Rearrangement of *S*-Methylbenzylsulfonium *S*-Alkylides in Non-Basic Media

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S-Methylbenzylsulfonium *S*-alkylides, prepared by fluoride ion-induced desilylation of *S*-methyl-*S*-[1-(trimethylsilyl)alkyl](2,4-disubstituted benzyl)sulfonium salts **8** in dimethyl sulfoxide, rearranged exclusively to Sommelet–Hauser products without contamination of Stevens products.

Although the Stevens rearrangement is a typical route for the isomerization of nitrogen and sulfur ylides and it has been the subject of many reports,[1] few have dealt with benzylsulfonium ylides. Hayashi and Oda[2] reported the formation of Sommelet–Hauser products in 3–56% yields on treatment of dimethyl(substituted benzyl)sulfonium salts with sodium methoxide in methanol, but they failed to mention Stevens products. They also stated that in the reaction of dibenzylmethylsulfonium perchlorate with sodium hydroxide, the ratio of the Sommelet–Hauser to the Stevens rearrangement product was increased as the concentration of the base rose, but no experimental results were reported.

We have reported[3] from studies of ammonium ylides in non-basic media that benzylammonium *N*-alkylides **1** are initially isomerized to isotoluene derivatives **2** *via* a [2,3] sigmatropic migration pathway, and are then converted into the products of Sommelet–Hauser rearrangement **3** and/or Stevens rearrangement **4** (Scheme 1). The former **3** are predominantly formed when an R^1 group is an electron-releasing or a weak electron-withdrawing substituent (Hammett *para*-substituent constant, $\sigma_p > 0.6$) and R^2 is a hydrogen. The latter **4** are produced when R^1 is a strong electron-withdrawing group (*e.g.* NO_2) and/or R^2 is an alkyl group. However, the ylides giving **4** as the main product in non-basic media are converted into **3** in the presence of a strong basic amine (*e.g.* DBU) *via* a proton–dissociation and –recombination pathway.[4]

These results suggest that only Sommelet–Hauser products are formed in basic media. Because the chemical behaviours of benzylsulfonium and benzylammonium alkylides are similar,[1] the Stevens products from the sulfonium ylides might be formed in non-basic media, especially from 4-nitrobenzylsulfonium *S*-methylides and benzylsulfonium *S*-alkylides. We examined the fluoride ion-induced desilylation of *S*-methyl-*S*-[1-(trimethylsilyl)alkyl](substituted benzyl)sulfonium salts **8**.†

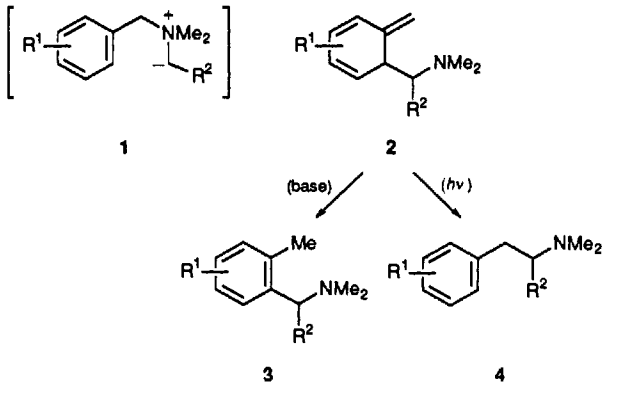
The starting salts **8** were prepared by one of the three routes shown in Scheme 2. The results are summarized in Table 1.

Reaction of **8** with cesium fluoride in dimethyl sulfoxide‡ (DMSO) gave only the corresponding Sommelet–Hauser product **12** after 24 h at room temperature, except for a (2-methyl-4-methoxybenzyl) analogue **8h** (entry 13 in Table 2). We were somewhat surprised that no Stevens product **13** was detected in any reaction mixture. The yield of methyl 1-(2-methyl-5-nitrophenyl)ethyl sulfide **12j** was low at room temperature but improved when the reaction was carried out at 0 °C (entries 17 and 18).

Table 1 *S*-Methyl-*S*-[1-(trimethylsilyl)alkyl] (substituted benzyl)-sulfonium salts **8**

	R^1	R^2	R^3	X	Route[a]	Total yield (%)
a	H	H	H	OTf	A	88
b	H	H	Me	OTf	B	85
c	Me	H	H	OTf	A	42
d	H	Me	H	Br	C	58
e	H	Br	H	Br	C	88
f	H	MeO	H	OTf	A	58
g	H	MeO	Me	OTf	B	40
h	Me	MeO	H	OTf	A	56
i	H	NO_2	H	Br	C	41
j	H	NO_2	Me	OTf	B	30

[a] Route A: **5**→**6**→**8**; B: **7**→**6**→**8**; C: **5**→**8**.



Scheme 1

To examine the reaction path, the reactions of **8a**, **d**, **f** were carried out at 10 °C and quenched after 0.5 h. No change of the product from **8a** (entry 1) was observed, but the products from **8d**, **f** changed to complex mixtures (entries 5 and 9). These results suggest that 2-methyl- or 2-methoxy-substituted 6-[(methylthio)methyl]-5-methylenecyclohexa-1,3-dienes **11d**, **f** (isotoluene derivatives), which were initially formed from the ylides **9d**, **f** existed in the reaction mixtures after 0.5 h but were decomposed during the aqueous work-up.

During this research, we noticed that polymethoxy-substituted 6-(dimethylamino)methyl-5-methylenecyclohexa-1,3-dienes (isotoluene derivatives), which were [2,3] sigmatropic migration products of (polymethoxy-substituted benzyl)-ammonium *N*-methylides, were stable at room temperature, but quickly hydrolysed during aqueous work-up to polymethoxytoluenes, dimethylamine, and formaldehyde. However,

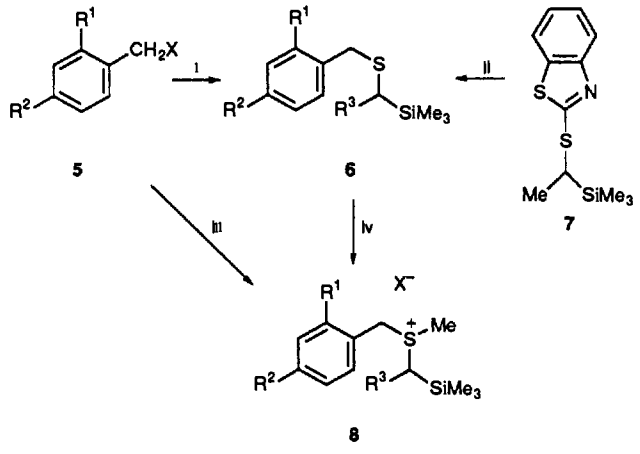
† It has been reported[5] that a sulfonium ylide which was produced by fluoride-induced desilylation of *S*-methyl-*S*-[(trimethylsilyl)methyl](2-methylbenzyl)sulfonium triflate **8c** in dimethoxyethane (DME), changed to a 1:2 mixture of **10c** and **12c** in 64% yield, and that **10c** was converted into **12c** on a silica gel column. We are unable to reproduce this interesting conversion, however.

‡ The reactions in DMSO proceeded more quickly to give higher yields of the products than in dimethylformamide or 1,2-dimethoxyethane.

Table 2 Reaction of *S*-methyl-*S*-[(trimethylsilyl)methyl](substituted benzyl)sulfonium salts **8** with CsF in DMSO

Entry		Reaction Temp. (°C)	Time (h)	Condition[b]	Total yield (%)	Product ratio[a] **10**	**11**	**12**
1	**8a**	10	0.5	A[c]	75	—	0	100
2	**8a**	RT	24	A	83	—	0	100
3	**8b**	RT	24	A	80	—	0	100
4	**8c**	RT	24	A	74	15	0	85
5	**8d**	10	0.5	A[c]	Complex mixture			
6	**8d**	10	0.5	B[c]	59	—	10	90
7	**8d**	RT	24	A	81	—	0	100
8	**8e**	RT	24	A	74	—	0	100
9	**8f**	10	0.5	A[c]	Complex mixture			
10	**8f**	10	0.5	B[c]	60	—	92	8
11	**8f**	RT	24	A	75	—	0	100
12	**8g**	RT	72	A	87	—	0	100
13	**8h**	RT	24	A	Complex mixture			
14	**8h**	RT	24	B	80	15	0	85
15	**8h**	RT	24	C	78	12	0	88
16	**8i**	RT	24	A	78	—	0	100
17	**8j**	0	0.5	A[d]	64	—	0	100
18	**8j**	RT	24	A	31	—	0	100

[a] Determined from the proton ratios of ^{1}H NMR spectra. [b] Condition A: the reaction was quenched with water; B: quenched with 12 mol dm^{-3} aqueous NaOH; C: the reaction was carried out in the presence of DBU (5 mol equiv.). [c] DMSO–THF (3:1) was used as the solvent. [d] DMSO–THF (5:3) was used as the solvent.



Scheme 2 *Reagents and conditions:* i, Me_3SiCH_2SLi, Et_2O, −20 °C, overnight; ii, Bu^{t}Li, THF, −66 °C, $R^2C_6H_4CH_2X$, room temp., 3 h or overnight; iii, Me_3SiCH_2SMe, acetone or acetonitrile, room temp., overnight; iv, MeOTf, benzene, 0 °C, or ether, −15 °C, overnight

when the reaction was quenched with 12 mol dm^{-3} sodium hydroxide, the hydrolysis was suppressed and Sommelet–Hauser rearrangement products or isotoluene derivatives were isolable.[6]

When the reactions of **8d, f** were carried out at 10 °C and worked up with 12 mol dm^{-3} aqueous sodium hydroxide, the products were mixtures of **11d, f** and **12d, f** (entries 6 and 10). A similar treatment of **8h** gave a mixture of 2-methoxy-6-methyl-5-methylene-6-[(methylthio)methyl]cyclohexa-1,3-diene **10h** and **12h** (entry 14). The same result was obtained when the reaction of **8h** was carried out in the presence of DBU and worked up with water (entry 15). These results support that methoxy-substituted isotoluenes **11d, f, h** exist in the reaction mixtures at room temperature but quickly react with water to form complex mixtures. It is still unclear what types of decomposition occur in water.

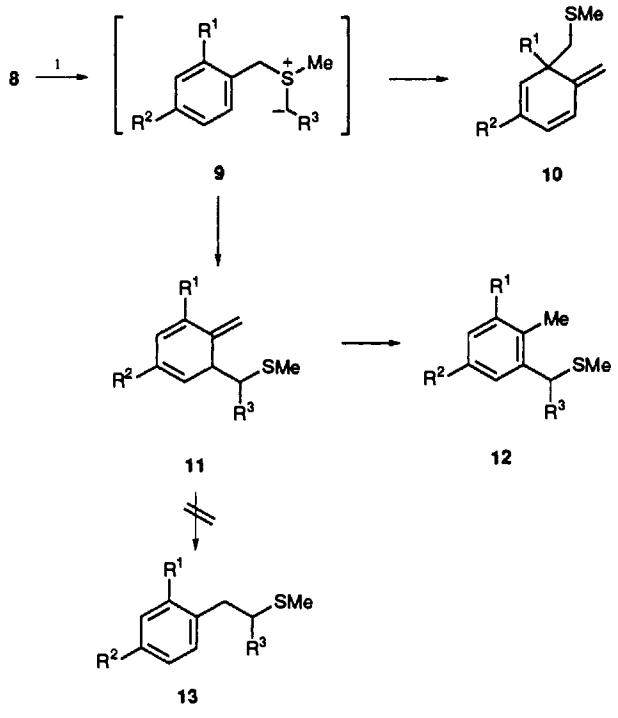
Thus, no Stevens rearrangement product was formed in the isomerization of benzylsulfonium ylides. It is interesting but unclear why such difference exists between the chemical behaviour of the *N*-ylides and the *S*-ylides.

Experimental

All reactions were carried out in N_2 or Ar. 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. ^{1}H NMR spectra were recorded at 270, 400 or 500 MHz. All melting and boiling points are uncorrected. *J*-Values are given in Hz.

4-Methoxybenzyl (Trimethylsilyl)methyl Sulfide **6f**.—A solution of (trimethylsilyl)methanethiol (4.33 g, 36.0 mmol) in ether (100 cm^3) was added at −20 °C to butyllithium (1.61 mol dm^{-3} in hexane; 23 cm^3, 37.0 mmol) followed, after 2 h by 4-methoxybenzyl bromide (5.60 g, 35.7 mmol); stirring was then continued overnight at the same temperature. The reaction was quenched with water (100 cm^3) and the mixture was extracted with ether (3 × 100 cm^3). The combined extracts were washed with saturated brine, dried ($MgSO_4$), concentrated, and distilled under reduced pressure to give the *title compound* **6f** (5.77 g, 60%), b.p. 120 °C/1.0 mmHg (Found: C, 60.2; H, 8.2. $C_{12}H_{20}OSSi$ requires C, 59.95; H, 8.4%); ν_{max}(film)/cm^{-1} 1174 (OMe), 1250 and 846 (CSi); δ_H(270 MHz; $CDCl_3$; Me_3Si) 0.05 (9 H, s, $SiMe_3$), 1.68 (2 H, s, CH_2Si), 3.65 (2 H, s, CH_2S), 3.80 (3 H, s, OMe), 6.84 (2 H, d, *J* 8.6, Ph) and 7.21 (2 H, d, *J* 8.6, Ph).

4-Methoxybenzyl 1-(Trimethylsilyl)ethyl Sulfide **6g**.—A solution of benzothiazol-2-yl 1-(trimethylsilyl)ethyl sulfide[7] **7** (5.35 g, 20.0 mmol) in THF (200 cm^3) was added at −60 °C to *tert*-butyllithium (1.70 mol dm^{-3} in pentane; 11.7 cm^3, 20.0 mmol) and the mixture stirred for 2 h. 4-Methoxybenzyl chloride (2.7 cm^3, 20.0 mmol) was then added to the mixture after which stirring was continued overnight at the same temperature, and then for 3 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (100 cm^3) and the mixture was extracted with ether (3 × 200 cm^3). The combined extracts were washed with water and saturated brine, dried ($MgSO_4$), concentrated, and distilled under reduced pressure. The distillate at 138–139 °C/4 mmHg was chromatographed on silica gel (hexane–trichloromethane, 4:1) to give the *title sulfide* **6g** (2.14 g, 42%) (Found: C, 61.2; H, 8.8. $C_{13}H_{22}OSSi$ requires C, 61.4; H, 8.7%); ν_{max}(film)/cm^{-1} 1250 and 837 (CSi); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.02 (9 H, s, $SiMe_3$), 1.28 (3 H, d, *J* 7.3, CMe), 1.82 (1 H, q, *J* 7.3, CHSi), 3.71 (2 H, s,



Scheme 3 *Reagents and conditions:* i, CsF, DMSO, 10 °C or room temp., 0.5–24 h

CH_2S), 3.80 (3 H, s, OMe), 6.84 (2 H, d, *J* 8.6, Ph) and 7.24 (2 H, d, *J* 8.6, Ph).

4-*Methoxy*-2-*methylbenzyl* (*Trimethylsilyl*)*methyl Sulfide* **6h**.—In a manner similar to that described for **6f**, (trimethylsilyl)methanethiol (3.132 g, 26.04 mmol), butyllithium (1.60 mol dm^{-3} in hexane; 16.3 cm^3, 26.1 mmol), and 4-methoxy-2-methylbenzyl bromide * were treated to give the *title sulfide* **6h** (3.81 g, 58%), b.p. 127 °C/0.7 mmHg (Found: C, 61.1; H, 8.6. $C_{13}H_{22}OSSi$ requires C, 61.4; H, 8.7%); ν_{max}(film)/cm^{-1} 1253 and 848 (C–Si); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.05 (9 H, s, $SiMe_3$), 1.69 (2 H, s, CH_2Si), 2.37 (3 H, s, PhMe), 3.66 (2 H, s, CH_2S), 3.78 (3 H, s, OMe), 6.67 (1 H, dd, *J* 8.2, 2.8, Ph), 6.73 (1 H, d, *J* 2.8, Ph) and 7.09 (1 H, d, *J* 8.2, Ph).

4-*Nitrophenyl* 1-(*Trimethylsilyl*)*ethyl Sulfide* **6j**.—In a manner similar to that described for **6g**, a solution of **7** (5.35 g, 20.0 mmol) in THF (200 cm^3), *tert*-butyllithium (11.7 cm^3, 20.0 mmol), and 4-nitrobenzyl bromide (6.48 cm^3, 30.0 mmol) was treated to give the *title sulfide* **6g** (1.93 g, 36%), b.p. 149 °C/0.9 mmHg (Kugelrohr) (Found: C, 53.3; H, 7.0; N, 5.1. $C_{12}H_{19}NO_2SSi$ requires C, 53.5; H, 7.1; N, 5.2%); ν_{max}(film)/cm^{-1} 1250 and 853 (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.03 (9 H, s, $SiMe_3$), 1.29 (3 H, d, *J* 7.2, CMe), 1.78 (1 H, q, *J* 7.2, CHSi), 3.78 and 3.83 (2 H, AB q, *J* 13.6, CH_2S), 7.48 (2 H, d, *J* 8.7, Ph) and 8.17 (2 H, d, *J* 8.7, Ph).

S-*Methyl*-S-[1-(*trimethylsilyl*)*ethyl*]*benzylsulfonium Triflate* **8b**.—A solution of **6b** (4.42 g, 19.7 mmol) and methyl triflate (2.7 cm^3, 23.64 mmol) in ether (44 cm^3) was stirred at −15 °C overnight. The solvent was evaporated under reduced pressure and the residue was washed with ether to give the *title salt* **8b** (7.29 g, 95%), m.p. 73–74 °C (Found: C, 43.0; H, 5.85. $C_{14}H_{23}F_3O_3S_2Si$ requires C, 43.30; H, 6.0%); ν_{max}(KBr)/cm^{-1} 1263 and 847 (C–Si). The presence of the diastereoisomers was observed on the ^1H NMR spectrum but assignment was difficult (isomer-1/isomer-2, 5:1); δ_H(500 MHz; $CDCl_3$; Me_4Si); isomer-1: 0.21 (9 H, s, $SiMe_3$), 1.54 (3 H, d, *J* 7.3, CMe), 2.71 (3 H, s, SMe), 2.94 (1 H, q, *J* 7.3, CHS), 4.70 and 4.76 (2 H, AB q, *J* 12.3, CH_2S) and 7.37–7.41 (5 H, m, Ph); isomer-2: 0.25 (9 H, s, $SiMe_3$), 1.58 (3 H, d, *J* 7.4, CMe), 2.79 (3 H, s, SMe), 3.29 (1 H, q, *J* 7.4, CHS), 4.48 and 4.68 (2 H, AB q, *J* 12.8, CH_2S) and 7.51–7.53 (5 H, m, Ph).

S-*Methyl*-S-[(*trimethylsilyl*)*methyl*](4-*methylbenzyl*)*sulfonium Bromide* **8d**.—A solution of 4-methylbenzyl bromide **5d** (2.56 g, 14.90 mmol) and methyl (trimethylsilyl)methyl sulfide [9] (1.47 g, 10.9 mmol) in acetone (15 cm^3) was stirred overnight at room temperature. The solvent was evaporated under reduced pressure and the residue was washed with ether to give the *title salt* **8d** (2.02 g, 58%), m.p. 114–116 °C (Found: C, 48.7; H, 7.2. $C_{13}H_{23}BrSSi$ requires C, 48.9; H, 7.3%); ν_{max}(KBr)/cm^{-1} 1251 and 854 (CSi); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.10 (9 H, s, $SiMe_3$), 1.79 (2 H, s, CH_2Si), 2.15 (3 H, s, SMe), 2.20 (3 H, s, CMe), 4.98 (2 H, s, CH_2S), 7.15 (2 H, d, *J* 8.3, Ph) and 7.28 (2 H, d, *J* 8.3, Ph).

S-*Methyl*-S-[(*trimethylsilyl*)*methyl*](4-*bromobenzyl*)*sulfonium Bromide* **8e**.—In the same way, a solution of 4-bromobenzyl bromide **5e** (2.50 g, 10.0 mmol) and methyl (trimethylsilyl)methyl sulfide (1.38 g, 10.3 mmol) in acetonitrile (15 cm^3) was treated to give the *title salt* **8e** (3.38 g, 88%), m.p. 112–113 °C (Found: C, 37.4; H, 5.2. $C_{12}H_{20}Br_2SSi$ requires C, 37.5; H, 5.2%); ν_{max}(KBr)/cm^{-1} 1251 and 854 (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.10 (9 H, s, $SiMe_3$), 1.79 (2 H, s, CH_2Si), 2.15 (3 H, s, SMe), 4.43 (2 H, s, CH_2S), 7.27 (2 H, d, *J* 8.6, Ph) and 7.47 (2 H, d, *J* 8.6, Ph).

S-*Methyl*-S-[(*trimethylsilyl*)*methyl*](4-*methoxybenzyl*)*sulfonium Triflate* **8f**.—A solution of **6f** (3.24 g, 13.5 mmol) and methyl triflate (1.5 cm^3, 13.3 mmol) in dry ether (15 cm^3) was stirred overnight at −10 °C. The solvent was evaporated under reduced pressure and the residue was washed with ether to give the *title salt* **8f** (5.24 g, 96%), m.p. 65–67 °C (Found: C, 41.4; H, 5.8. $C_{14}H_{23}F_3O_4S_2Si$ requires C, 41.6; H, 5.7%); ν_{max}(KBr)/cm^{-1} 1159 (OMe), 1263 and 852 (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.24 (9 H, s, $SiMe_3$), 2.57 (2 H, s, CH_2Si), 2.79 (3 H, s, SMe), 3.82 (3 H, s, OMe), 4.70 and 4.73 (2 H, AB q, *J* 12.8, CH_2Si), 6.93 (2 H, d, *J* 8.4, Ph) and 7.40 (2 H, d, *J* 8.4, Ph).

S-*Methyl*-S-[1-(*trimethylsilyl*)*ethyl*](4-*methoxybenzyl*)*sulfonium Triflate* **8g**.—A solution of **6g** (2.11 g, 8.3 mmol) and methyl triflate (1.1 cm^3, 9.9 mmol) in ether (13 cm^3) was stirred overnight at −16 °C. The solvent was evaporated and the residue washed with ether to give the *title salt* **8g** (3.26 g, 94%), m.p. 86–87 °C (Found: C, 42.8; H, 6.0. $C_{15}H_{25}F_3O_4S_2Si$ requires C, 43.0; H, 6.0%); ν_{max}(KBr)/cm^{-1} 1254 and 849 (C–Si). The presence of diastereoisomers was observed on the ^1H NMR spectrum but assignment was difficult (isomer-1/isomer-2, 5:1); δ_H(270 MHz; $CDCl_3$; Me_4Si); isomer-1: 0.23 (9 H, s, $SiMe_3$), 1.53 (3 H, d, *J* 7.3, CMe), 2.71 (3 H, s, SMe), 2.89 (1 H, q, *J* 7.3, CHS), 3.81 (3 H, s, OMe), 4.63 and 4.77 (2 H, AB q, *J* 12.5, CH_2S), 6.91 (2 H, d, *J* 8.6, Ph) and 7.42 (2 H, d, *J* 8.6, Ph); isomer-2: 0.28 (9 H, s, $SiMe_3$), 1.59 (3 H, d, *J* 7.3, CMe), 2.78 (3 H, s, SMe), 3.31 (1 H, q, *J* 7.3, CHS), 3.82 (3 H, s, OMe), 4.48 and 4.69 (2 H, AB q, *J* 12.5, CH_2S), 6.89 (2 H, d, *J* 8.3, Ph) and 7.43 (2 H, d, *J* 8.3, Ph).

S-*Methyl*-S-[(*trimethylsilyl*)*methyl*](4-*methoxy*-2-*methylbenzyl*)*sulfonium Triflate* **8h**.—A solution of **6h** (1.63 g, 6.42 mmol) and methyl triflate (0.73 cm^3, 6.45 mmol) in benzene

* This compound was prepared from 3,4-dimethylanisole (3.43 g, 25.18 mmol) with NBS prior to use.[8]

(10 cm^3) was stirred overnight at 0 °C. The solvent was evaporated and the residue was recrystallized from ethyl acetate–ether to give the *title salt* **8h** (2.59 g, 96%), m.p. 106–107 °C (Found: C, 43.3; H, 5.9. $C_{15}H_{25}F_3O_4S_2Si$ requires C, 43.0; H, 6.0%); ν_{max}(KBr)/cm^{-1} 1263 and 850 (C–Si); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.25 (9 H, s, $SiMe_3$), 2.39 (3 H, s, PhMe), 2.57 (1 H, d, *J* 13.7, CH_2Si), 2.89 (1 H, d, *J* 13.7, CH_2Si), 2.89 (3 H, s, SMe), 3.80 (3 H, s, OMe), 4.67 (1 H, d, *J* 12.6, CH_2S), 4.80 (1 H, d, *J* 12.6, CH_2S), 6.75 (1 H, d, *J* 2.7, Ph), 6.77 (1 H, dd, *J* 2.7, 8.1, Ph) and 7.38 (1 H, d, *J* 8.1, Ph).

S-*Methyl*-S-[(*trimethylsilyl*)*methyl*](4-*nitrobenzyl*)*sulfonium Bromide* **8i**.—In a manner similar to that described for **8d**, a solution of 4-nitrobenzyl bromide **5i** (3.24 g, 15.0 mmol) and methyl (trimethylsilyl)methyl sulfide (2.10 g, 15.6 mmol) in acetone (15 cm^3) was treated to give the *title salt* **8i** (2.02 g, 41%), m.p. 119–120 °C (Found: C, 41.1; H, 5.6; N, 4.2. $C_{12}H_{20}BrNO_2SSi$ requires C, 41.1; H, 5.75; N, 4.0%); ν_{max}(KBr)/cm^{-1} 1249 and 854 (C–Si); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.10 (9 H, s, $SiMe_3$), 1.79 (2 H, s, CH_2Si), 2.15 (3 H, s, SMe), 4.51 (2 H, s, CH_2S), 7.56 (2 H, d, *J* 9.6, Ph) and 8.10 (2 H, d, *J* 9.6, Ph).

S-*Methyl*-S-[1-(*trimethylsilyl*)*ethyl*](4-*nitrobenzyl*)*sulfonium Triflate* **8j**.—In a manner similar to that described for **8b**, a solution of **6j** (1.93 g, 7.14 mmol) and methyl triflate (0.97 cm^3, 8.56 mmol) in ether (11 cm^3) was treated to give the *title salt* **8j** (2.54 g, 82%), m.p. 81–82 °C (Found: C, 38.9; H, 5.1; N, 3.0. $C_{14}H_{22}F_3NO_5S_2Si$ requires C, 38.8; H, 5.1; N, 3.2%); ν_{max}(KBr)/cm^{-1} 1262 and 855 (C–Si). The presence of diastereoisomers was observed on the ^1H NMR spectrum but assignment was difficult (isomer–1/isomer–2, 4:1); δ_H(270 MHz; $CDCl_3$; Me_4Si); isomer–1: 0.24 (9 H, s, $SiMe_3$), 1.59 (3 H, d, *J* 6.9, CMe), 2.78 (3 H, s, SMe), 2.95 (1 H, q, *J* 6.9, CHS), 4.88 and 4.99 (2 H, AB q, *J* 12.9, CH_2S), 7.80 (2 H, d, *J* 8.9, Ph) and 8.23 (2 H, d, *J* 8.9, Ph); isomer–2: 0.28 (9 H, s, $SiMe_3$), 1.61 (3 H, d, *J* 7.3, CMe), 2.89 (3 H, s, SMe), 3.35 (1 H, q, *J* 7.3, CHS), 4.69 and 4.99 (2 H, AB q, *J* 12.9, CH_2Ph), 7.77 (2 H, d, *J* 8.9, Ph) and 8.26 (2 H, d, *J* 8.9, Ph).

Reaction of S-*Methyl*-S-[(*trimethylsilyl*)*methyl*]*benzylsulfonium Iodide*[5] **8a** *with* CsF.—The salt **8a** (375 mg, 1.0 mmol) was placed in a 20 cm^3-flask equipped with a magnetic stirrer, a septum, and a test tube which was connected to the flask by a short piece of rubber tubing. CsF (0.76 g, 5 mmol) was placed in the test tube. After the apparatus had been dried under reduced pressure and flushed with N_2, a mixture of DMSO–THF (3:1; 4 cm^3) was introduced at 10 °C with a syringe followed by CsF added from the test tube. The mixture was stirred at 10 °C for 0.5 h and then poured into water (100 cm^3) and extracted with ether (4 × 50 cm^3). The combined extracts were dried ($MgSO_4$), concentrated, and distilled under reduced pressure to give methyl 2-methylbenzyl sulfide[5] **12a** (114 mg, 75%), b.p. 129 °C/1.5 mmHg (Kugelrohr).

When the same reaction was carried out in DMSO (3 cm^3) and quenched after 24 h at room temperature, **12a** (126 mg, 83%) was obtained.

Reaction of **8b** *with* CsF.—In a manner similar to that described above, a mixture of **8b** (388 mg, 1.0 mmol) and CsF (0.76 g, 5 mmol) in DMSO (3 cm^3) was stirred for 24 h at room temperature and worked up to give *methyl* 1-(2-*methylphenyl*)-*ethyl sulfide* **12b** (133 mg, 80%), b.p. 120 °C/2 mmHg (Kugelrohr) (Found: C, 71.95; H, 8.5. $C_{10}H_{14}S$ requires C, 72.2; H, 8.5%); ν_{max}(film)/cm^{-1} 2969, 2916, 1489 and 669; δ_H(500 MHz; $CDCl_3$; Me_4Si) 1.58 (3 H, d, *J* 6.7, CMe), 1.94 (3 H, s, SMe), 2.38 (3 H, s, PhMe), 4.16 (1 H, q, *J* 6.7, CHS), 7.11–7.25 (3 H, m, Ph) and 7.44 (1 H, d, *J* 7.3, Ph).

Reaction of S-*Methyl*-S-[(*trimethylsilyl*)*methyl*](4-*methylbenzyl*)*sulfonium Iodide*[5] **8c** *with* CsF.—In the same way, a mixture of the salt **8c** (766 mg, 2.0 mmol) and CsF (1.52 g, 10.0 mmol) in DMSO (6 cm^3) was stirred for 24 h at room temperature and then worked up. ^1H NMR spectroscopy of the residual oil indicated the presence of 6-methyl-5-methylene-6-[(methylthio)methyl]cyclohexa-1,3-diene[5] **10c** and methyl 1-(2,3-dimethylphenyl)ethyl sulfide[5] **12c**. The ratio was calculated on the basis of the proton ratios of the ^1H NMR spectra (entry 4 in Table 2). The samples were isolated on a HPLC column (Waters μ Bondasphere 5μ Silica-100A, 150 × 19 mm, hexane–dichloromethane, 3:1).

Compound **10c**; λ_{max}(ether)/nm 305 (log ε 3.75); δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.22 (3 H, s, CMe), 2.10 (3 H, s, SMe), 2.55 and 2.68 (2 H, AB q, *J* 12.6, CH_2S), 5.10 (1 H, d, *J* 1.1, $=CH_2$), 5.15 (1 H, s, $=CH_2$), 5.71 (1 H, dd, *J* 9.5, 1.1, 4-H), 5.87 (1 H, m, 2-H), 5.99 (1 H, ddd, *J* 9.5, 5.6, 1.1, 3-H) and 6.16 (1 H, d, *J* 9.3, 1-H).

Reaction of **8d** *with* CsF.—In the same way, a mixture of the sulfonium salt **8d** (320 mg, 1.0 mmol) and CsF (0.76 g, 5.0 mmol) in DMSO–THF (3:1) (4 cm^3) was stirred at 10 °C for 0.5 h and then quenched with water. TLC and ^1H NMR spectra of the ethereal extract indicated that the products were composed of a complex mixture and were difficult to isolate (entry 5 in Table 2).

The same reaction was carried out and quenched with 12 mol dm^{-3} NaOH. The ethereal extract was dried and concentrated. ^1H NMR spectra of the residue (98 mg, 59%) indicated the presence of two isomers: 2-methyl-5-methylene-6-[(methylthio)methyl]cyclohexa-1,3-diene **11d** and methyl 2,5-dimethylbenzyl sulfide[2] **12d**.

Compound **11d** (not isolated); δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.79 (3 H, s, CMe), 2.17 (3 H, s, SMe), 2.60 (2 H, s, CH_2S), 3.07 (1 H, m, CCH), 4.96 (1 H, s, $=CH_2$), 5.08 (1 H, d, *J* 1.0, $=CH_2$), 5.72 (2 H, m, 1-H, 3-H) and 6.10 (1 H, d, *J* 9.5, 4-H).

The same reaction was carried out at room temperature and quenched with water after 24 h. Distillation of the ethereal extract gave **12d** (134 mg, 81%), b.p. 80 °C/2.5 mmHg (Kugelrohr), δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.04 (3 H, s, SMe), 2.30 (3 H, s, PhMe), 2.34 (3 H, s, PhMe), 3.72 (2 H, s, CH_2S), 6.98 (2 H, m, Ph) and 7.05 (1 H, d, *J* 7.5, Ph).

Reaction of **8e** *with* CsF.—In the same way, a mixture of **8e** (320 mg, 1.0 mmol) and CsF (0.76 g, 5.0 mmol) was treated in DMSO (3 cm^3) to give 5-*bromo*-2-*methylbenzyl methyl sulfide* **12e** (171 mg, 74%), b.p. 124 °C/1.5 mmHg (Kugelrohr) (Found: C, 47.0; H, 4.8. $C_9H_{11}BrS$ requires C, 46.8; H, 4.8%); ν_{max}(film)/cm^{-1} 2914, 1485, 1435 and 869; δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.03 (3 H, s, SMe), 2.32 (3 H, s, PhMe), 3.61 (2 H, s, CH_2S), 7.03 (1 H, d, *J* 7.9, Ph) and 7.28–7.32 (2 H, m, Ph).

Reaction of **8f** *with* CsF.—In a manner similar to that described for **8d**, a mixture of **8f** (405 mg, 1.0 mmol) and CsF (0.76 g, 5.0 mmol) in DMSO–THF (3:1, 3 cm^3) was stirred at 10 °C for 0.5 h and worked up with water. The products were a complex mixture (entry 9).

The same reaction was carried out and quenched with 12 mol dm^{-3} NaOH and extracted with ether. The extract was dried and concentrated. ^1H NMR spectroscopy of the residue (109 mg, 60%) showed the presence of 2-methoxy-5-methylene-6-[(methylthio)methyl]cyclohexa-1,3-diene **11f** and 5-methoxy-2-methylbenzyl methyl sulfide[2] **12f**. The ratio was determined from the proton ratios of ^1H NMR spectra (entry 10).

Compound **11f** (not isolated); δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.04 (3 H, s, SMe), 2.51–2.69 (2 H, m, CH_2S), 3.31 (1 H, m, CCH), 3.57 (3 H, s, OMe), 4.92 (1 H, dd, *J* 6.0, 2.4, 1-H), 5.02

(1 H, s, =CH_2), 5.12 (1 H, s, =CH_2), 5.72 (1 H, d, *J* 9.8, 3-H) and 6.15 (1 H, d, *J* 9.8, 4-H).

The same reaction was carried out in DMSO (3 cm^3) at room temperature and quenched with water after 24 h (entry 11). Distillation of the ether extract gave **12f** (136 mg, 75%), b.p. 126 °C/1.5 mmHg (Kugelrohr); δ_H(270 MHz; $CDCl_3$; Me_4Si) 2.03 (3 H, s, SMe), 2.31 (3 H, s, PhMe), 3.63 (2 H, s, CH_2S), 3.78 (3 H, s, OMe), 6.72 (2 H, m, Ph) and 7.06 (1 H, d, *J* 7.5, Ph).

Reaction of **8g** *with* CsF.—In the same way, a mixture of **8g** (420 mg, 1.0 mmol) and CsF (0.76 g, 5 mmol) in DMSO (3 cm^3) was stirred for 72 h at room temperature and worked up to give *methyl* 1-(*2-methyl-5-methoxyphenyl*)*ethyl sulfide* **12g** (170 mg, 87%), b.p. 135 °C/1.5 mmHg (Kugelrohr) (Found: C, 67.0; H, 8.2. $C_{11}H_{16}OS$ requires C, 67.3; H, 8.2%); ν_{max}(film)/cm^{-1} 2967, 2917, 1456 and 1038; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.55 (3 H, d, *J* 6.9, CMe), 1.94 (3 H, s, SMe), 2.30 (3 H, s, PhMe), 3.79 (3 H, s, OMe), 4.11 (1 H, q, *J* 6.9, CHS), 6.69 (1 H, dd, *J* 8.3, 2.6, Ph) and 7.02–7.09 (2 H, m, Ph).

Reaction of **8h** *with* CsF.—In the same way, a mixture of the sulfonium salt **8h** (420 mg, 1.0 mmol) and CsF (0.76 g, 5.0 mmol) in DMSO (3 cm^3) was stirred for 24 h at room temperature and then quenched with water. ^1H NMR spectroscopy of the ethereal extract indicated that the products were a complex mixture.

The same reaction was carried out and quenched with 12 mol dm^{-3} NaOH. ^1H NMR spectroscopy of the residual oil indicated the presence of 2-methoxy-6-methyl-5-methylene-6-[(methylthio)methyl]cyclohexa-1,3-diene **10h** and 5-methoxy-2,3-dimethylbenzyl methyl sulfide **12h**. The ratio was calculated on the basis of the proton ratios of ^1H NMR spectra (entry 14).

The samples were isolated on an HPLC column (Waters μ Bondasphere 5μ Silica-100A, 150 × 19 mm, hexane–ether, 97:3).

Compound **10h** (an undistillable oil); λ_{max}(ether)/nm 310 (log ε 3.90); δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.25 (3 H, s, CMe), 2.10 (3 H, s, SMe), 2.57 and 2.66 (2 H, AB q, *J* 12.6, CH_2S), 3.57 (3 H, s, OMe), 4.63 (1 H, s, 1-H), 5.13 (1 H, s, =CH_2), 5.16 (1 H, s, =CH_2), 5.75 (1 H, d, *J* 9.8, 3-H) and 6.18 (1 H, d, *J* 9.8, 4-H).

Compound **12h**; b.p. 150 °C/1.5 mmHg (Kugelrohr) (Found: C, 67.0; H, 8.1. $C_{11}H_{16}OS$ requires C, 67.3; H, 8.2%); ν_{max}(film)/cm^{-1} 2970, 2917, 1455 and 1038; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.05 (3 H, s, SMe), 2.19 (3 H, s, PhMe), 2.27 (3 H, s, PhMe) 3.66 (2 H, s, CH_2S), 3.77 (3 H, s, OMe), 6.60 (1 H, d, *J* 2.7, Ph) and 6.64 (1 H, d, *J* 2.7, Ph).

A mixture of **8h** (420 mg, 1.0 mmol), CsF (0.76 g, 5.0 mmol) and DBU (0.76 g, 5.0 mmol) in DMSO (3 cm^3) was stirred for 24 h at room temperature and then poured into water (100 cm^3). The ethereal extract was dried ($MgSO_4$), and concentrated under reduced pressure. ^1H NMR spectroscopy of the residual oil showed the presence of **10h** and **12h** (entry 16).

Reaction of **8i** *with* CsF.—In the same way, a mixture of **8i** (351 mg, 1.0 mmol), CsF (0.76 g, 5 mmol) in DMSO (3 cm^3) was stirred for 24 h at room temperature and worked up with water (100 cm^3) to give *methyl 2-methyl-5-nitrobenzyl sulfide* **12i** (153 mg, 78%), b.p. 120 °C/1.5 mmHg (Kugelrohr) (Found: C, 55.0; H, 5.55; N, 7.05. $C_9H_{11}NO_2S$ requires C, 54.8; H, 5.6; N, 7.1%); ν_{max}(film)/cm^{-1} 2968, 2920, 1568, 1493 and 850; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.05 (3 H, d, SMe), 2.49 (3 H, s, PhMe), 3.72 (2 H, s, CH_2S), 7.33 (1 H, d, *J* 8.2, Ph) and 8.05–8.15 (2 H, m, Ph).

Reaction of **8j** *with* CsF.—In the same way, a mixture of **8j** (435 mg, 1.0 mmol) and CsF (0.76 g, 5 mmol) in DMSO–THF (5:3, 4.8 cm^3) was stirred at 0 °C for 0.5 h and then treated to give *methyl* 1-(*2-methyl-5-nitrophenyl*)*ethyl sulfide* **12j** (135 mg, 64%), b.p. 170 °C/0.9 mmHg (Kugelrohr) (Found: C, 56.7; H, 6.1; N, 6.9. $C_{10}H_{13}NO_2S$ requires C, 56.85; H, 6.2; N, 6.6%); ν_{max}(film)/cm^{-1} 2980, 2924, 1586 and 1053; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.62 (3 H, d, *J* 6.9, CMe), 1.96 (3 H, s, SMe), 2.49 (3 H, s, PhMe), 4.16 (1 H, q, *J* 6.9, CHS), 7.30 (1 H, d, *J* 8.3, Ph), 7.99 (1 H, dd, *J* 8.3, 2.3, Ph) and 8.31 (1 H, d, *J* 2.3, Ph).

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