4,7,8,10-*tetrahydro*-5H-*thieno*[2,3-f][1,4]*oxathionine* **17** (92 mg, 46%), bp 115 °C (0.6 mmHg) (Found: C, 53.9; H, 6.1. $C_9H_{12}OS_2$ requires C, 54.0; H, 6.0%); ν_{max}(film)/cm^{-1} 1435, 1110 and 1045; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.13 (2 H, d, *J* 5.0, 8-H_2), 2.73 (2 H, t, *J* 4.6, 4-H_2), 3.61 (2 H, t, *J* 4.6 and 10.6, 5-H_2), 3.80 (2 H, d, *J* 5.0, 7-H_2), 4.24 (2 H, s, 10-H_2), 6.70 (1 H, d, *J* 5.3, ArH) and 7.20 (1 H, d, *J* 5.3, ArH); δ_C(67.9 MHz; $CDCl_3$) 27.0, 29.7, 31.0, 71.8, 75.0, 124.1, 128.9, 136.0 and 140.1; *m*/*z* 200 (M^+, 100%), 123 (50), 110 (72) and 89 (30).

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Paper 7/07379H
Received 13*th October* 1997
Accepted 12*th January* 1998