Synthesis of 3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionines by *S*-ylide rearrangement

Tomoko Kitano, Naohiro Shirai and Yoshiro Sato*

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

Substituted 3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionines 4 have been synthesized by the base-assisted aromatization of [2,3] sigmatropic rearrangement products 7 (substituted 1,3,4,11a-tetrahydro-6*H*-5,2-benzoxathionines) of the *S*-ylides 3, which were generated by the reaction of *trans*-3-(substituted phenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate 2 with caesium fluoride in dimethyl sulfoxide (DMSO) at room temperature.

Introduction

Sommelet–Hauser rearrangement of α-aryl-cycloammonium or -cyclosulfonium ylides is useful for three-carbon enlargement of cyclic compounds.[1,2] Fluoride ion-induced desilylation of [(trimethylsilyl)methyl]-ammonium or -sulfonium salts is suitable for these ylide reactions, since the ylides are regioselectively generated in quantitative yields. For example, we previously reported the syntheses of eight- to ten-membered cyclic amines and sulfides starting from 2-phenyl-1-[(trimethylsilyl)methyl]-cycloammonium[3] or -cyclosulfonium salts.[4] In this paper, we describe the synthesis of 3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionines.

Results and discussion

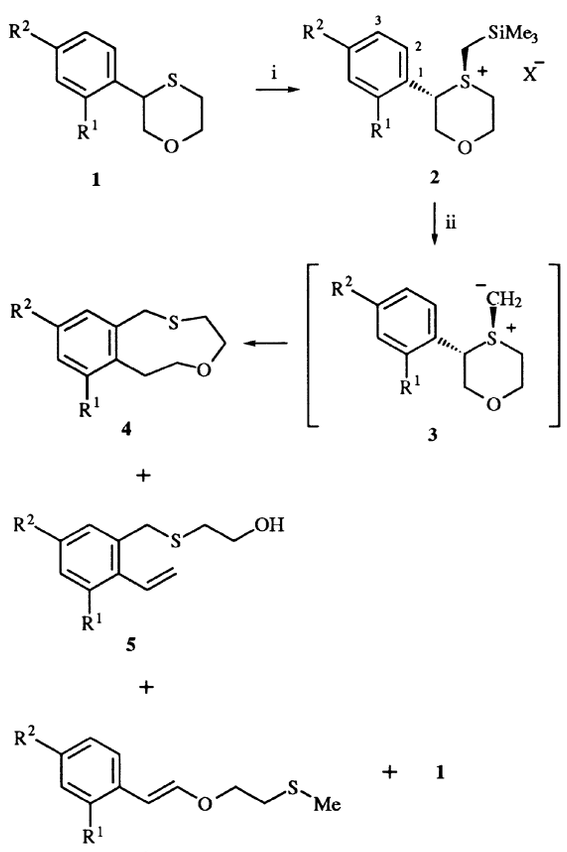
Reaction of 3-(substituted phenyl)-1,4-oxathianes **1a**–**h** with (trimethylsilyl)methyl triflate (trifluoromethanesulfonate) gave mixtures of *cis*- and *trans*-isomers of 3-(substituted phenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium triflates which were crystallized as perchlorates **2a**–**h** (Scheme 1, Table 1). The *trans*-configuration of the main products of **2b** was confirmed by observation of NOE enhancement of a proton of the CH_2Si group upon irradiation of the proton at position 3. The relation of the chemical shifts of the $SiCH_2$ groups of *trans*-**2b** and *cis*-**2b** (*cis* < *trans*) is the same as those of *cis*- and *trans*-1-phenyl-3,4-dihydro-1*H*-2-benzothiopyranium salts.[4] Therefore, the major isomers of **2** were assigned a *trans* configuration and the minor isomers were *cis*.

When **2c** was treated with caesium fluoride at room temperature in dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO), which is a standard condition for desilylations,[3] the product was a complex mixture in which the expected ring-expansion products were not detected by spectroscopic analyses (Table 2, entries 1, 3).

We previously reported that the reaction of *S*-methyl-*S*-[(trimethylsilyl)methyl](4-methoxybenzyl)sulfonium triflate with caesium fluoride also gave a complex mixture, but afforded methyl 2-methyl-4-methoxybenzyl sulfide (Sommelet–Hauser rearrangement product) in high yield in the presence of DBU.[5]

When the reactions of **2c** were repeated in the presence of DBU (5 mol equiv.), the product changed to a mixture of 3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4c**, 2-(2-vinylbenzylsulfanyl)ethanol **5c**, 2-(methylsulfanyl)ethyl 2-phenylvinyl ether **6c** and **1c** (entries 2, 4). The best result was obtained from the reaction in DMSO overnight (entry 5). The results with **2a**–**g** under these conditions are shown in Table 3.

The total yields for all of the reactions are high, however, the ratios of **4** in the products from **2** increase in decreasing



Scheme 1 *Reagents and conditions:* i, Me_3SiCH_2OTf, CH_2Cl_2, RT, 3 h; ii, CsF, DBU, DMSO, RT, 24 h

order of the electron-donating effect of the *para*- and *ortho*-substituents (R^3 and R^1), which is in direct opposition to the results with **1**. Compounds **4** are aromatization products of substituted 1,3,4,11a-tetrahydro-6*H*-5,2-benzoxathionines **7** which are [2,3] sigmatropic migration products of ylides **3** (Scheme 2), and **5** may also be formed from **7** by an intramolecular [1,5] proton transfer. Compounds **1** and **6** may be formed from **3** by the elimination of carbene or by a Hofmann degradation process.

[2,3] Sigmatropic rearrangement of benzylammonium *N*-methylides occurs more quickly to electron-deficient benzene rings than to electron-rich rings.[6] Similarly, the speed of the [2,3] sigmatropic migration of **3** to **7** also decreases with an increase in the electron-donating abilities of the substituents

Table 1 3-(Substituted phenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorates **2**

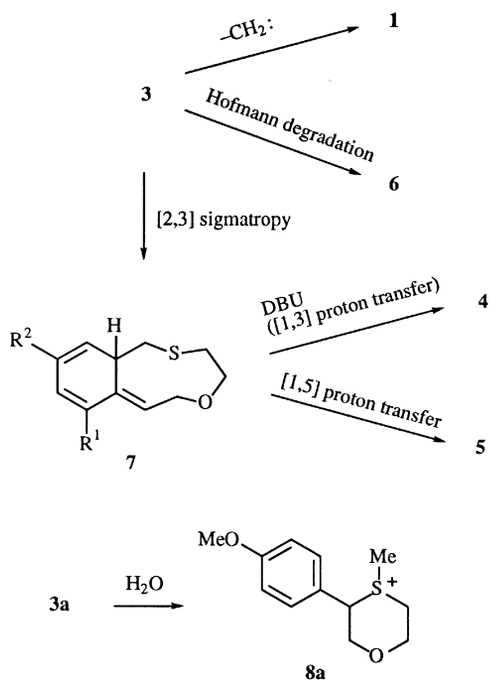
						δ_H(500 MHz; $CDCl_3$; Me_4Si) $SiCH_2$[a]			
		R^1	R^2	Yield (%)	Ratio of *cis* to *trans*	*cis*		*trans*	
1	**2a**	H	OMe	60	4:96	1.98	2.41	2.20	3.02
2	**2b**	H	Me	73	5:95	2.00	2.23	2.19	3.08
3	**2c**	H	H	83	5:95	1.98	2.48	2.23	3.05
4	**2d**	H	CF_3	30	0:100	—	—	2.59[b]	2.93[b]
5	**2e**	OMe	H	83	5:95	1.98	2.33	2.37	3.01
6	**2f**	Me	H	52	7:93	1.92	3.00	2.19	3.08
7	**2g**	CF_3	H	20	0:100	—	—	2.16	2.80

[a] Two hydrogens appeared as an AB quartet. [b] Measured in CD_3OD.

Table 2 Reaction of 3-phenyl-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate **2c** with CsF

					Product ratio[a]			
Entry	Solvent	Additive	Reaction time (h)	Total yield (%)	**4c**	**5c**	**6c**	**1c**
1	**DMF**	—	1	—	Complex mixture			
2	**DMF**	DBU	1	69	75	3	1	21
3	**DMSO**	—	1	—	Complex mixture			
4	**DMSO**	DBU	1	83	78	5	2	16
5	**DMSO**	DBU	24	96	80	6	1	13

[a] Ratios of the products determined by integration of the ^1H signals at 500 MHz.



Scheme 2

and, consequently, the ratio of degradation from **3** to **1** and **6** increases.

When the ^1H NMR spectrum of the reaction mixture of **2a** with caesium fluoride in [$^2H_6$]dimethyl sulfoxide ([$^2H_6$]-DMSO) was measured after 30 min at room temperature, **7a** and 4-methyl-3-(4-methoxyphenyl)-1,4-oxathianium salt **8a** were observed in a 15:85 ratio without **1a**. Detection of **8a** shows that the ylide **3a** still remained in the reaction mixture and was protonated when the mixture was transferred into an NMR glass tube. The amount of **7a** gradually increases in the absence of DBU, while it is decomposed to a complex mixture by water.

To clarify the relationship between the substituent effects of the R^1 or R^2 groups and the [2,3] sigmatropic pathway, we examined the relationship between electronic effect of the substituents (*e.g.* chemical shifts in ^1H and ^{13}C NMR spectra of the benzene rings, Hammett substituent constants of R^2, *etc.*) and the total yields of **4** and **5**. We found a linear relationship between the chemical shift in the ^{13}C NMR at the C-1 carbons of the phenyl groups of **2** and the total yields of **4** and **5**, except for *ortho*-methyl compound **2f** (Fig. 1). However, it is still unclear how to explain this relationship, and why there is no correlation between the chemical shift of the C-2 carbons at which C–C bond-formation occurs.

Table 3 Reaction of 3-(substituted phenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorates **2** with CsF at RT for 24 h in DMSO in the presence of DBU

			Product ratio[a]			
Entry	Salt	Total yield (%)	**4**	**5**	**6**	**1**
1	**2a**	97	46	12	5	38
2	**2b**	95	63	8	2	27
3	**2c**	96	80	6	1	13
4	**2d**	99	96	4	0	0
5	**2e**	91	30	3	6	62
6	**2f**	99	38	3	8	51
7	**2g**	90	60	10	12	18

[a] Ratios of the products determined by integration of the ^1H signals at 500 MHz.

Experimental

All reactions were carried out under N_2. DMSO was dried by distillation under reduced pressure from CaH_2. Diethyl ether (referred to as ether) was distilled from Na benzophenone ketyl. Benzene was distilled from Na. CsF was dried over P_2O_5 at 180 °C. Distillation was performed on a Büchi Kugelrohr distillation apparatus. All melting points and boiling points (oven temperature) are uncorrected. *J* Values are given in Hz.

3-(4-Methoxyphenyl)-1,4-oxathiane 1a

3-Chloro-1,4-oxathiane was prepared from 1,4-oxathiane (2.5 g, 24 mmol) with *N*-chlorosuccinimide (3.2 g, 24 mmol) in benzene (25 cm^3) as previously reported.[7] This benzene solution was added to a solution of (4-methoxyphenyl)magnesium bromide, prepared from 4-bromoanisole (4.5 g, 24 mmol) and magnesium turnings (0.6 g, 25 mmol) in Et_2O (25 cm^3). The mixture was stirred for 24 h at RT and quenched with 20% H_2SO_4 (25 cm^3). The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with 10% aqueous NaOH and water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue

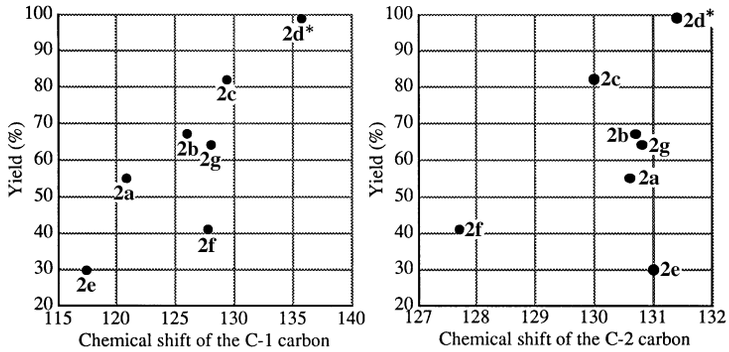


Fig. 1 Relation of the chemical shift (δ_C, $CDCl_3$) of the C-1 or C-2 carbon to the total yield (%) of **4** and **5**.* Measured in CD_3OD.

was chromatographed on a silica gel column (hexane–ether, 8:2), and the eluent was distilled to give the *oxathiane* **1a** (2.3 g, 45%), bp 140 °C/0.4 mmHg; mp 61–63 °C (Found: C, 62.5; H, 6.8. $C_{11}H_{14}O_2S$ requires C, 62.8; H, 6.7%); ν_{max}(KBr)/cm^{-1} 1610, 1100 and 675; δ_H(270 MHz; $CDCl_3$) 2.49 (1 H, ddd, *J* 1.8, 2.4, 14.0, 5-H), 3.09 (1 H, ddd, *J* 3.1, 11.6, 14.0, 5-H), 3.72 (1 H, ddd, *J* 1.8, 11.6, 12.2, 6-H), 3.73 (1 H, dd, *J* 10.4, 11.6, 2-H), 3.79 (3 H, s, OCH_3), 4.01 (1 H, dd, *J* 3.1, 10.4, 3-H), 4.14 (1 H, dd, *J* 3.1, 11.6, 2-H), 4.19 (1 H, ddd, *J* 2.4, 3.1, 12.2, 6-H), 6.87 (2 H, d, *J* 8.6, ArH) and 7.27 (2 H, d, *J* 8.6, ArH).

3-(4-Methylphenyl)-1,4-oxathiane 1b

In a reaction similar to that described above, a benzene solution of 3-chloro-1,4-oxathiane (52 mmol) was added to a solution of (4-methylphenyl)magnesium bromide, prepared from 4-bromotoluene (8.7 g, 50 mmol) and magnesium (1.2 g, 50 mmol) in Et_2O (50 cm^3). The reaction mixture was treated as above to give the *oxathiane* **1b** (4.7 g, 49%), bp 120 °C/0.5 mmHg (Found: C, 67.7; H, 7.15. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3%); ν_{max}(film)/cm^{-1} 1510, 1280 and 1105; δ_H(270 MHz; $CDCl_3$) 2.33 (3 H, s, CH_3), 2.49 (1 H, ddd, *J* 2.0, 2.3, 14.2, 5-H), 3.09 (1 H, ddd, *J* 3.3, 11.6, 14.2, 5-H), 3.73 (1 H, ddd, *J* 2.0, 11.6, 11.7, 6-H), 3.75 (1 H, dd, *J* 9.9, 11.7, 2-H), 4.03 (1 H, dd, *J* 3.0, 9.9, 3-H), 4.15 (1 H, dd, *J* 3.0, 11.7, 2-H), 4.20 (1 H, ddd, *J* 2.3, 3.3, 11.7, 6-H) and 7.11–7.26 (4 H, m, ArH).

3-[4-(Trifluoromethyl)phenyl]-1,4-oxathiane 1d

In a reaction similar to that described above, a benzene solution of 3-chloro-1,4-oxathiane (9.6 mmol) was added to a solution of 4-(trifluoromethyl)phenylmagnesium bromide, prepared from 4-bromo(trifluoromethyl)benzene (2.0 g, 8.9 mmol) and magnesium (0.2 g, 9.0 mmol) in Et_2O (20 cm^3). The reaction mixture was worked up to give the *oxathiane* **1d** (1.2 g, 54%), mp 55–57 °C (Found: C, 52.9; H, 4.55. $C_{11}H_{11}F_3OS$ requires C, 53.2; H, 4.5%); ν_{max}(Nujol)/cm^{-1} 1620, 1325 and 1110; δ_H(270 MHz; $CDCl_3$) 2.47 (1 H, ddd, *J* 2.2, 3.3, 13.9, 5-H), 3.06 (1 H, ddd, *J* 3.3, 11.0, 13.9, 5-H), 3.78 (1 H, ddd, *J* 2.2, 11.0, 11.7, 6-H), 3.80 (1 H, dd, *J* 9.5, 12.1, 2-H), 4.08 (1 H, dd, *J* 3.3, 9.5, 3-H), 4.17 (1 H, dd, *J* 3.3, 12.1, 2-H), 4.20 (1 H, ddd, *J* 3.3, 3.3, 11.7, 6-H), 7.49 (2 H, d, *J* 8.4, ArH) and 7.59 (2 H, d, *J* 8.4, ArH).

3-(2-Methoxyphenyl)-1,4-oxathiane 1e

In a reaction similar to that described above, a benzene solution of 3-chloro-1,4-oxathiane (53 mmol) and a solution of (2-methoxyphenyl)magnesium bromide, prepared from 2-bromoanisole (9.9 g, 53 mmol) and magnesium (1.3 g, 53 mmol) in Et_2O (50 cm^3) were treated as above to give the *oxathiane* **1e** (3.25 g, 29%), mp 71–73 °C (Found: C, 62.65; H, 6.6. $C_{11}H_{14}O_2S$ requires C, 62.8; H, 6.7%); ν_{max}(KBr)/cm^{-1} 1600, 1495, 1250 and 1100; δ_H(270 MHz; $CDCl_3$) 2.54 (1 H, ddd, *J* 2.3, 2.6, 13.9, 5-H), 3.08 (1 H, ddd, *J* 3.3, 10.9, 13.9, 5-H), 3.71 (1 H, dd, *J* 9.6, 11.6, 2-H), 3.70–3.90 (1 H, m, 6-H), 3.84 (3 H, s, OCH_3), 4.13 (1 H, dd, *J* 3.0, 11.6, 2-H), 4.18 (1 H, ddd, *J* 2.6, 3.3, 11.9, 6-H), 4.58 (1 H, dd, *J* 3.0, 9.6, 3-H), 6.86 (1 H, d, *J* 8.3, ArH), 6.93 (1 H, dd, *J* 7.6, 7.6, ArH), 7.23 (1 H, ddd, *J* 1.3, 7.6, 8.3, ArH) and 7.42 (1 H, dd, *J* 1.3, 7.6, ArH).

3-(2-Methylphenyl)-1,4-oxathiane 1f

In the same way, a benzene solution of 3-chloro-1,4-oxathiane (100 mmol) and a solution of (2-methylphenyl)magnesium bromide, prepared from 2-bromotoluene (17.1 g, 100 mmol) and magnesium (2.4 g, 100 mmol) in Et_2O (100 cm^3) were treated as above to give the *oxathiane* **1f** (10.5 g, 54%), bp 140 °C/1.0 mmHg (Found: C, 67.7; H, 7.45. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3%); ν_{max}(film)/cm^{-1} 1490, 1250 and 1105; δ_H(270 MHz; $CDCl_3$) 2.42 (3 H, s, CH_3), 2.53 (1 H, ddd, *J* 2.2, 2.9, 13.6, 5-H), 3.12 (1 H, ddd, *J* 3.3, 11.4, 13.6, 5-H), 3.78 (1 H, ddd, *J* 2.2, 11.4, 11.7, 6-H), 3.82 (1 H, dd, *J* 9.9, 11.7, 2-H), 4.14 (1 H, ddd, *J* 0.7, 2.9, 11.7, 2-H), 4.22 (1 H, ddd, *J* 2.9, 3.3, 11.7, 6-H), 4.26 (1 H, dd, *J* 2.9, 9.9, 3-H), 7.16–7.20 (3 H, m, ArH) and 7.38–7.41 (1 H, m, ArH).

3-[2-(Trifluoromethyl)phenyl]-1,4-oxathiane 1g

In a reaction similar to that described above, a benzene solution of 3-chloro-1,4-oxathiane (53 mmol) and a solution of [2-(trifluoromethyl)phenyl]magnesium bromide, prepared from 2-bromo(trifluoromethyl)benzene (11.9 g, 53 mmol) and magnesium (1.3 g, 53 mmol) in Et_2O (80 cm^3), were treated as above to give the *oxathiane* **1g** (3.5 g, 27%); bp 105 °C/0.9 mmHg (Found: C, 53.1; H, 4.6. $C_{11}H_{11}F_3OS$ requires C, 53.2; H, 4.5%); ν_{max}(film)/cm^{-1} 1605, 1315 and 1110; δ_H(270 MHz; $CDCl_3$) 2.54 (1 H, ddd, *J* 2.0, 2.0, 13.9, 5-H), 3.17 (1 H, ddd, *J* 3.3, 11.6, 13.9, 5-H), 3.71 (1 H, dd, *J* 9.9, 11.6, 2-H), 3.77 (1 H, ddd, *J* 2.0, 11.6, 11.6, 6-H), 4.13 (1 H, dd, *J* 3.0, 11.6, 2-H), 4.24 (1 H, ddd, *J* 2.0, 3.0, 11.6, 6-H), 4.46 (1 H, dd, *J* 3.0, 9.9, 3-H), 7.37 (1 H, dd, *J* 7.6, 7.9, ArH), 7.54 (1 H, dd, *J* 7.3, 7.9, ArH), 7.65 (1 H, d, *J* 7.3, ArH) and 7.75 (1 H, d, *J* 7.6, ArH).

3-(4-Methoxyphenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate 2a

(Trimethylsilyl)methyl triflate (5.2 g, 22 mmol) was added to a solution of **1a** (4.21 g, 20 mmol) in CH_2Cl_2 (50 cm^3) at 3 °C and the mixture was stirred at RT for 3 h. It was then evaporated under reduced pressure and the residue (viscous oil) was washed with Et_2O, dissolved in $CHCl_3$ (20 cm^3) and stirred with aqueous 5 M $NaClO_4$ (8 cm^3) for 18 h. The mixture was extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$) and concentrated to give the *title salt* **2a** (4.76 g, 60%), mp 137–140 °C (from EtOH) (Found: C, 45.3; H, 6.3. $C_{15}H_{25}ClO_6SSi$ requires C, 45.4; H, 6.35%); ν_{max}(KBr)/cm^{-1} 1610, 1510, 1085 and 855; δ_H(500 MHz; $CDCl_3$) *trans*-**2a**: 0.15 (9 H, s, $SiMe_3$), 2.20 (1 H, d, *J* 14.0, CH_2), 3.02 (1 H, d, *J* 14.0, CH_2), 3.67–3.73 (2 H, m, 5-H), 3.79 (3 H, s, OCH_3), 4.06 (1 H, dd, *J* 10.6, 13.4, 2-H), 4.18 (1 H, ddd, *J* 5.5, 7.9, 14.0, 6-H), 4.24 (1 H, dd, *J* 3.1, 13.4, 2-H), 4.45 (1 H, ddd, *J* 3.1, 3.1, 14.0, 6-H),

4.75 (1 H, dd, *J* 3.1, 10.4, 3-H), 6.94 (2 H, d, *J* 8.5, ArH) and 7.42 (2 H, d, *J* 8.5, ArH); *cis*-**2a**: 0.14 (9 H, s), 1.98 (1 H, d, *J* 14.0), 2.41 (1 H, d, *J* 14.0), 4.25–4.29 (1 H, m), 4.32–4.39 (1 H, m), 4.57–4.62 (1 H, m), 5.07–5.10 (1 H, m) and 7.50 (2 H, d, *J* 8.9) (other signals overlapped *trans*-**2a**); δ_C(125.7 MHz; $CDCl_3$); *trans*-**2a**: −1.4 (3 C), 25.0, 40.0, 55.4, 58.9, 64.5, 70.6, 115.4 (2 C), 120.8, 130.6 (2 C) and 161.3.

3-(4-Methylphenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate 2b

In a reaction similar to that described above, (trimethylsilyl)-methyl triflate (4.2 g, 18 mmol) was added to a solution of **1b** (2.3 g, 12 mmol) in CH_2Cl_2 (10 cm^3) and the mixture was worked up to give the *title salt* **2b** (3.3 g, 73%), mp 140–147 °C (not recrystallized) (Found: C, 47.2; H, 6.6. $C_{15}H_{25}ClO_5SSi$ requires C, 47.3; H, 6.6%); ν_{max}(Nujol)/cm^{-1} 1515 and 855; δ_H(400 MHz, $CDCl_3$) *trans*-**2b**: 0.16 (9 H, s, $SiMe_3$), 2.19 (1 H, d, *J* 13.9, CH_2), 2.36 (3 H, s, CH_3), 3.08 (1 H, d, *J* 13.9, CH_2), 3.71 (1 H, ddd, *J* 1.8, 2.6, 12.1, 5-H), 3.78 (1 H, ddd, *J* 3.3, 11.7, 12.1, 5-H), 4.04 (1 H, dd, *J* 10.6, 13.6, 2-H), 4.16 (1 H, ddd, *J* 1.8, 11.7, 14.7, 6-H), 4.27 (1 H, dd, *J* 3.3, 13.6, 2-H), 4.49 (1 H, ddd, *J* 2.6, 3.3, 14.7, 6-H), 4.80 (1 H, dd, *J* 3.3, 10.6, 3-H), 7.26 (2 H, d, *J* 8.1, ArH) and 7.38 (2 H, d, *J* 8.1, ArH); *cis*-**2b**: 0.15 (9 H, s), 2.00 (1 H, d, *J* 13.9), 2.23 (1 H, d, *J* 13.9), 4.33–4.42 (1 H, m), 4.57–4.65 (1 H, m), 5.19–5.21 (1 H, m) and 7.45 (2 H, d, *J* 8.1) (other signals overlapped *trans*-**2b**). NOE enhancement was observed 3% at δ 3.05 (CH_2) and 6% at δ 4.26 (2-H) under irradiation at δ 4.95 (3-H); δ_C(125.7 MHz; $CDCl_3$) *trans*-**2b**: −1.3 (3 C), 21.3, 24.9, 39.8, 59.0, 64.6, 70.6, 126.0, 129.0 (2 C), 130.7 (2 C) and 141.1.

3-Phenyl-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate 2c

In a reaction similar to that described above, (trimethylsilyl)-methyl triflate (12.6 g, 53 mmol) was added to a solution of phenyl-1,4-oxathiane[7] **1c** (8.0 g, 44 mmol) in CH_2Cl_2 (50 cm^3) and the mixture was worked up to give the *title salt* **2c** (13.5 g, 83%), mp 113 °C (not recrystallized) (Found: C, 45.6; H, 6.2. $C_{14}H_{23}ClO_5SSi$ requires C, 45.8; H, 6.3%); ν_{max}(KBr)/cm^{-1} 1585, 1075 and 845; δ_H(500 MHz; $CDCl_3$) *trans*-**2c**: 0.14 (9 H, s, $SiMe_3$), 2.23 (1 H, d, *J* 13.9, CH_2), 3.05 (1 H, d, *J* 13.9, CH_2), 3.70–3.78 (2 H, m, 5-H), 4.07 (1 H, dd, *J* 10.6, 13.4, 2-H), 4.15–4.23 (1 H, m, 6-H), 4.27 (1 H, dd, *J* 3.3, 13.4, 2-H), 4.43–4.50 (1 H, m, 6-H), 4.83 (1 H, dd, *J* 3.3, 10.6, 3-H), 7.42–7.47 (3 H, m, ArH) and 7.48–7.53 (2 H, m, ArH); *cis*-**2c**: 0.11 (9 H, s), 1.98 (1 H, d, *J* 14.3), 2.48 (1 H, d, *J* 14.3), 3.87–3.96 (2 H, m), 4.28–4.42 (2 H, m), 4.62–4.67 (1 H, m), 5.13–5.17 (1 H, m) and 7.54–7.58 (m, 2 H) (other signals overlapped *trans*-**2c**); δ_C(125.7 MHz; $CDCl_3$) *trans*-**2c**: −1.4 (3 C), 25.2. 40.0, 59.0, 64.5, 70.5, 129.1 (2 C), 129.4, 130.0 (2 C) and 130.7.

trans-3-[4-(Trifluoromethyl)phenyl]-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate *trans*-2d

In a reaction similar to that described above, (trimethylsilyl)-methyl triflate (9.5 g, 40 mmol) was added to a solution of **1d** (8.0 g, 32 mmol) in CH_2Cl_2 (50 cm^3) and the mixture was worked up to give the *title salt trans*-**2d** (4.15 g, 30%), mp 193 °C (not recrystallized) (Found: C, 41.1; H, 5.1. $C_{15}H_{22}ClF_3O_5SSi$ requires C, 41.4; H, 5.1%); ν_{max}(KBr)/cm^{-1} 1620, 1325 and 855; δ_H(500 MHz; CD_3OD) 0.21 (9 H, s, $SiMe_3$), 2.59 (1 H, d, *J* 14.0, CH_2), 2.93 (1 H, d, *J* 14.0, CH_2), 3.62 (1 H, ddd, *J* 3.7, 11.0, 12.8, 5-H), 3.88 (1 H, ddd, *J* 2.4, 3.0, 12.8, 5-H), 4.18 (1 H, ddd, *J* 2.4, 11.0, 14.0, 6-H), 4.27 (1 H, dd, *J* 10.4, 14.0, 2-H), 4.41 (1 H, dd, *J* 3.1, 14.0, 2-H), 4.53 (1 H, ddd, *J* 3.0, 3.7, 14.0, 6-H) and 4.81–4.83 (1 H, 3-H; the *J* value was not determined due to overlapping with a signal of CD_3OH) and 7.82–7.89 (4 H, m, ArH); δ_C(125.7 MHz; CD_3OD) −1.4 (3 C), 26.4, 41.0, 59.9, 65.3, 70.9, 125.1 (q, *J* 271), 127.8 (2 C, q, *J* 3), 131.4 (2 C), 133.5 (q, *J* 32) and 135.7.

3-(2-Methoxyphenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate 2e

In a reaction similar to that described above, (trimethylsilyl)-methyl triflate (3.7 g, 16 mmol) was added to a solution of **1e** (3.0 g, 14 mmol) in CH_2Cl_2 (15 cm^3) and the mixture was worked up to give the *title salt* **2e** (4.7 g, 83%), mp 127 °C (not recrystallized) (Found: C, 45.2; H, 6.1. $C_{15}H_{25}ClO_6SSi$ requires C, 45.4; H, 6.35%); ν_{max}(Nujol)/cm^{-1} 1600, 1080 and 850; δ_H(500 MHz, $CDCl_3$) *trans*-**2e**: 0.17 (9 H, s, $SiMe_3$), 2.37 (1 H, d, *J* 14.1, CH_2), 3.01 (1 H, d, *J* 14.1, CH_2), 3.65 (1 H, ddd, *J* 3.6, 9.5, 12.6, 5-H), 3.73 (1 H, ddd, *J* 2.2, 4.0, 12.6, 5-H), 3.92 (3 H, s, OCH_3), 4.12 (1 H, ddd, *J* 2.2, 9.5, 13.9, 6-H), 4.29 (2 H, d, *J* 6.2, 2-H), 4.47 (1 H, ddd, *J* 3.6, 4.0, 13.9, 6-H), 4.86 (1 H, t, *J* 6.2, 3-H), 6.99 (1 H, d, *J* 8.1, ArH), 7.05 (1 H, dd, *J* 7.3, 7.7, ArH), 7.45 (1 H, ddd, *J* 1.5, 7.3, 8.1, ArH) and 7.56 (1 H, dd, *J* 1.5, 7.7, ArH); *cis*-**2e**: 0.07 (9 H, s), 1.98 (1 H, d, *J* 14.1), 2.33 (1 H, d, *J* 14.1), 4.35–4.42 (1 H, m), 4.65–4.71 (1 H, m) and 5.16–5.20 (1 H, m) (other signals overlapped *trans*-**2e**); δ_C(125.7 MHz; $CDCl_3$) *trans*-**2e**: −1.4 (3 C), 25.2, 39.2, 53.9, 55.7, 63.7, 68.4, 111.6, 117.4, 121.8, 131.0, 132.4 and 157.6.

3-(2-Methylphenyl)-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate 2f

In a reaction similar to that described above, (trimethylsilyl)-methyl triflate (2.0 g, 8 mmol) was added to a solution of **1f** (1.33 g, 7 mmol) in CH_2Cl_2 (10 cm^3) and the mixture was worked up to give the *title salt* **2f** (1.4 g, 52%), mp 149–153 °C (from EtOH–Et_2O) (Found: C, 47.1; H, 6.6. $C_{15}H_{25}ClO_5SSi$ requires C, 47.3; H, 6.6%); ν_{max}(Nujol)/cm^{-1} 1460, 1090 and 855; δ_H(400 MHz; $CDCl_3$) *trans*-**2f**: 0.15 (9 H, s, $SiMe_3$), 2.19 (1 H, d, *J* 13.8, CH_2), 2.53 (3 H, s, CH_3), 3.08 (1 H, d, *J* 13.8, CH_2), 3.73–3.79 (1 H, m, 5-H), 3.86–3.98 (2 H, m, 2-H, 5-H), 4.15–4.22 (2 H, m, 2-H, 6-H), 4.47 (1 H, ddd, *J* 3.0, 3.0, 14.0, 6-H), 4.99 (1 H, dd, *J* 3.1, 10.4, 3-H), 7.25–7.38 (3 H, m, ArH) and 7.43–7.47 (1 H, m, ArH); *cis*-**2f**: 0.07 (9 H, s), 1.92 (1 H, d, *J* 14.7), 2.53 (3 H, s), 3.00 (1 H, d, *J* 14.7), 4.05–4.15 (1 H, m), 4.23–4.38 (2 H, m), 4.69–4.75 (1 H, m) and 5.11–5.16 (1 H, m) (other signals overlapped *trans*-**2f**); δ_C(125.7 MHz; $CDCl_3$) *trans*-**2f**: −1.5 (3 C), 19.6, 25.4, 40.0, 55.9, 64.5, 70.6, 127.5, 127.7, 127.8, 130.2, 132.0 and 138.3.

trans-3-[2-(Trifluoromethyl)phenyl]-4-(trimethylsilyl)methyl-1,4-oxathianium perchlorate *trans*-2g

In a reaction similar to that described above, (trimethylsilyl)-methyl triflate (3.2 g, 14 mmol) was added to a solution of **1g** (3.0 g, 12 mmol) in CH_2Cl_2 (15 cm^3) and the mixture was worked up to give the *title salt trans*-**2g** (1.1 g, 20%), mp 148 °C (not recrystallized) (Found: C, 41.2; H, 4.9. $C_{15}H_{22}ClF_3O_5SSi$ requires C, 41.4; H, 5.1%); ν_{max}(Nujol)/cm^{-1} 1315 and 850; δ_H(500; $CDCl_3$) 0.13 (9 H, s, $SiMe_3$), 2.16 (1 H, d, *J* 14.0, CH_2), 2.80 (1 H, d, *J* 14.0, CH_2), 3.65 (1 H, ddd, *J* 3.1, 10.4, 12.2, 5-H), 4.98–4.03 (1 H, m, 5-H), 4.08 (1 H, dd, *J* 10.4, 14.0, 2-H), 4.24 (1 H, dd, *J* 3.7, 14.0, 2-H), 4.37 (1 H, ddd, *J* 1.8, 10.4, 13.4, 6-H), 4.49 (1 H, ddd, *J* 3.1, 3.1, 13.4, 6-H), 4.69 (1 H, dd, *J* 3.7, 10.4, 3-H), 7.62 (1 H, dd, *J* 7.3, 7.9, ArH), 7.78–7.86 (2 H, m, ArH) and 8.00 (1 H, d, *J* 7.9, ArH); δ_C(125.7 MHz, $CDCl_3$) −1.5 (3 C), 27.3, 41.7, 56.5, 64.4, 71.0, 123.6 (q, *J* 273), 127.3 (q, *J* 5), 128.0, 129.8 (q, *J* 30), 130.8 (2 C) and 134.1.

Reaction of 2a with CsF in the presence of DBU

Salt **2a** (397 mg, 1 mmol) was placed in a 20-cm^3 flask equipped with a magnetic stirrer, a septum and a test tube connected to the flask by a short piece of rubber tubing. CsF (0.76 g, 5 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with N_2. DMSO (4 cm^3) and DBU (0.76 g, 5 mmol) were added to the flask with syringes and then CsF was added from the test tube. The mixture was stirred for 24 h at RT, 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 (213 mg)

was chromatographed on a silica gel column (Et_2O–hexane, 10:90 to 50:50) to give 2-(5-methoxy-2-vinylbenzylsulfanyl)-ethanol **5a**, 2-(4-methoxyphenyl)vinyl 2-(methylsulfanyl)ethyl ether **6a** and a mixture of 10-methoxy-3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4a** and **1a**. Compounds **4a** and **1a** were separated by an HPLC column (μBondasphere 5 μ Si–100 Å, Et_2O–hexane, 5:95 to 50:50). The product ratio was determined from the integrated values of the proton signals in the ^{1}H NMR spectrum of the residue. The results are listed in Table 2.

Compound **4a**: bp 90 °C/0.8 mmHg (Found: C, 64.2; H, 7.2. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.2%); ν_{max}(film)/cm^{-1} 1610, 1500, 1260 and 1110; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.04 (2 H, t, *J* 5.0, 3-H), 2.76 (2 H, br, 7-H), 3.76 (2 H, t, *J* 5.0, 6-H), 3.80 (2 H, br, 4-H), 3.81 (3 H, s, OCH_3), 4.00 (2 H, s, 1-H), 6.75 (1 H, dd, *J* 3.0, 8.9, ArH), 6.97 (1 H, d, *J* 3.0, ArH) and 6.98 (1 H, d, *J* 8.9, ArH).

Compound **5a**: an oil (Found: C, 63.9; H, 6.95. $C_{12}H_{16}O_2S$ requires C, 64.2; H, 7.2%); ν_{max}(film)/cm^{-1} 3425, 1605, 1495 and 1255; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.13 (1 H, br, OH), 2.69 (2 H, t, *J* 5.9, SCH_2), 3.70 (2 H, t, *J* 5.9, OCH_2), 3.77 (2 H, s, $ArCH_2$), 3.80 (3 H, s, OCH_3), 5.25 (1 H, dd, *J* 1.3, 10.9, CH=CH_2), 5.58 (1 H, dd, *J* 1.3, 17.5, CH=CH_2), 6.76–6.83 (2 H, m, ArH), 6.99 (1 H, dd, *J* 10.9, 17.5, C*H*=CH_2) and 7.46 (1 H, d, *J* 7.9, ArH).

Compound **6a**: an oil (Found: C, 64.0; H, 7.05. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.2%); ν_{max}(film)/cm^{-1} 1650, 1510, 1245 and 1155; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.19 (3 H, s, SCH_3), 2.80 (2 H, t, *J* 6.6, SCH_2), 3.79 (3 H, s, OCH_3), 3.99 (2 H, t, *J* 6.6, OCH_2), 5.84 (1 H, d, *J* 12.9, ArCH=C*H*), 6.82 (2 H, d, *J* 8.7, ArH), 6.86 (1 H, d, *J* 12.9, ArC*H*=CH) and 7.15 (2 H, d, *J* 8.7, ArH).

Reaction of 2a with CsF in [$^2H_6$]-DMSO

In a manner similar to that described above, **2a** (119 mg, 0.3 mmol) was treated with CsF (0.22 g, 1.5 mmol) in [$^2H_6$]-DMSO (1.2 cm^3) for 0.5 h. An aliquot of the mixture was placed in a glass tube and the ^{1}H NMR spectra were measured. The presence of 10-methoxy-1,3,4,11a-tetrahydro-6*H*-5,2-benzoxathionine **7a** and 3-(4-methoxyphenyl)-4-methyl-1,4-oxathianium salt **8a** in a 15:85 ratio was estimated by the integrated values.

Compound **7a**: δ_H(270 MHz; [$^2H_6$]-DMSO) 1.75–1.90 (1 H, m), 2.00–2.10 (1 H, m), 2.57–2.77 (2 H, m), 2.94 (1 H, dd, *J* 4.0, 14.2), 3.46 (3 H, s, OCH_3), 5.08 (1 H, dd, *J* 2.3, 5.9, 11-H), 5.75–5.88 (2 H, m, 7-H, 9-H) and 6.60 (1 H, d, *J* 9.9, 8-H); other signals overlapped with the signals of **8a** and are difficult to specify.

Compound **8a**: δ_H(270 MHz; [$^2H_6$]-DMSO) 2.90 (3 H, s, SCH_3), 3.43 (1 H, m 5-H), 3.73–3.83 (1 H, m), 3.75 (3 H, s, OCH_3), 4.00 (1 H, t, *J* 12.2), 4.23–4.30 (2 H, m), 4.37 (1 H, d, *J* 13.9), 4.76 (1 H, t, *J* 6.7), 7.05 (2 H, d, *J* 8.4, ArH) and 7.45 (2 H, d, *J* 8.4, ArH).

Reaction of 2b with CsF in the presence of DBU

In a manner similar to that described for compound **2a**, a mixture of **2b** (381 mg, 1 mmol), CsF (0.76 g, 5 mmol) and DBU (0.76 g, 5 mmol) in DMSO (4 cm^3) was treated as above. The residue (195 mg) of the ethereal extract was chromatographed on a silica gel column (ether–hexane, 10:90 to 50:50) to give 2-(5-methyl-2-vinylbenzylsulfanyl)ethanol **5b**, 2-(4-methylphenyl)-vinyl 2-(methylsulfanyl)ethyl ether **6b** and a mixture of 10-methyl-3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4b** and **1b**. Compound **4b** was isolated by distillation of the mixture. The presence of **1b** was confirmed by ^{1}H NMR and GLC analyses.

Compound **4b**: bp 110 °C/1.0 mmHg (Found: C, 69.0; H, 7.7. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(film)/cm^{-1} 1500, 1110 and 1045; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.04 (2 H, t, *J* 5.3, 3-H), 2.33 (3 H, s, CH_3), 2.78 (2 H, t, *J* 4.6, 7-H), 3.71 (2 H, br s, 6-H), 3.77 (2 H, t, *J* 5.3, 4-H), 4.01 (2 H, s, 1-H), 6.94–6.98 (2 H, m, ArH) and 7.25 (1 H, s, ArH).

Compound **5b**: an oil (Found: C, 68.8; H, 7.8. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(film)/cm^{-1} 3395, 1610 and 1045; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.87 (1 H, br s, OH), 2.33 (3 H, s, CH_3), 2.70 (2 H, t, *J* 5.9, SCH_2), 3.71 (2 H, t, *J* 5.9, OCH_2), 3.77 (2 H, s, $ArCH_2$), 5.31 (1 H, dd, *J* 1.3, 11.2, CH=CH_2), 5.66 (1 H, dd, *J* 1.3, 17.5, CH=CH_2), 6.99–7.10 (3 H, m, C*H*=CH_2, ArH) and 7.42 (1 H, d, *J* 7.6, ArH).

Compound **6b**: an oil (Found: C, 68.9; H, 7.7. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(film)/cm^{-1} 1640 and 1154; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.19 (3 H, s, SCH_3), 2.31 (3 H, s, $ArCH_3$), 2.81 (2 H, t, *J* 6.6, SCH_2), 4.01 (2 H, t, *J* 6.6, OCH_2), 5.85 (1 H, d, *J* 13.0, ArCH=C*H*), 6.95 (1 H, d, *J* 13.0, Ar-C*H*=CH) and 7.05–7.14 (4 H, m, ArH).

Reaction of 2c with CsF in the presence of DBU

In a manner similar to that described for **2b**, **2c** (381 mg, 1 mmol), CsF (0.76 g, 5 mmol) and DBU (0.76 g, 5 mmol) were allowed to react in DMSO (4 cm^3). The residue (130 mg) of the ethereal extract was chromatographed to give 2-(2-vinylbenzylsulfanyl)ethanol **5c**, 2-(methylsulfanyl)ethyl 2-phenylvinyl ether **6c** and a mixture of 3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4c** and **1c**. Compound **4c** was isolated by distillation of the mixture.

Compound **4c**: bp 100 °C/0.5 mmHg (Found: C, 67.8; H, 7.35. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3%); ν_{max}(film)/cm^{-1} 1490 and 1110; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.15 (2 H, t, *J* 4.9, 3-H), 2.95 (2 H, br s, 7-H), 3.85 (2 H, br s, 6-H), 3.90 (2 H, t, *J* 4.9, 4-H), 4.18 (2 H, s, 1-H), 7.18–7.20 (1 H, m, ArH), 7.28–7.32 (1 H, m, ArH), 7.37–7.41 (1 H, m, ArH) and 7.56–7.58 (1 H, m, ArH).

Compound **5c**: bp 120 °C/1.0 mmHg (Found: C, 67.7; H, 7.4. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.3%); ν_{max}(film)/cm^{-1} 3395, 1050 and 770; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.10 (1 H, s, OH), 2.68 (2 H, t, *J* 6.1, SCH_2), 3.69 (2 H, t, *J* 6.1, OCH_2), 3.80 (2 H, s, $ArCH_2$), 5.36 (1 H, dd, *J* 1.2, 11.0, CH=CH_2), 5.70 (1 H, dd, *J* 1.2, 17.4, CH=CH_2), 7.09 (1 H, dd, *J* 11.0, 17.4, C*H*=CH_2), 7.20–7.30 (3 H, m, ArH) and 7.52 (1 H, d, *J* 7.3, ArH).

Compound **6c**: an oil (Found: C, 67.8; H, 7.2. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.2%); ν_{max}(film)/cm^{-1} 1640, 1230, 1150, 750 and 695; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.20 (3 H, s, SCH_3), 2.81 (2 H, t, *J* 6.6, SCH_2), 4.02 (2 H, t, *J* 6.6, OCH_2), 5.87 (1 H, d, *J* 12.9, ArCH=C*H*), 6.99 (1 H, d, *J* 12.9, ArC*H*=CH) and 7.13–7.42 (5 H, m, ArH).

Reaction of 2c with CsF

In a reaction similar to that described above, **2c** and CsF were allowed to react in DMF or DMSO in the presence or absence of DBU. The results are listed in Table 2.

Reaction of 2d with CsF in the presence of DBU

In a reaction similar to that described for **2b**, **2d** (435 mg, 1 mmol), CsF (0.76 g, 5 mmol) and DBU (0.76 g, 5 mmol) were allowed to react in DMSO (4 cm^3). The residue (258 mg) of the ethereal extract was chromatographed to give 10-(trifluoromethyl)-3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4d** and 2-[5-(trifluoromethyl)-2-vinylbenzylsulfanyl]ethanol **5d**.

Compound **4d**: bp 90 °C/0.2 mmHg (Found: C, 54.9; H, 5.1. $C_{12}H_{13}F_3OS$ requires C, 54.95; H, 5.0%); ν_{max}(film)/cm^{-1} 1620, 1335 and 1110; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.04 (2 H, t, *J* 5.5, 3-H), 2.88 (2 H, br s, 7-H), 3.74 (2 H, br s, 6-H), 3.79 (2 H, t, *J* 5.5, 4-H), 4.09 (2 H, s, 1-H), 7.19 (1 H, d, *J* 7.9, ArH), 7.42 (1 H, dd, *J* 1.5, 7.9, ArH) and 7.73 (1 H, d, *J* 1.5, ArH).

Compound **5d**: an oil (Found: C, 54.8; H, 5.0. $C_{12}H_{13}F_3OS$ requires C, 54.95; H, 5.0%); ν_{max}(film)/cm^{-1} 3410, 1330 and 1120; δ_H(270 MHz; $CDCl_3$; Me_4Si), 2.00 (1 H, br, OH), 2.68 (2 H, t, *J* 5.9, SCH_2), 3.73 (2 H, t, *J* 5.9, OCH_2), 3.83 (2 H, s, $ArCH_2$), 5.48 (1 H, d, *J* 10.9, CH=CH_2), 5.70 (1 H, d, *J* 17.2, CH=CH_2), 7.06 (1 H, dd, *J* 10.9, 17.2, C*H*=CH_2), 7.45–7.49 (2 H, m, ArH) and 7.59 (1 H, d, *J* 8.6, ArH).

Reaction of 2e with CsF in the presence of DBU

In a reaction similar to that described for **2b**, **2e** (397 mg, 1 mmol), CsF (0.76 g, 5 mmol) and DBU (0.76 g, 5 mmol) were allowed to react in DMSO (4 cm^3). The residue (196 mg) of the ethereal extract was chromatographed to give 2-(3-methoxy-2-vinylbenzylsulfanyl)ethanol **5e**, 2-(2-methoxyphenyl)vinyl 2-(methylsulfanyl)ethyl ether **6e** and a mixture of 8-methoxy-3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4e** and **1e**. Compound **4e** was isolated by distillation of the mixture.

Compound **4e**: bp 110 °C/1.5 mmHg (Found: C, 63.85; H, 6.8. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.2%); ν_{max}(film)/cm^{-1} 1580, 1465, 1250 and 1110; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.05 (2 H, t, *J* 4.6, 3-H), 2.91 (2 H, br, 7-H), 3.65–3.88 (4 H, m, 4-H, 6-H), 3.81 (3 H, s, OCH_3), 4.04 (2 H, s, 1-H), 6.75 (1 H, dd, *J* 1.0, 8.4, ArH), 7.02 (1 H, dd, *J* 1.0, 7.6, ArH) and 7.22 (1 H, dd, *J* 7.6, 8.4, ArH).

Compound **5e**: an oil (Found: C, 63.9; H, 7.0. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.2%); ν_{max}(film)/cm^{-1} 3395, 1575 and 1260; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.07 (1 H, br s, OH), 2.70 (2 H, t, *J* 5.9, SCH_2), 3.71 (2 H, t, *J* 5.9, OCH_2), 3.82 (2 H, s, $ArCH_2$), 3.83 (3 H, s, OCH_3), 5.58 (1 H, dd, *J* 2.3, 13.9, CH=CH_2), 5.71 (1 H, dd, *J* 2.3, 17.8, CH=CH_2), 6.75–7.00 (2 H, m, C*H*=CH_2, ArH), 6.94 (1 H, d, *J* 7.6, ArH) and 7.18 (1 H, t, *J* 7.6, ArH).

Compound **6e**: an oil (Found: C, 64.0; H, 7.1. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.2%); ν_{max}(film)/cm^{-1} 1720 and 1245; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.20 (3 H, s, SCH_3), 2.82 (2 H, t, *J* 6.6, SCH_2), 3.85 (3 H, s, OCH_3), 4.04 (2 H, t, *J* 6.6, OCH_2), 6.07 (1 H, d, *J* 12.9, ArCH=C*H*), 6.85 (1 H, d, *J* 8.2, ArH), 6.91 (1 H, t, *J* 7.6, ArH), 7.09 (1 H, d, *J* 12.9, ArC*H*=CH), 7.14 (1 H, ddd, *J* 1.7, 7.6, 8.2, ArH) and 7.23 (1 H, dd, *J* 1.7, 7.6, ArH).

Reaction of 2f with CsF in the presence of DBU

In a manner similar to that described for **2b**, **2f** (381 mg, 1 mmol), CsF (0.76 g, 5 mmol) and DBU (0.76 g, 5 mmol) were allowed to react in DMSO (4 cm^3). The residue (200 mg) of the ethereal extract was chromatographed on a silica gel column (ether–hexane, 5:95 to 50:50) to give 8-methyl-3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4f**, 2-(3-methyl-2-vinylbenzylsulfanyl)ethanol **5f**, 2-(2-methylphenyl)vinyl 2-(methylsulfanyl)ethyl ether **6f** and **1f**.

Compound **4f**: bp 110 °C/0.4 mmHg (Found: C, 68.9; H, 7.7. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(film)/cm^{-1} 1460 and 1110; δ_H(270 MHz; $CDCl_3$; Me_4Si), 1.99 (2 H, t, *J* 5.0, 3-H), 2.28 (3 H, s, CH_3), 2.85 (2 H, t, *J* 5.0, 7-H), 3.72 (4 H, t, *J* 5.0, 4-H, 6-H), 4.05 (2 H, s, 1-H), 7.05 (1 H, d, *J* 7.4, ArH), 7.14 (1 H, t, *J* 7.4, ArH) and 7.28 (1 H, d, *J* 7.4, ArH).

Compound **5f**: an oil (Found: C, 69.0; H, 7.8. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(film)/cm^{-1} 3395, 1575, 1465, 1260 and 1070; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.10 (1 H, br, OH), 2.30 (3 H, s, CH_3), 2.69 (2 H, t, *J* 5.9, SCH_2), 3.70 (2 H, t, *J* 5.9, OCH_2), 3.78 (2 H, s, $ArCH_2$), 5.36 (1 H, dd, *J* 1.8, 18.0, CH=CH_2), 5.59 (1 H, dd, *J* 1.8, 11.4, CH=CH_2), 6.80 (1 H, dd, *J* 11.4, 18.0, C*H*=CH_2) and 7.08–7.29 (3 H, m, ArH).

Compound **6f**: an oil (Found: C, 69.0; H, 7.8. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(film)/cm^{-1} 1720, 1600, 1245, 1025 and 755; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.21 (3 H, s, SCH_3), 2.30 (3 H, s, $ArCH_3$), 2.83 (2 H, t, *J* 6.6, SCH_2), 4.04 (2 H, t, *J* 6.6, OCH_2), 6.00 (1 H, d, *J* 12.7, ArCH=C*H*), 6.82 (1 H, d, *J* 12.7, ArC*H*=CH) and 7.08–7.28 (4 H, m, ArH).

Reaction of 2g with CsF in the presence of DBU

In a reaction similar to that described above, **2g** (435 mg, 1 mmol), CsF (0.76 g, 5 mmol) and DBU (0.76 g, 5 mmol) were allowed to react in DMSO (4 cm^3). The residue (236 mg) of the ethereal extract was chromatographed on a silica gel column to give 8-(trifluoromethyl)-3,4,6,7-tetrahydro-1*H*-5,2-benzoxathionine **4g** and 2-[3-(trifluoromethyl)-2-vinylbenzylsulfanyl]-ethanol **5g**. Isolation of pure samples of **1g** and 2-[2-(trifluoromethyl)phenyl]vinyl 2-(methylsulfanyl)ethyl ether **6g** failed because of insufficient separation from **4g**.

Compound **4g**: mp 106–107 °C (Found: C, 54.8; H, 5.1. $C_{12}H_{13}F_3OS$ requires C, 54.95; H, 5.0%); ν_{max}(film)/cm^{-1} 1590, 1465, 1320 and 1115; δ_H(500 MHz; [$^2H_6$]-DMSO; Me_4Si; 120 °C) 2.14 (2 H, t, *J* 4.9, 3-H), 3.00–3.06 (2 H, m, 7-H), 3.75 (2 H, t, *J* 4.9, 4-H), 3.77 (2 H, t, *J* 4.9, 6-H), 4.16 (2 H, s, 1-H), 7.49 (1 H, dd, *J* 7.3, 7.9, ArH), 7.66 (1 H, d, *J* 7.9, ArH) and 7.75 (1 H, d, *J* 7.3, ArH).

Compound **5g**: an oil (Found: C, 54.8; H, 5.0. $C_{12}H_{13}F_3OS$ requires C, 54.95; H, 5.0%); ν_{max}(Nujol)/cm^{-1} 3350, 1460, 1320 and 1125; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.05 (1 H, t, OH), 2.69 (2 H, t, *J* 5.9, SCH_2), 3.73 (2 H, q, *J* 5.9, OCH_2), 3.83 (2 H, s, $ArCH_2$), 5.24 (1 H, dd, *J* 1.3, 17.8, CH=CH_2) 5.57 (1 H, dd, *J* 1.3, 11.9, CH=CH_2), 6.90 (1 H, dd, *J* 11.9, 17.8, C*H*=CH_2), 7.33 (1 H, t, *J* 7.6, ArH) and 7.53–7.60 (2 H, m, ArH).

Compound **6g**: δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.21 (3 H, s, SCH_3), 2.83 (2 H, t, *J* 6.6, SCH_2), 4.06 (2 H, t, *J* 6.6, OCH_2), 6.18 (1 H, d, *J* 12.5, ArCH=C*H*) and 6.94 (1 H, d, *J* 12.5, ArC*H*=CH) (aromatic proton signals overlapped with those of **4g**).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 08672437) provided by the Ministry of Education, Science and Culture, Japan.

References

1 M. Hesse, *Ring Enlargement in Organic Chemistry*, VCH, New York, 1991, p. 83; E. Vedejs, *Acc. Chem. Res.*, 1984, **17**, 358; I. E. Markó, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 3, p. 913; R. Brückner, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 6, p. 873.

2 V. Ceré, C. Paolucci, S. Pollicino, E. Sandri and A. Fava, *J. Org. Chem.*, 1981, **46**, 3315; P. Cotelle, B. Hasiak, D. Barbry and D. Couturier, *Chem. Lett.*, 1987, 1007

3 N. Shirai, F. Sumiya, Y. Sato and M. Hori, *J. Org. Chem.*, 1989, **54**, 836; F. Sumiya, N. Shirai and Y. Sato, *Chem. Pharm. Bull.*, 1991, **39**, 36; T. Kitano, N. Shirai and Y. Sato, *Synthesis*, 1991, 996; T. Kitano, N. Shirai and Y. Sato, *Chem. Pharm. Bull.*, 1992, **40**, 768; T. Kitano, N. Shirai, M. Motoi and Y. Sato, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2851; Y. Sato, N. Shirai, Y. Machida, E. Ito, T. Yasui, Y. Kurono and K. Hatano, *J. Org. Chem.*, 1992, **57**, 6711; A. Sakuragi, N. Shirai, Y. Sato, Y. Kurono and K. Hatano, *J. Org. Chem.*, 1994, **59**, 148; N. Kawanishi, N. Shirai, Y. Sato, K. Hatano and Y. Kurono, *J. Org. Chem.*, 1995, **60**, 4272.

4 T. Tanzawa, N. Shirai, Y. Sato, K. Hatano and Y. Kurono, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2845.

5 T. Tanzawa, M. Ichioka, N. Shirai and Y. Sato, *J. Chem. Soc., Perkin Trans. 1*, 1995, 431.

6 T. Tanaka, N. Shirai and Y. Sato, *Chem. Pharm. Bull.*, 1992, **40**, 518.

7 D. L. Tuleen and R. H. Bennett, *J. Heterocycl. Chem.*, 1969, **6**, 115.

Paper 6/05423D
Received 2*nd August* 1996
Accepted 29*th October* 1996