# Rearrangement of 1-phenyl-3,4-dihydro-1*H*-2-benzothiopyranium 2-methylides

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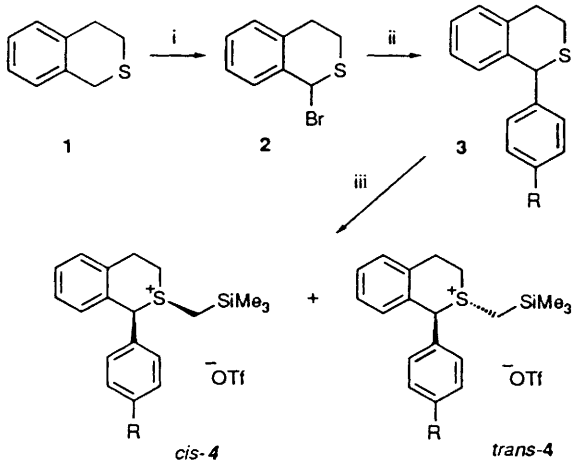
*trans*-1-Phenyl-2-benzothiopyranium 2-methylides (*trans*-**5**), generated by fluoride ion-induced desilylation of *trans*-1-(4-substituted phenyl)-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflates (*trans*-**4**) in DMSO, rearranged to 3-substituted 7,8-dihydro-5*H*,13*H*-dibenzo[*c*,*f*]thionines **6** (Sommelet–Hauser rearrangement products), 1-(4-substituted phenyl)-1,2,4,5-tetrahydro-3-benzothiepines **7** (Stevens rearrangement products) and (4-substituted phenyl)(2-vinylphenyl)methyl methyl sulfides **8** (Hofmann degradation products). Reactions carried out in the presence of oxygen, gave (4-substituted phenyl) 2-[2-(methylsulfanyl)ethyl]phenyl ketones **9** as the main products.

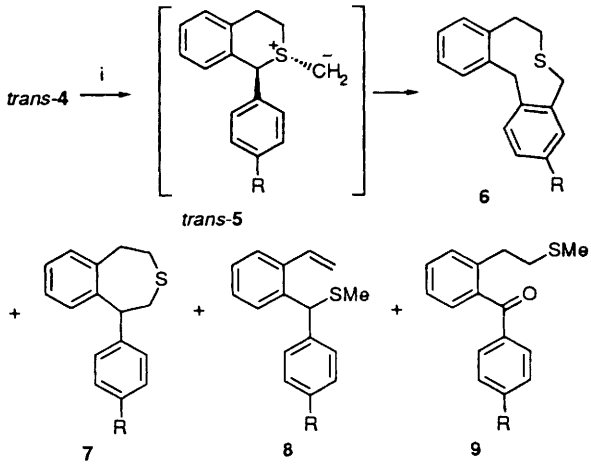
Sulfur ylides have been used as versatile reagents in organic syntheses.[1] Although Sommelet–Hauser rearrangement of stabilized sulfur ylides is applicable to ring enlargement of thiacyclic compounds,[2] that of unstabilized ylides is usually inadequate under basic conditions because plural ylides are simultaneously formed.[3] Fluoride ion-induced desilylation of *S*-[1-(trimethylsilyl)alkyl]sulfonium salts is suitable for the regio- and stereo-selective ylide formation.[4,5] We report herein the rearrangement of 1-phenyl-3,4-dihydro-1*H*-2-benzothiopyranium 2-methylides prepared by desilylation.

1-(4-Substituted phenyl)-3,4-dihydro-1*H*-2-benzothiopyrans **3** were prepared by bromination of 3,4-dihydro-1*H*-2-benzothiopyran **1** followed by reaction with (4-substituted phenyl)-magnesium bromides (Scheme 1). Reaction of **3** with (trimethylsilyl)methyl triflate gave only one isomer of 1-(4-substituted phenyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflate **4a,c,d**, except for a (4-methoxyphenyl) analogue **4b** (see Table 1). The configuration of **4a** was determined by X-ray crystallographic analysis to have a *trans* and diaxial conformation.† The major isomers of **4b–d** were assigned as *trans* and the minor as *cis* by comparison of the $^1$H NMR chemical shifts of the $SiCH_2$ groups (*cis* < *trans*).




**Scheme 1** *Reagents and conditions:* i, NBS, $CCl_4$, reflux, 0.5 h; ii, $RC_6H_4MgBr$, THF, room temp., overnight; iii, $Me_3SiCH_2OTf$, $Et_2O$, room temp., overnight

† Supplementary data (tables of atomic coordinates, bond lengths and angles) have been deposited at the Cambridge Crystallographic Data Centre (see *Instructions for Authors*, in the January issue) of *J. Chem. Soc., Perkin Trans. 1*.




**Scheme 2** *Reagents and conditions:* i, CsF, DMSO, room temp., overnight

Reaction of **4** with cesium fluoride in dimethyl sulfoxide (DMSO) at room temperature gave mixtures of 3-substituted 7,8-dihydro-5*H*,13*H*-dibenzo[*c*,*f*]thionines **6** (Sommelet–Hauser rearrangement products), 1-(4-substituted phenyl)-1,2,4,5-tetrahydro-3-benzothiepines **7** (Stevens rearrangement products), (4-substituted phenyl)(2-vinylphenyl)methyl methyl sulfides **8** (Hofmann degradation products) and (4-substituted phenyl) 2-[2-(methylsulfanyl)ethyl]phenyl ketones **9**, except for the reaction of **4b** (Scheme 2, Table 2).

When the reaction of **4a**, **c**, **d** with cesium fluoride was carried out in the presence of DBU,‡ the proportion of **6** formed increased, whilst that of **7** and **9** decreased (compare conditions A and B in Table 2). These results clearly support that the Stevens products **7**, as well as the Sommelet–Hauser products **6**, are formed from [2,3] sigmatropic migration products **10** (isotoluenes) of the ylides (*trans*-**5**) (Scheme 3). There is no [1,2] rearrangement pathway from *trans*-**5** to **7** *via* a diradical intermediate **11**, similar to the cases of the rearrangement of

‡ In the rearrangement of benzylammonium ylides, the Stevens and the Sommelet–Hauser rearrangement products are competitively formed from the same [2,3] sigmatropic migration products (isotoluenes) of the ylides. When the reaction giving the Stevens products as the main products is carried out in the presence of a strong basic amine (*e.g.*, DBU), the main products change to Sommelet–Hauser products by the acceleration of a hydrogen transfer.[6]

**Table 1** 1-(4-Substituted phenyl)-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflate **4**

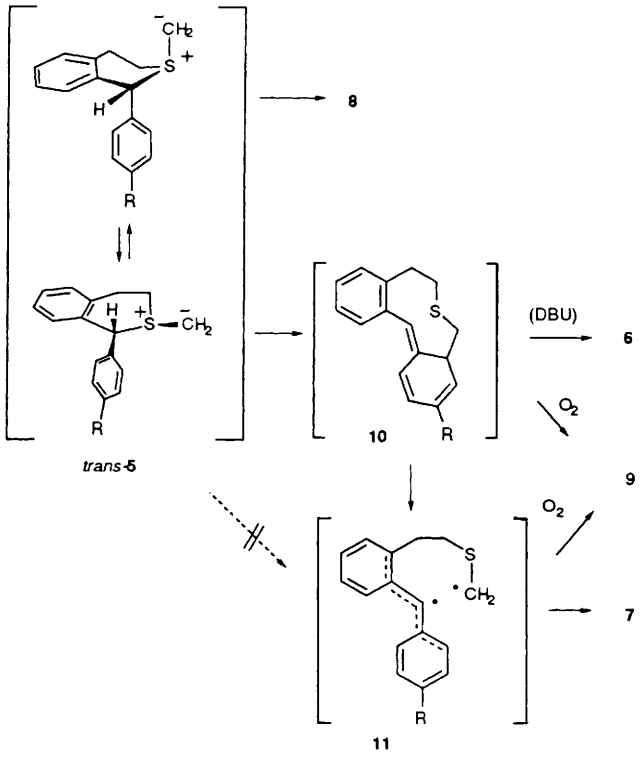
| | $R^1$ | Yield from **1** (%) | Ratio of *cis* to *trans* | $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) $SiCH_2$[a] | | | |
|---|---|---|---|---|---|---|---|
| | | | | *cis* | | *trans* | |
| **4a** | H | 45 | 0:100 | | — | 2.35 | 2.99 |
| **4b** | MeO | 23 | 4:96 | 1.30 | 2.65 | 2.23 | 3.18 |
| **4c** | Cl | 23 | 0:100 | — | — | 2.36 | 3.06 |
| **4d** | $CF_3$ | 31 | 0:100 | — | — | 2.41 | 3.12 |

[a] Two hydrogens appeared as an AB quartet.

**Table 2** Reaction of 1-(4-substituted phenyl)-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflate **4** with CsF in DMF for 24 h

| Entry | Salt | Reaction condition[b] | Total yield (%) | Product ratio[a] | | | |
|---|---|---|---|---|---|---|---|
| | | | | **6** | **7** | **8** | **9** |
| 1 | *trans*-**4a** | A | 89 | 45 | 27 | 15 | 13 |
| 2 | *trans*-**4a** | B | 92 | 74 | 13 | 7 | 6 |
| 3 | *trans*-**4a** | C | 80 | 20 | 20 | 3 | 57 |
| 5 | **4b**[c] | A | — | Complex mixture | | | |
| 6 | **4b**[c] | B | — | Complex mixture | | | |
| 7 | **4b**[c] | C | — | Complex mixture | | | |
| 8 | *trans*-**4c** | A | 92 | 69 | 18 | 11 | 2 |
| 9 | *trans*-**4c** | B | 98 | 92 | 0 | 6 | 2 |
| 10 | *trans*-**4c** | C | 81 | 17 | 12 | 3 | 68 |
| 11 | *trans*-**4d** | A | 88 | 73 | 5 | 5 | 17 |
| 12 | *trans*-**4d** | B | 94 | 97 | 2 | 1 | 0 |
| 13 | *trans*-**4d** | C | 82 | 9 | 5 | 0 | 86 |

[a] Ratios of the products determined by integration of the $^1H$ signals in the 500 MHz. [b] Conditions A: The reaction was carried out under $N_2$; B: the reaction was carried out in the presence of DBU (5 mol equiv.) under $N_2$; C: the reaction was carried out in dry air. [c] *cis*-**4b**:*trans*-**4b** = 4:96.




**Scheme 3**

benzylammonium ylides.[6] Hofmann products **8** may be formed from diaxial forms of *trans*-**5**, and isotoluenes **10** from diequatorial forms.[3c,7]

Initially we thought that formation of the unexpected ketones **9** was a result of oxidation of the reaction intermediate with DMSO which was used as the solvent. However, there was no appreciable change of the product ratio when the reaction of **4a** was carried out in dimethylformamide (DMF) instead of DMSO, although the total yield decreased to 75%. This ylide reaction may be very sensitive to oxygen, a minor contaminant in the reaction flask, although the flask was charged with nitrogen (>99%). Indeed, **9** was transformed into the main product when the reaction was carried out in dry air (conditions C in Table 2). The path from **5** to **9** is still unclear, but may be formed by rapid oxidation of the diradical intermediates **11** or isotoluenes **10**.

All reactions of the 4-methoxyphenylsulfonium salt **4b** gave complex mixtures (entries 5–7). [2,3] Sigmatropic rearrangement products (isotoluenes) of polymethoxybenzylammonium ylides[8] and methoxybenzylsulfonium ylides[5] were stable at room temperature, but they were decomposed during aqueous work-up to give complex mixtures. These isotoluenes were aromatized to Sommelet–Hauser products when the reactions were carried out in the presence of DBU, and were detected in the reaction mixture when worked up with 12 mol $dm^{-3}$ aqueous sodium hydroxide. Although we tried adding DBU to the reaction of **4b**, or a work-up with 12 mol $dm^{-1}$ aqueous sodium hydroxide, neither **6b** nor **10b** could be detected. We are currently investigating the effect of a *para*-methoxy substituent.

## Experimental

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

**1-Phenyl-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflate 4a**

Trimethylsilylmethyl triflate (1.2 g, 5.1 mmol) was added to a solution of 1-phenyl-3,4-dihydro-1*H*-2-benzothiopyran§[9] **3a** (1.1 g, 4.8 mmol) in $Et_2O$ (20 $cm^3$) at −78 °C and the mixture was stirred overnight; it was then stirred for 3 h at room temperature. After this the mixture was evaporated under reduced pressure and the residue was washed with $Et_2O$ to give the *title salt* **4a** (2.1 g, 94%), mp 136–137 °C (Found: C, 51.7; H, 5.55. $C_{20}H_{25}F_3O_3S_2Si$ requires C, 51.9; H, 5.5%); $\nu_{max}$ (KBr)/$cm^{-1}$ 3024, 1491, 1446, 1254, 858, 736 and 695; $\delta_H$(270 MHz; $CDCl_3$; $Me_4Si$) 0.22 (9 H, s), 2.35 (1 H, d, *J* 13.9), 2.99 (1 H, d, *J* 13.9), 3.39–3.48 (2 H, m), 3.51–3.58 (2 H, m), 6.20 (1 H, s), 7.01 (1 H, d, *J* 7.6), 7.26–7.31 (2 H, m), 7.36–7.42 (3 H, m) and 7.44–7.49 (3 H, m).

**1-(4-Methoxyphenyl)-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflate 4b**

A solution of 3,4-dihydro-1*H*-2-benzothiopyran[10] **1** (1.5 g, 10 mmol) and *N*-bromosuccinimide (NBS) (2.2 g, 12 mmol) in $CCl_4$ (200 $cm^3$) was heated at reflux for 0.5 h after which the solution was filtered and concentrated to give crude 1-bromo-3,4-dihydro-1*H*-2-benzothiopyran **2**. This was dissolved in THF (20 $cm^3$) and added to a solution of (4-methoxyphenyl)-magnesium bromide (25 mmol) in THF (10 $cm^3$). The mixture was stirred overnight at room temperature after which it was treated with saturated aqueous $NH_4Cl$ (100 $cm^3$) to quench the reaction and extracted with $Et_2O$ (4 × 50 $cm^3$). The combined extracts were washed with water and saturated brine, dried ($MgSO_4$) and concentrated. Distillation of the residual oil gave 1-(4-methoxyphenyl)-3,4-dihydro-1*H*-2-benzothiopyran **3b** which was unstable at room temperature and subsequently used as prepared, for the next step.

Trimethylsilylmethyl triflate (1.2 g, 5.1 mmol) was added at −78 °C to a solution of **3b** in $Et_2O$ (20 $cm^3$) and the mixture was stirred at the same temperature overnight; it was stirred at room temperature for 3 h. After this the mixture was evaporated under reduced pressure and the residue was washed with $Et_2O$ to give the *title salt* **4b** (1.4 g, 28%), mp 107–109 °C (Found: C, 51.1; H, 5.7. $C_{21}H_{27}F_3O_4S_2Si$ requires C, 51.2; H, 5.5%); $\nu_{max}$(KBr) $cm^{-1}$ 2957, 1610, 1514, 1462, 1261, 1143, 848 and 636. The $^1H$ NMR spectrum indicated the presence of two isomers. The major isomer was assigned as *trans* and the minor as *cis* by comparison of the chemical shifts for the $SiCH_2$ groups (see Table 1, *cis*-**4b**/*trans*-**4b**, 4:96); $\delta_H$(400 MHz; $CDCl_3$; $Me_4Si$) *cis*-**4b**: 0.26 (9 H, s), 1.30 (1 H, d, *J* 13.5), 2.65 (1 H, d, *J* 13.5), 3.35–3.46 (2 H, m), 3.59–3.70 (1 H, m), 3.80–3.87 (1 H, m), 3.84 (3 H, s), 6.42 (1 H, s), 6.99–7.04 (3 H, m), 7.17–7.27 (1 H, m) and 7.29–7.42 (4 H, m); *trans*-**4b**: 0.23 (9 H, s), 2.23 (1 H, d, *J* 13.9), 3.18 (1 H, d, *J* 13.9), 3.35–3.46 (2 H, m), 3.59–3.70 (1 H, m), 3.80–3.87 (1 H, m), 3.86 (3 H, s), 6.11 (1 H, s), 6.99–7.04 (3 H, m), 7.17–7.27 (1 H, m) and 7.29–7.42 (4 H, m).

**1-(4-Chlorophenyl)-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-2-benzothiopyranium triflate 4c**

In a manner similar to that described for **4b**, a solution of **2** in THF was added to a solution of 4-(chlorophenyl)magnesium bromide (25 mmol) in THF (10 $cm^3$) and treated to give 1-(4-chlorophenyl)-3,4-dihydro-1*H*-2-benzothiopyran **3c**. This compound was subsequently treated with (trimethylsilyl)methyl triflate (1.2 g, 5.1 mmol) to give the *title salt* **4c** (2.1 g, 42%), mp 156–157 °C (Found: C, 48.1; H, 4.9. $C_{20}H_{24}ClF_3O_3S_2Si$ requires C, 48.3; H, 4.9%); $\nu_{max}$(KBr)/$cm^{-1}$ 1263, 1148, 1032, 853 and 637; $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) 0.25 (9 H, s), 2.36 (1 H, d, *J* 14.0), 3.06 (1 H, d, *J* 14.0), 3.38–3.50 (2 H, m), 3.58–3.64 (2 H, m), 6.25 (1 H, s), 7.00 (1 H, d, *J* 7.9) and 7.30–7.48 (7 H, m).

**1-(4-Trifluoromethylphenyl)-2-(trimethylsilylmethyl)-3,4-dihydro-1*H*-benzothiopyranium triflate 4d**

In the same way, a solution of **2** in THF was treated with a solution of 4-trifluoromethylphenylmagnesium bromide (25 mmol) in THF (10 $cm^3$) to give 1-(4-trifluoromethylphenyl)-3,4-dihydro-1*H*-2-benzothiopyran **3d**. This compound was subsequently treated with trimethylsilylmethyl triflate (1.2 g, 5.1 mmol) to give the *title salt* **4d** (2.5 g, 47%), mp 158–160 °C (Found: C, 47.3; H, 4.6. $C_{21}H_{24}F_6O_3S_2Si$ requires C, 47.5; H, 4.6%); $\nu_{max}$(KBr)/$cm^{-1}$ 2955, 1487, 1460, 1263, 1145, 1032, 852 and 636; $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) 0.26 (9 H, s), 2.41 (1 H, d, *J* 13.8), 3.12 (1 H, d, *J* 13.8), 3.35–3.63 (2 H, m), 3.65–3.72 (1 H, m), 3.73–3.82 (1 H, m), 6.43 (1 H, s), 6.98 (1 H, d, *J* 7.6), 7.30–7.48 (3 H, m), 7.63 (2 H, d, *J* 8.6) and 7.77 (2 H, d, *J* 8.6).

**Reaction of 4a with CsF**

**Conditions A.** A 30-$cm^3$ flask equipped with a magnetic stirrer, septum and a test tube which was connected to the flask by a short piece of rubber tubing was charged with the sulfonium salt **4a** (0.215 g, 0.5 mmol). CsF (0.38 g, 2.5 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with $N_2$ (dry air was used instead of $N_2$ under Conditions C). DMSO (5 $cm^3$) [and DBU (0.38 g, 2.5 mmol) under Conditions B] was added to the flask with a syringe, followed by CsF, added from the test tube. The mixture was stirred at room temperature for 24 h after which it was poured into water and extracted with $Et_2O$. The ethereal extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was distilled (bp 160 °C/0.7 mmHg) to give a mixture of 7,8-dihydro-5*H*,13*H*-dibenzo-[*c*,*f*]thionine **6a**, 1-phenyl-1,2,4,5-tetrahydro-3-benzothiepine **7a**, phenyl(2-vinylphenyl)methyl methyl sulfide **8a**, 2-[2-(methylsulfanyl)ethyl]phenyl phenyl ketone **9a**. The products were separated on a silica gel column (hexane–ethyl acetate, 100:1 to 50:1) and distilled under reduced pressure. Isolation of pure **7a** was difficult because of inefficient separation from **6a**. The product ratios were determined from the integrated values of the proton signals in the $^1H$ NMR spectra of the mixtures. The results are summarized in Table 2.

*Compound* **6a**: bp 160 °C/0.7 mmHg (Found: C, 79.7; H, 6.8. $C_{16}H_{16}S$ requires C, 80.0; H, 6.7%); $\nu_{max}$(KBr)/$cm^{-1}$ 2955, 1491, 1446, 1060, 736 and 695; $\delta_H$(270 MHz; $CDCl_3$; $Me_4Si$) 2.60 (2 H, t, *J* 6.5), 3.26 (2 H, t, *J* 6.5), 3.79 (2 H, s), 4.31 (2 H, s), 7.05–7.23 (6 H, m), 7.25–7.29 (1 H, m) and 7.38 (1 H, d, *J* 8.1).

*Compound* **7a** (not isolated): $\delta_H$(270 MHz; $CDCl_3$; $Me_4Si$) 3.15–3.20 (2 H, m), 3.22–3.26 (2 H, m), 3.32–3.34 (1 H, m), 3.45–3.48 (1 H, m), 4.70 (1 H, dd, *J* 8.2, 3.8), 6.78 (1 H, d, *J* 7.1) and 7.06–7.39 (8 H, m) (Found: $M^+$, 240.096. Calc. for $C_{16}H_{16}S$: *M*, 240.097).

*Compound* **8a**: bp 160 °C/0.7 mmHg (Found: C, 79.7; H, 6.8. $C_{16}H_{16}S$ requires C, 79.95; H, 6.7%); $\nu_{max}$(film)/$cm^{-1}$ 3026, 2914, 1491, 1448, 765 and 698; $\delta_H$(400 MHz; $CDCl_3$; $Me_4Si$) 2.00 (3 H, s), 5.32 (1 H, dd, *J* 11.0, 1.3), 5.37 (1 H, s), 5.60 (1 H, dd, *J* 17.3, 1.3), 7.08–7.14 (1 H, m), 7.17–7.35 (5 H, m), 7.44 (2 H, d, *J* 7.5), 7.41 (1 H, dd, *J* 7.5, 1.6) and 7.56 (1 H, dd, *J* 7.5, 1.5).

*Compound* **9a**: bp 170 °C/0.7 mmHg (Found: C, 75.2; H, 6.6. $C_{16}H_{16}OS$ requires C, 75.0; H, 6.3%); $\nu_{max}$(film)/$cm^{-1}$ 2918, 1662, 1597, 1267, 925 and 730; $\delta_H$(400 MHz; $CDCl_3$; $Me_4Si$) 2.01 (3 H, s), 2.68–2.73 (2 H, m), 2.95–2.99 (2 H, m), 7.28–7.37 (3 H, m), 7.36 (1 H, d, *J* 7.7), 7.42–7.47 (2 H, m), 7.56–7.61 (1 H, m) and 7.80–7.82 (2 H, m); $\delta_C$(100.5 MHz; $CDCl_3$; $Me_4Si$) 15.4, 33.4, 35.8, 125.8, 128.5, 128.9 (2 C), 130.3, 130.4, 130.7 (2 C), 133.3, 137.8, 138.5, 139.7 and 198.3.

§ $\delta_H$(400 MHz; $CDCl_3$; $Me_4Si$) 2.83–2.95 (2 H, m), 3.06–3.20 (2 H, m), 5.16 (1 H, s), 6.89 (1 H, d, *J* 7.8), 7.07–7.13 (2 H, m) and 7.18–7.32 (6 H, m).

**Reaction of 4b with CsF**

In a manner similar to that described above, **4b** (0.246 g, 0.5 mmol) and CsF (0.38 g, 2.5 mmol) were allowed to react. $^1$H NMR and TLC of the ethereal extracts from reactions carried out under Conditions A, B and C showed that the product mixtures were complex and difficult to separate.

**Reaction of 4c with CsF**

In the same way, **4c** (0.249 g, 0.5 mmol) and CsF (0.38 g, 2.5 mmol) were treated under Conditions A, B and C to give a mixture of 3-chloro-7,8-dihydro-5*H*,13*H*-dibenzo[*c*,*f*]thionine **6c**, 1-(4-chlorophenyl)-1,2,4,5-tetrahydro-3-benzothiepine **7c**, (4-chlorophenyl)(2-vinylphenyl)methyl methyl sulfide **8c**, 2-[2-(methylsulfanyl)ethyl]phenyl 4-chlorophenyl ketone **9c**. The products were separated on a silica gel column and distilled under reduced pressure.

*Compound* **6c**: mp 121–123 °C (Found: C, 69.8; H, 5.6. $C_{16}H_{15}ClS$ requires C, 69.9; H, 5.5%); $\nu_{max}$(KBr)/cm$^{-1}$ 2920, 1451, 1047, 702 and 619; $\delta_H$(400 MHz; $C_6D_6$; $Me_4Si$) 2.26 (2 H, t, *J* 6.3), 2.84 (2 H, t, *J* 6.3), 3.30 (2 H, s), 3.96 (2 H, s), 6.75–6.78 (1 H, m), 6.88 (2 H, d, *J* 8.1) and 6.96–7.00 (4 H, m).

*Compound* **7c** (not isolated): $\delta_H$(400 MHz; $CDCl_3$; $Me_4Si$) 2.74–2.79 (2 H, m), 3.13–3.18 (2 H, m), 3.29–3.36 (2 H, m), 4.67 (1 H, dd, *J* 7.6, 4.0), 6.77 (1 H, d, *J* 7.3) and 7.05–7.34 (7 H, m) (Found: M$^+$, 274.058. Calc. for $C_{16}H_{15}ClS$: *M*, 274.058).

*Compound* **8c**: bp 150 °C/2 mmHg (Found: C, 69.7; H, 5.7. $C_{16}H_{15}ClS$ requires C, 69.9; H, 5.5%); $\nu_{max}$(film)/cm$^{-1}$ 3061, 2917, 1489, 1090, 1015 and 768; $\delta_H$(400 MHz; $CDCl_3$; $Me_4Si$) 1.99 (3 H, s), 5.33 (1 H, s), 5.33 (1 H, dd, *J* 10.7, 1.5), 5.60 (1 H, dd, *J* 17.4, 1.5), 7.02–7.07 (1 H, m), 7.15–7.34 (6 H, m), 7.44 (1 H, dd, *J* 7.3, 1.2) and 7.51 (1 H, dd, *J* 7.6, 1.5).

*Compound* **9c**: bp 150 °C/2 mmHg (Found: C, 66.0; H, 5.2. $C_{16}H_{15}ClOS$ requires C, 66.1; H, 5.2%); $\nu_{max}$(film)/cm$^{-1}$ 1665, 1586, 1262, 1090 and 685; $\delta_H$(400 MHz; $CD_3OD$; $Me_4Si$) 1.92 (3 H, s), 2.61–2.67 (2 H, m), 2.89–2.95 (2 H, m), 7.22–7.49 (6 H, m) and 7.70–7.75 (2 H, m); $\delta_C$(67.9 MHz; $CD_3OD$; $Me_4Si$) 15.3, 34.0, 34.6, 126.8, 129.7, 129.8 (2 C), 131.8, 131.9, 132.7 (2 C), 137.4, 139.2, 140.7, 140.9 and 198.4.

**Reaction of 4d with CsF**

In the same way, **4d** (0.265 g, 0.5 mmol) and CsF (0.38 g, 2.5 mmol) were allowed to react under Conditions A, B and C to give a mixture (bp 175 °C/0.8 mmHg) of 3-(trifluoromethyl)-7,8-dihydro-5*H*,13*H*-dibenzo[*c*,*f*]thionine **6d**, 1-(4-trifluoromethylphenyl)-1,2,4,5-tetrahydro-3-benzothiepine **7d**, (4-trifluoromethylphenyl)(2-vinylphenyl)methyl methyl sulfide **8d**, 2-[2-(methylsulfanyl)ethyl]phenyl [4-(trifluoromethyl)phenyl] ketone **9c**.

*Compound* **6d**: mp 132–134 °C (Found: C, 66.1; H, 5.1. $C_{17}H_{15}F_3S$ requires C, 66.2; H, 4.9%); $\nu_{max}$(KBr)/cm$^{-1}$ 2924, 1471, 1415, 1334, 1169, 1120, 841 and 648; $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) 2.66 (2 H, t, *J* 6.2), 3.27 (2 H, t, *J* 6.2), 3.75 (2 H, s), 4.41 (2 H, s), 7.08–7.20 (4 H, m), 7.35 (1 H, d, *J* 5.6) and 7.43–7.52 (2 H, m).

*Compound* **7d** (not isolated): $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) 2.76–2.81 (2 H, m), 3.18–3.21 (2 H, m), 3.33–3.43 (2 H, m), 4.75 (1 H, dd, *J* 8.2, 2.7), 6.76 (1 H, d, *J* 7.2) and 7.02–7.65 (7 H, m) (Found: M$^+$, 308.083. Calc. for $C_{17}H_{15}F_3S$: *M*, 308.084).

*Compound* **8d**: bp 175 °C/0.8 mmHg (Found: C, 63.3; H, 5.0. $C_{17}H_{15}F_3S$ requires C, 66.2; H, 4.9%); $\nu_{max}$(film)/cm$^{-1}$ 2926, 1417, 1124, 1016 and 769; $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) 2.0 (3 H, s), 5.33 (1 H, dd, *J* 10.4, 1.3), 5.37 (1 H, s), 5.60 (1 H, dd, *J* 17.3, 1.3), 7.04–7.14 (1 H, m), 7.19–7.31 (2 H, m) and 7.32–7.57 (6 H, m).

*Compound* **9d**: bp 165–168 °C/0.8 mmHg (Found: C, 62.8; H, 4.8. $C_{17}H_{15}F_3OS$ requires C, 62.95; H, 4.7%); $\nu_{max}$(film)/cm$^{-1}$ 2920, 1670, 1325, 1170, 1130 and 756; $\delta_H$(500 MHz; $CDCl_3$; $Me_4Si$) 2.02 (3 H, s), 2.70–2.75 (2 H, m), 2.99–3.05 (2 H, m), 7.30 (2 H, d, *J* 3.6), 7.36–7.40 (1 H, m), 7.44–7.52 (1 H, m), 7.73 (2 H, d, *J* 8.9) and 7.92 (2 H, d, *J* 8.9); $\delta_C$(100.5 MHz; $CDCl_3$; $Me_4Si$) 15.5, 33.2, 35.9, 123.6 (d, $J_{C,F}$ 272.1), 125.5 (q, 2 C, $J_{C,F}$ 3.6), 125.9 (2 C), 129.3, 130.5, 131.1, 131.6, 134.4 (q, $J_{C,F}$ 33.1), 137.5, 140.3, 140.8 and 196.9.

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