Comparison of the Reaction of Benzylammonium *N*-Methylides with That of Benzylsulfonium *S*-Methylides

Tomofumi NISHIMURA, Chen ZHANG, Yasuhiro MAEDA,* Naohiro SHIRAI, Shin-ichi IKEDA, and Yoshiro SATO

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467–8603, Japan.
Received September 30, 1998; accepted November 19, 1998

Allylbenzylsulfonium *S*-methylides 8*S* and dibenzylsulfonium *S*-methylides 18*S* have been generated by the fluoride ion-induced desilylation of *S*-benzyl-*S*-[(trimethylsilyl)methyl](alk-2-enyl)sulfonium salts 4*S* and *S*-benzyl-*S*-[(trimethylsilyl)methyl](4-substituted benzyl)sulfonium salts 7*S*, and the isomerized products are compared with those of the corresponding *N*-methylides. *S*-Methylides 8*S* selectively rearrange toward the allyl groups (path *a* in Chart 2), whereas rearrangement to the benzyl groups (path *b*) competitively occurs in *N*-methylides 8*N*. Isomerization of *S*-methylides 18*S* to *S*-benzylides 19*S* and 20*S* competes with sigmatropic rearrangement to the benzyl groups (paths *a* and *b* in Chart 3), whereas the isomerization of *N*-methylides 18*N* is not observed.

Key words ammonium ylide; sulfonium ylide; Sommelet–Hauser rearrangement; Stevens rearrangement; sigmatropic rearrangement

Stevens rearrangement and Sommelet–Hauser rearrangement are common and competing isomerization routes for benzylammonium and benzylsulfonium ylides.[1,2] Benzylammonium *N*-alkylides, prepared by the fluoride ion-induced desilylation of *N*-methyl-*N*-[1-(trimethylsilyl)alkyl]benzylammonium salts, are initially isomerized to isotoluene derivatives *via* a [2, 3] sigmatropic migration pathway, and are then converted into Sommelet–Hauser rearrangement and/or Stevens rearrangement. The former route is superior when the *para*-substituent of the benzene ring is an electron-releasing or a weak electron-withdrawing group, and the latter becomes the main route when the substituent is a strong electron-withdrawing group.[2]

However, benzylsulfonium *S*-alkylides, which are similarly generated by desilylation of *S*-methyl-*S*-[1-(trimethylsilyl)-alkyl]benzylsulfonium salts, rearrange exclusively to Sommelet–Hauser products. The formation of Stevens products is not observed regardless of the physicochemical relationships of the *para*-substituents of the benzene rings.[3] These results conflict with previous papers describing the Stevens rearrangement of *S*-ylides, *e.g.*, the formation of 1-(methylsulfanyl)-1,2-diphenylethane (**28**) from *S*-methylbenzylsulfonium *S*-benzylide (**19*S*a**) (Chart 4).[4]

To compare the chemical behavior of *S*-methylides with *N*-methylides, *S*-benzyl-*S*-[(trimethylsilyl)methyl](alk-2-enyl)-sulfonium salts **4*S*** and *S*-benzyl-*S*-[(trimethylsilyl)methyl](4-substituted benzyl)sulfonium salts **7*S*** which are analogous compounds of the reported ammonium salts, were prepared and allowed to react with cesium fluoride.[5—7]

Results and Discussion

The required starting compounds, **4*S*** and **7*S*** were prepared by reacting phenylmethanethiol (**1**) with 3-substituted prop-2-enyl bromides **2** or 4-substituted benzyl bromides **5** followed by treatment with (trimethylsilyl)methyl triflate (Chart 1).

The allylbenzylsulfonium salts **4*S*** were treated with cesium fluoride in *N*,*N*-dimethylformamide (DMF) at room temperature, in a manner similar to that reported for the desilylation of *N*-benzyl-*N*-methyl-*N*-[(trimethylsilyl)methyl]-(alk-2-enyl)ammonium salts **4*N*** (Chart 2).[5,6] The results are listed in Table 1 together with those of **4*N***. The reaction of **4*N*** gives a variety of products. Two [2, 3] sigmatropic rearrangement routes of **8*N*a—d** to allyl groups (path *a*) and to benzyl groups (path *b*) compete with each other to give **9*N*a—d** and **11*N*a—d** (entries 1—4). Stevens rearrangement products **12*N*f**, silyl-compounds **13*N*e, f**, fluoro-compounds **14*N*e, f** and aldehydes **15*N*f** are formed when R^1 is a strong electron-withdrawing group (**4*N*e, f**) (entries 5—7). These formation routes were discussed in a previous paper.[6]

In contrast to these complex results with *N*-methylides, *S*-methylides **8*S*a—f**, which were generated from **4*S*a—f**, rearranged selectively toward the allyl groups to give **9*S*a—f** (path *a*), while **9*S*e, f** in which R^2 is an acidic hydrogen, isomerized to **10*S*e, f** (entries 8—13), and **9*S*d**, in which R^1 is chlorine, hydrolyzed to **16** and **17** during aqueous workup. The formyl group of **17** should originate from DMF because **17** was not formed when the same reaction was carried out in dimethoxyethane (DME). The formation of fluoro-compounds **14*N*e, f** from *N*-ylides **8*N*e, f** increased when a solution of **4*N*e, f** in DMF was added to a suspension of cesium fluoride in DMF at 60 °C (entries 6, 7).[6] However, changes in the product from **4*S*f** were not observed under similar reaction conditions (entry 14).

Dibenzylsulfonium salts **7*S*a—e** were similarly treated with cesium fluoride in DMF at room temperature and the results are listed in Table 2 together with those reported for dibenzylammonium salts **7*N*** (Chart 3, Table 2).[7] Competitive rearrangement toward both benzene rings occurred in *N*-methylide **18*N*b**, in which R is a methyl group (paths *a* and *b*), to give two Sommelet–Hauser rearrangement products **23*N*b** and **25*N*b** (entry 2). When R was a methoxy group, rearrangement occurred selectively toward the non-substituted benzyl group to give **23*N*c** (entry 3). When R was a strong electron-withdrawing group (CN or NO_2), rearrangement occurred toward the substituted benzyl groups, and Stevens rearrangement to give **26*N*d, e** becomes the main path (entries 4, 5). Thus, the rearrangement of *N*-methylide is favored with electron-deficient benzene rings, and Sommelet–Hauser and Stevens rearrangements then compete with each other.

* To whom correspondence should be addressed.

In the reaction of dibenzylsulfonium **7*S*a** and benzyl(4-methylbenzyl)sulfonium salts **7*S*b**, methyl benzyl sulfides **21*S*a**, **b** and **22*S*a**, **b** were formed together with the expected Sommelet–Hauser rearrangement products **23*S*a**, **b** and **25*S*a**, **b** of *S*-methylides **18*S*a**, **b** (entries 6, 8). *S*-Methylides **18*S*d**, **e** (R=CN or NO_2) rearranged selectively toward electron-deficient benzene rings (path *b*) to give Sommelet–Hauser rearrangement products **25*S*d**, **e**. The presence of Stevens products **24*S*** and **26*S*** was not observed. Methoxy-substituted *S*-ylide **18*S*c** led to a complex mixture which was difficult to separate (entry 9).

Compounds **21*S*** and **22*S*** should be produced from sulfonium benzylides **19*S*** and **20*S*** *via* a respective [2, 3] sigmatropic rearrangement pathway. When the reaction of **7*S*a** was repeated at 0 °C, the only product was **21*S*a** (=**22*S*a**). Thus, even in non-basic media, isomerization of *S*-methylide **18*S*a** to *S*-benzylide **19*S*a** (=**20*S*a**) occurs more quickly than sigmatropic rearrangement to give **23*S*a** (=**25*S*a**) at 0 °C.

Padwa and Gasdaska[8] reported in the reaction of *S*-methyl-*S*-[(trimethylsilyl)methyl]benzylsulfonium salts with cesium fluoride in the presence of aldehydes that the initially formed *S*-methylides rapidly come to equilibrium with the thermodynamically more stable benzylides. This report coincides with our results, however, [1, 2] migration of the benzyl groups (Stevens rearrangement) of **19*S*** and/or **20*S*** has not been observed, despite several studies[4] on the competitive formation of Stevens products; *e.g.*, Boekelheide and a

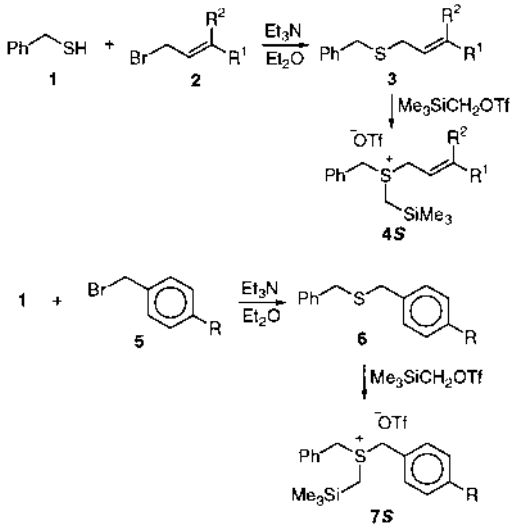

Chart 1

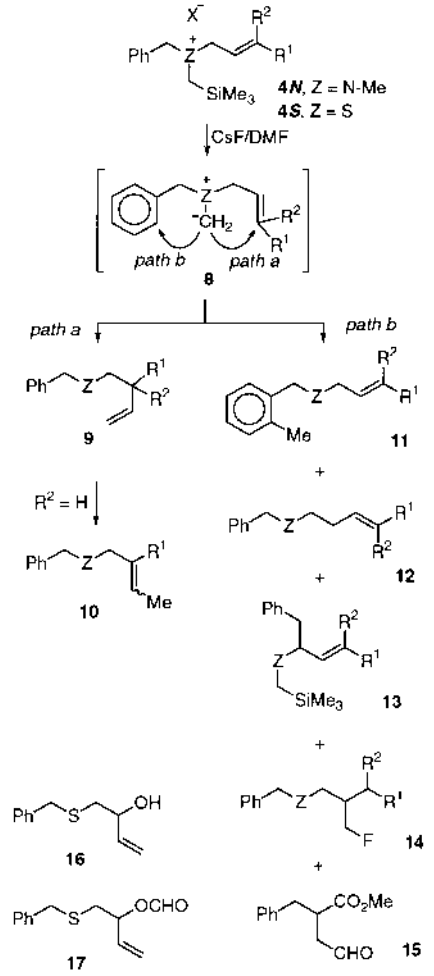

Chart 2

Table 1. Reaction of *N*-Benzyl-*N*-methyl-*N*-[(trimethylsilyl)methyl](alk-2-enyl)ammonium Salts **4*N*** and *S*-Benzyl-*S*-[(trimethylsilyl)methyl](alk-2-enyl)sulfonium Salts **4*S*** with CsF in DMF at Room Temperature

Entry		Z	R^1	R^2	X	Total yield (%)	Product ratio[a]						
							9	**10**	**11**	**12**	**13**	**14**	**15**
1	**4*N*a**	N-Me	H	H	Br	61	50	0	50	0	0	0	0
2	**4*N*b**	N-Me	Me	H	Cl	50	34	0	66	0	0	0	0
3	**4*N*c**	N-Me	Me	Me	Br	74	0	0	100	0	0	0	0
4	**4*N*d**	N-Me	Cl	H	PF_6	94	45	0	50	5	0	0	0
5	**4*N*e**	N-Me	CN	H	PF_6	90[b]	0	8	0	0	10	82	0
6	**4*N*f**	N-Me	CO_2Me	H	PF_6	32	0	9	0	9	66	0	16
7	**4*N*f**	N-Me	CO_2Me	H	ClO_4	84[b]	0	0	0	13	15	67	5
8	**4*S*a**	S	H	H	OTf	60[c]	100	0	0	0	0	0	0
9	**4*S*b**	S	Me	H	OTf	93[c]	100	0	0	0	0	0	0
10	**4*S*c**	S	Me	Me	OTf	98	100	0	0	0	0	0	0
11	**4*S*d**	S	Cl	H	ClO_4	76[d]	0	0	0	0	0	0	0
12	**4*S*e**	S	CN	H	OTf	33[c]	0	100	0	0	0	0	0
13	**4*S*f**	S	CO_2Me	H	ClO_4	90	0	100	0	0	0	0	0
14	**4*S*f**	S	CO_2Me	H	ClO_4	90[b]	0	100	0	0	0	0	0

a) Ratio of the products determined by integration of the ^1H signals at 500 MHz. *b*) A solution of **4*N*e**, **f** or **4*S*f** in DMF was slowly added to a suspension of CsF in DMF at 60 °C. *c*) Yield from **3**. *d*) Compounds **16** and **17** were obtained in 76% yield (ratio, 76 : 24).

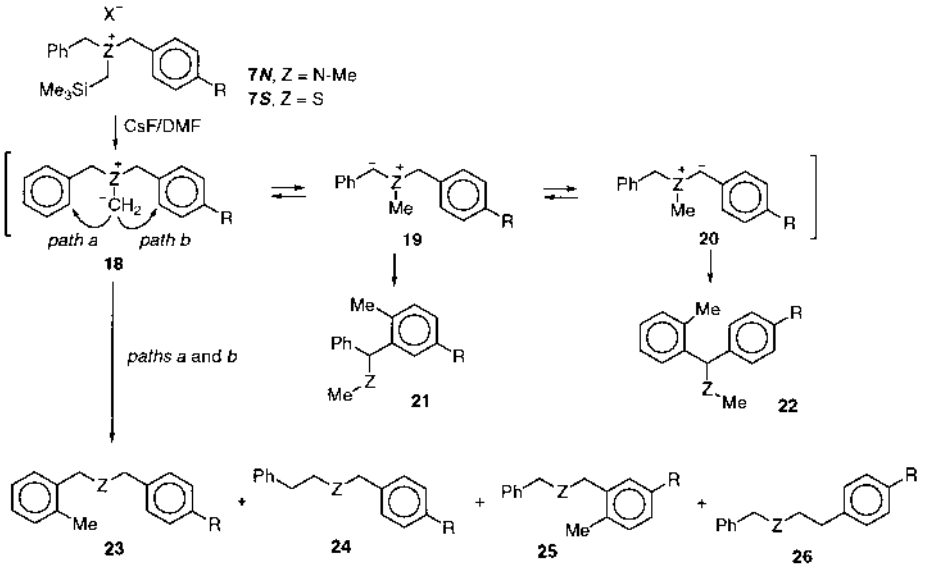

Chart 3

Table 2. Reaction of *N*-Benzyl-*N*-[(trimethylsilyl)methyl](substituted benzyl)ammonium Salts **7*N*** and *S*-Benzyl-*S*-[(trimethylsilyl)methyl](substituted benzyl)sulfonium Salts **7*S*** with CsF in DMF at Room Temperature

Entry		Z	R	X	Total yield (%)	Product ratio[a]					
						21	**22**	**23**	**24**	**25**	**26**
1	**7*N*a**	N-Me	H	I	95	0	0	49	1	49	1
2	**7*N*b**	N-Me	Me	I	63	0	0	60	0	40	0
3	**7*N*c**	N-Me	OMe	I	75	0	0	100	0	0	0
4	**7*N*d**	N-Me	CN	Br	67	0	0	15	0	25	60
5	**7*N*e**	N-Me	NO_2	Br	68	0	0	6	0	0	94
6	**7*S*a**	S	H	OTf	100	27	27	23	0	23	0
7	**7*S*a**	S	H	OTf	71[b]	50	50	0	0	0	0
8	**7*S*b**	S	Me	ClO_4	100	34	21	31	0	14	0
9	**7*S*c**	S	OMe	OTf	—	Complex mixture					
10	**7*S*d**	S	CN	ClO_4	81	0	0	0	0	100	0
11	**7*S*e**	S	NO_2	ClO_4	89	0	0	0	0	100	0

a) Ratio was determined based on the integrated values in GLC analysis of the mixture. *b*) The reaction was carried out at 0 °C.

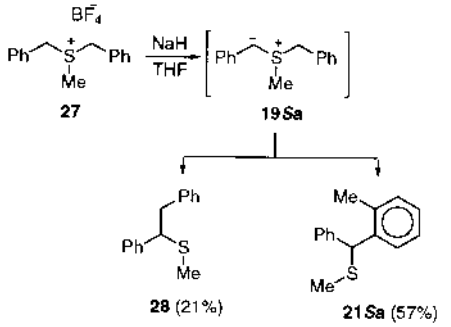

Chart 4

coworker[4d] obtained a Stevens product **28** (21%) and a Sommelet–Hauser product **21*S*a** (57%) *via* ylide **19*S*a** in the reaction of methyldiphenylsulfonium tetrafluoroborate (**27**) with sodium hydride in tetrahydrofuran (THF) (Chart 4).

We previously reported that Stevens rearrangement of ammonium ylides occurs *via* one of the following three processes: i) a [1, 2] radical shift when the radical of the migrating group is stabilized by adjacent group(s); ii) a [1, 2] (ionic?) shift when the migrating group has no adjacent stabilizing group(s) in the presence of a strong base; and iii) a [1, 3] shift from isotoluene intermediates when a [2, 3] sigmatropic rearrangement of ylides is allowed.[9]

Stevens rearrangement of benzylsulfonium ylides occurs only in the aid of strong bases, and the route *via* a [2, 3] sigmatropic rearrangement followed by a [1, 3] shift was not observed (*cf.*, process iii of ammonium ylides). Equilibrium between isomeric ylides is important in sulfonium ylides (*e.g.*, among **18**, **19** and **20**) but not in ammonium ylides.

Experimental

All reactions were carried out under nitrogen. DMF was dried by distillation from BaO under reduced pressure. CsF was dried over P_2O_5 at 190 °C under reduced pressure. Distillation was carried out using a Kugelrohr distillation apparatus. All melting and boiling points are uncorrected.

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]allylsulfonium Triflate (4*S*a) with CsF (Entry 8 in Table 1) A solution of allyl benzyl sulfide[10] (**3*S*a**) (164 mg, 1 mmol) and (trimethylsilyl)methyl triflate (260 mg, 1.1 mmol) in CH_2Cl_2 (3 ml) was stirred at room temperature for 12 h to give **4*S*a**. The solution was mixed with DMF (30 ml) and then concentrated under reduced pressure at 80 °C to *ca.* 10 ml. CsF (460 mg, 3 mmol) was added to the remaining solution and the mixture was stirred for 12 h at room temperature. The mixture was poured into water (100 ml) and extracted with Et_2O. The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distilled to give benzyl but-3-enyl

sulfide (**9*Sa***) (106 mg, 60%), bp 75 °C (0.7 mmHg). IR (film) cm^{-1}: 2917, 1640, 1495, 1452, 916, 700. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 2.20—2.28 (2H, m), 2.39—2.45 (2H, m), 3.66 (2H, s), 4.93—5.02 (2H, m), 5.66—5.81 (1H, m), 7.20—7.26 (5H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 30.7, 34.5, 36.3, 115.8, 126.9, 128.4 (2C), 128.8 (2C), 136.7, 138.4. *Anal*. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 73.77; H, 7.98.

The structure of **4*Sa*** was confirmed by ^{1}H-NMR spectroscopic analysis after the reaction mixture of allyl benzyl sulfide and (trimethylsilyl)methyl triflate was concentrated to give a viscous oil, ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.15 (9H, s), 2.48, 2.55 (2H, ABq, J=14.5 Hz), 4.05 (2H, m), 4.54, 4.72 (2H, ABq, J=12.5 Hz), 5.60 (1H, d, J=9.6 Hz), 5.72 (1H, d, J=16.7 Hz), 5.77—5.89 (1H, m), 7.34—7.39 (3H, m), 7.40—7.51 (2H, m).

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]but-2-enylsulfonium Triflate (4*Sb*) with CsF (Entry 9 in Table 1) In a manner similar to that described above, benzyl but-2-enyl sulfide[11] (**3*Sb***) ($E:Z$=4 : 1) (178 mg, 1 mmol) and (trimethylsilyl)methyl triflate (260 mg, 1.1 mmol) were treated in CH_2Cl_2 (5 ml). A solution of **4*Sb*** in DMF was allowed to react with CsF (460 mg, 3 mmol) and worked up to give benzyl (2-methylbut-3-enyl) sulfide (**9*Sb***) (154 mg, 80%), bp 90 °C (1.0 mmHg). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.05 (3H, d, J=6.3 Hz), 2.31—2.45 (3H, m), 3.70 (2H, s), 4.95—5.00 (2H, m), 5.67—5.79 (1H, m), 7.19—7.31 (5H, m). *Anal*. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.74; H, 8.37.

The structure of **4*Sb*** ($E:Z$=4 : 1) was confirmed by ^{1}H-NMR spectroscopic analysis after concentration of the reaction mixture: a viscous oil, ^{1}H-NMR (270 MHz, $CDCl_3$) (*E*): δ: 0.16 (9H, s), 1.78 (3H, d, J=6.9 Hz), 2.45, 2.56 (2H, ABq, J=14.5 Hz), 4.00 (2H, m), 4.53, 4.72 (2H, ABq, J=12.5 Hz), 5.40 (1H, m), 6.12 (1H, m), 7.40—7.50 (5H, m); (*Z*): δ: 0.18 (9H, s), other signals overlapped with those of the *E*-isomer.

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-3-methylbut-2-enylsulfonium Triflate (4*Sc*) with CsF (Entry 10 in Table 1) A solution of benzyl 3-methylbut-2-enyl sulfide[12] (**3*Sc***) (577 mg, 3 mmol) and (trimethylsilyl)methyl triflate (827 mg, 3.5 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature for 12 h. After evaporation of the solvent under reduced pressure, the residue was washed with Et_2O and recrystallized to give **4*Sc*** (503 mg, 40%), mp 69—71 °C (acetone–Et_2O). IR (KBr) cm^{-1} 2965, 1261, 1032, 851. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 0.18 (9H, s), 1.77 (3H, s), 1.82 (3H, s), 2.53, 2.26 (2H, ABq, J=14.5 Hz), 4.09 (2H, d, J=7.9 Hz), 4.64, 4.76 (2H, ABq, J=12.5 Hz), 5.19 (1H, t, J=7.9 Hz), 7.41—7.51 (5H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: −1.3 (3C), 18.8, 22.5, 26.1, 41.5, 46.9, 109.4, 127.6, 129.8 (2C), 130.2, 130.7 (2C), 148.1. *Anal*. Calcd for $C_{16}H_{27}F_3O_3S_2Si$: C, 47.64; H, 6.35. Found: C, 47.40; H, 6.29.

Salt **4*Sc*** (429 mg, 1 mmol) was placed in a 30-ml flask equipped with a septum and a test tube which was connected to the flask by a short bent piece of glass tubing. CsF (460 mg, 3 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with N_2. DMF (10 ml) was added to the flask by a syringe and CsF was then added from the test tube. The mixture was stirred at room temperature for 12 h and worked up in a manner similar to that described for **4*Sa*** to give benzyl (2,2-dimethyl-but-3-enyl) sulfide (**9*Sc***) (204 mg, 98%), bp 110 °C (1.0 mmHg). IR (film) cm^{-1} 2962, 914, 700. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 1.06 (6H, s), 2.43 (2H, s), 3.70 (2H, s), 4.95 (1H, dd, J=10.6, 1.3 Hz), 4.97 (1H, dd, J=17.8, 1.3 Hz), 5.81 (1H, dd, J=17.8, 10.6 Hz), 7.22—7.31 (5H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 26.3 (2C), 37.9, 38.1, 44.7, 111.3, 126.3 (2C), 128.4 (2C), 128.9, 129.9, 146.8. *Anal*. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79. Found: C, 75.91; H, 8.93.

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-3-chloroprop-2-enylsulfonium Perchlorate (4*Sd*) with CsF (Entry 11 in Table 1) A solution of phenylmethanethiol (**1**) (1.21 g, 10 mmol), (*E*)-1,3-dichloropropene (1.20 g, 11 mmol) and triethylamine (1.11 g, 11 mmol) in Et_2O (100 ml) was stirred for 12 h at room temperature. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column to give benzyl (*E*)-3-chloroprop-2-enyl sulfide (**3*Sd***) (1.05 g, 52%), a colorless oil. IR (KBr) cm^{-1} 1452, 937, 698. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 3.00 (2H, dd, J=7.3, 0.7 Hz), 3.67 (2H, s), 5.89 (1H, dt, J=13.2, 7.3 Hz), 6.00 (1H, dt, J=13.2, 0.7 Hz), 7.21—7.46 (5H, m). *Anal*. Calcd for $C_{10}H_{11}ClS$: C, 60.44;H, 5.56. Found: C, 60.66; H, 5.74.

A solution of **3*Sd*** (0.99 g, 5 mmol) and (trimethylsilyl)methyl triflate (1.4 g, 6 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue (viscous oil) was dissolved in MeOH (10 ml) and mixed with saturated aqueous $NaClO_4$ (10 ml). The mixture was stirred for 0.5 h and extracted with $CHCl_3$ (50 ml×4). The extract was dried ($MgSO_4$) and concentrated under reduced pressure to give **4*Sd*** (1.1 g, 56%), mp 73—75 °C. IR (KBr) cm^{-1} 2361, 1260, 850. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 0.21 (9H, s), 2.56, 2.64 (2H, ABq, J=14.2 Hz), 4.21 (2H, d, J=7.9 Hz), 4.61, 4.80 (2H, ABq, J=12.5 Hz), 5.82 (1H, dt, J=13.2, 7.9 Hz), 6.76 (1H, d, J=13.2 Hz), 7.43—7.47 (5H, m). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 0.0 (3C), 24.0, 44.6, 49.0, 120.2, 126.0, 131.2 (2C), 131.7, 131.9 (2C), 132.8. *Anal*. Calcd for $C_{14}H_{22}C_{12}O_4SSi$: C, 43.63; H, 5.75. Found: C, 43.74; H, 5.82.

In a manner similar to that described for the reaction of **4*Sc*** with CsF (entry 10), **4*Sd*** (385 mg, 1 mmol) and CsF (460 mg, 3 mmol) were treated in DMF (10 ml) and worked up. The residue was chromatographed on a silica gel column (hexane : Et_2O = 5 : 1) to give 1-(benzylsulfanyl)but-3-en-2-ol (**16**) and 1-(benzylsulfanyl)but-3-en-2-yl formate (**17**) (153 mg, 76%).

Compound **16**: A colorless oil, IR (film) cm^{-1} 3420, 1494, 1454, 991, 927, 702. ^{1}H-NMR (400 MHz; $CDCl_3$) δ: 2.46 (1H, s), 2.51 (1H, dd, J=13.6, 8.1 Hz), 2.63 (1H, dd, J=13.6, 4.1 Hz), 3.75 (2H, s), 4.14—4.15 (1H, m), 5.15 (1H, d, J=10.6 Hz), 5.28 (1H, d, J=17.2 Hz), 5.83 (1H, ddd, J=17.2, 10.6, 5.9 Hz), 7.2—7.3 (5H, m). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 36.4, 38.8, 70.5, 115.9, 127.2, 128.6 (2C), 128.9 (2C), 137.9, 138.9. *Anal*. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 67.66; H, 7.24.

Compound **17**: A colorless oil, IR (film) cm^{-1} 1722, 1089, 626. ^{1}H-NMR (500 MHz; $CDCl_3$) δ: 2.61 (1H, dd, J=14.0, 6.1 Hz), 2.67 (1H, dd, J=14.0, 6.7 Hz), 3.71 (2H, s), 5.28 (1H, d, J=17.1 Hz), 5.37 (1H, m), 5.25 (1H, d, J=10.4 Hz), 5.78 (1H, ddd, J=6.7, 10.4, 17.1 Hz), 7.23—7.41 (5H, m), 8.01 (1H, s). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 34.9, 36.6, 73.1, 118.5, 127.2, 128.6 (2C), 129.0 (2C), 134.4, 137.8, 160.0. *Anal*. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35. Found: C, 64.54; H, 6.04.

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-3-cyanoprop-2-enylsulfonium Triflate (4*Se*) with CsF (Entry 12 in Table 1) In a manner similar to that described for entry 8, a solution of 4-(benzylsulfanyl)-crotononitrile[13] (**3*Se***) ($E:Z$=1 : 1) (189 mg, 1 mmol) and (trimethylsilyl)-methyl triflate (261 mg, 1.1 mmol) in CH_2Cl_2 (5 ml) was treated and concentrated after the addition of DMF (20 ml) to *ca.* 10 ml. CsF (460 mg, 3 mmol) was added and treated to give a mixture of 2-(benzylsulfanylmethyl)but-2-enonitrile (**10*Se***) ($E:Z$=5 : 1, determined by integration of the ^{1}H-NMR signals at 270 MHz), a colorless oil (67 mg, 33%), IR (film) cm^{-1} 2220, 1495, 1452, 702. ^{1}H-NMR (270 MHz; $CDCl_3$) (*Z*): δ: 1.70 (3H, d, J=7.2 Hz), 3.22 (2H, s), 3.83 (2H, s), 6.51 (1H, q, J=7.2 Hz), 7.22—7.43 (5H, m); (*E*): δ: 2.00 (3H, dd, J=6.9, 1.0 Hz), 3.08 (2H, t, J=1.0 Hz), 3.68 (2H, s), 6.22 (1H, q, J=6.9 Hz), 7.22—7.43 (5H, m); the nuclear overhauser effect (NOE) enhancement (4.6%) of vinyl proton (δ 6.22) was observed upon irradiation of the allyl proton (δ 3.08). ^{13}C-NMR (100 MHz; $CDCl_3$) (*Z*): δ: 17.1, 34.0, 35.6, 113.2, 116.7, 127.3, 127.3 (2C), 128.6 (2C), 137.2, 144.2; (*E*): δ: 14.5, 28.0, 35.8, 144.7 (other signals overlapped those of the (*Z*)-isomer). *Anal*. Calcd for $C_{12}H_{13}NS$: C, 70.90; H, 6.45; N, 6.89. Found: C, 70.69; H, 6.45; N, 6.74.

The structure of **4*Se*** ($E:Z$=1 : 1) was confirmed by ^{1}H-NMR spectroscopic analysis after concentration of the reaction mixture: a viscous oil, ^{1}H-NMR (500 MHz, $CDCl_3$) (*Z*): δ: 0.25 (9H, s), 2.63, 2.75 (2H, ABq, J=14.0 Hz), 4.19—4.38 (2H, m), 4.83, 4.86 (2H, ABq, J=7.6 Hz), 5.87 (1H, d, J=11.0 Hz), 6.49—6.56 (1H, m), 7.29—7.58 (5H, m); (*E*): δ: 0.21 (9H, s), 2.61, 2.72 (2H, ABq, J=14.6 Hz), 4.19—4.38 (2H, m), 4.61, 4.70 (2H, ABq, J=7.6 Hz), 5.98 (1H, d, J=15.9 Hz), 6.69—6.74 (1H, m), 7.29—7.58 (5H, m).

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-3-(methoxycarbonyl)-prop-2-enylsulfonium Perchlorate (4*Sf*) with CsF (Entries 13 and 14 in Table 1) A solution of methyl (*E*)-4-(benzylsulfanyl)crotonate[14] (**3*Sf***) (994 mg, 5 mmol) and (trimethylsilyl)methyl triflate (1.4 g, 6 mmol) in CH_2Cl_2 (10 ml) was allowed to react in a manner similar to that described for entry 11, and the counter ion was changed to perchlorate with saturated aqueous $NaClO_4$ to give **4*Sf*** (1.4 g, 69%), mp 108—110 °C. IR (KBr) cm^{-1} 1720, 1211, 850. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 0.24 (9H, s), 2.67 (2H, s), 3.74 (3H, s), 4.27 (2H, d, J=7.6 Hz), 4.67, 4.84 (2H, ABq, J=12.5 Hz), 6.65 (1H, d, J=5.0 Hz), 6.59—6.71 (1H, m), 7.47—7.53 (5H, m). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 0.0 (3C), 24.3, 44.2, 49.1, 53.3, 127.6, 131.2, 131.7 (2C), 131.8 (2C), 132.5, 133.3. *Anal*. Calcd for $C_{16}H_{25}ClO_6SSi$: C, 47.00; H, 6.16. Found: C, 46.82; H, 6.03.

(Method A): Salt **4*Sf*** (409 mg, 1 mmol) and CsF (460 mg, 3 mmol) were allowed to react in DMF (10 ml) in a manner similar to that described for entry 10, and worked up to give a mixture of methyl 2-(benzylsulfanylmethyl)but-2-enoate (**10*Sf***) ($E:Z$=10 : 1; determined by integration of the ^{1}H-NMR signals), a colorless oil (212 mg, 90%), bp 120 °C (0.4 mmHg). IR (film) cm^{-1} 1716, 1435, 1279, 1194. ^{1}H-NMR (270 MHz; $CDCl_3$) (*Z*): δ: 1.75 (3H, d, J=7.3 Hz), 3.39 (2H, s), 3.75 (5H, s), 6.93 (1H, q, J=7.3 Hz), 7.20—7.42 (5H, m); (*E*): δ: 2.02 (3H, d, J=6.9 Hz), 3.25 (2H, s), 3.77 (5H, s), 6.01 (1H, q, J=6.9 Hz), 7.20—7.42 (5H, m); the NOE enhancement (4.2%) of vinyl proton (δ 6.01) was observed upon irradiation of the allyl

proton (δ 3.25). ^{13}C-NMR (100 MHz; $CDCl_3$) (*Z*): δ: 14.5, 26.9, 36.8, 51.9, 127.0, 128.4 (2C), 128.9 (2C), 130.0, 138.2, 139.9, 167.3; (*E*): δ: 15.6, 35.5, 129.4, 130.0, 138.8 (other signals overlapped those of the (*Z*)-isomer). *Anal*. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.87; H, 6.75.

(Method B): A solution of **4*Sf*** (409 mg, 1 mmol) in DMF (10 ml) was added dropwise to a suspension of CsF (460 mg, 3 mmol) in DMF (15 ml) at 60 °C and stirring was continued for 3 h. The mixture was worked up to give **10*Sf*** (212 mg, 90%).

Reaction of [(Trimethylsilyl)methyl]dibenzylsulfonium Triflate (7*Sa*) with CsF (Entry 6 in Table 2) A solution of dibenzyl sulfide **6*Sa*** (1.1 g, 5.0 mmol) and (trimethylsilyl)methyl triflate (1.4 g, 6.0 mmol) in CH_2Cl_2 (15 ml) was stirred at room temperature for 12 h and the solvent was evaporated under reduced pressure. The residue was washed with Et_2O and recrystallized to give **7*Sa*** (2.1 g, 92%), mp 123—125 °C (EtOH–Et_2O). IR (KBr) cm^{-1} 2999, 1283, 1150, 849. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: −0.01 (9H, s), 2.56 (2H, s), 4.69, 4.81 (4H, ABq, *J*=12.5 Hz), 7.40—7.48 (10H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: −1.7 (3C), 22.3, 47.6 (2C), 127.3 (2C), 129.8 (4C), 130.2 (2C), 130.7 (4C). *Anal*. Calcd for $C_{18}H_{25}F_3O_3S_2Si$: C, 50.64; H, 5.59. Found: C, 50.59; H, 5.57.

Salt **7*Sa*** (451 mg, 1 mmol) and CsF (460 mg, 3 mmol) were treated in DMF (5 ml) and worked up in a manner similar to that described for entry 10 in Table 1. Silica gel column chromatography of the residue gave a mixture (228 mg, 100%) of methyl α-phenyl-2-methylbenzyl sulfide (**21*Sa***) (=**22*Sa***) and benzyl 2-methylbenzyl sulfide (**23*Sa***) (=**24*Sa***). The proportion was determined by GC analysis because separation was difficult.

A mixture of **21*Sa*** and **23*Sa***: a colorless oil. ^{1}H-NMR (270 MHz; $CDCl_3$) **21*Sa***: δ: 2.00 (3H, s), 2.34 (3H, s), 5.24 (1H, s), 7.13—7.60 (9H, m); **23*Sa***: δ: 2.31 (3H, s), 3.60 (2H, s), 3.66 (2H, s), 7.13—7.60 (9H, m). MS (EI, 70 eV) *m/z* (rel. int. %) **21*Sa***: 228 (M^+, 67), 181 (100, M−MeSH); **23*Sa***: 228 (M^+, 55), 105 (100, M−$C_6H_5CH_2S$), 91 (43). *Anal*. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 79.13; H, 7.10.

(Entry 7) The same reaction was carried out at 0 °C and worked up to give **21*Sa*** (=**22*Sa***) (162 mg, 71%).

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-4-methylbenzylsulfonium Perchlorate (7*Sb*) with CsF (Entry 8 in Table 2) A solution of benzyl 4-methylbenzyl sulfide[15] (**6*Sb***) (1.2 g, 5.0 mmol) and (trimethylsilyl)methyl triflate (1.4 g, 6 mmol) in CH_2Cl_2 (10 ml) was allowed to react and then treated with saturated aqueous $NaClO_4$, in a manner similar to that described for entry 11 in Table 1, to give **7*Sb*** (1.8 g, 85%), mp 121—123 °C. IR (KBr) cm^{-1} 845. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: −0.01 (9H, s), 2.34 (3H, s), 2.53 (2H, s), 4.58—4.78 (4H, m), 7.17—7.48 (9H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: −1.6 (3C), 21.3, 22.4, 47.7, 47.8, 124.0, 127.3, 130.0, 130.2 (2C), 130.5 (2C), 130.7 (2C), 130.7 (2C), 140.5. *Anal*. Calcd for $C_{19}H_{27}ClO_4SSi$: C, 54.99; H, 6.78. Found: C, 54.73; H, 6.65.

Salt **7*Sb*** (415 mg, 1 mmol) and CsF (460 mg, 3 mmol) were treated in DMF (5 ml) and worked up. Distillation of the residue gave a mixture of methyl α-phenyl-2,5-dimethylbenzyl sulfide (**21*Sb***), methyl α-(2-methylphenyl)-4-methylbenzyl sulfide (**22*Sb***), 2-methylbenzyl 4-methylbenzyl sulfide (**23*Sb***) and benzyl 2,5-dimethylbenzyl sulfide (**25*Sb***) (240 mg, 100%; ratio, 34 : 21 : 31 : 14), bp 105 °C (0.7 mmHg). *Anal*. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.49. Found: C, 79.47; H, 7.50. The structure of each compound was estimated by GC–mass spectrometry (5% SE–30, 2 m) because separation was difficult. The product ratio was determined by GC (5% SE–30, 2 m); ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 1.99 (s), 2.00 (s), 2.23 (s), 2.28 (s), 2.31 (s), 2.34 (s), 3.57 (s), 3.60 (s), 3.63 (s), 3.67 (s) 5.21 (s), 6.96—4.39 (m) (further assignment was difficult); MS (EI, 70 eV) *m/z* (rel. int. %) **21*Sb***: 242 (M^+, 8), 195 (100, M−MeS), 165 (33, M−C_6H_5), 137 (86, M−$Me_2C_6H_4$), 91 (8); **22*Sb***: 242 (M^+, 3), 195 (100, M−MeS), 152 (5, M−MeC_6H_5), 105 (2, 152−MeS); **23*Sb***: 242 (M^+, 79), 137 (17, M−$MeC_6H_5CH_2$), 105 (100, M−$MeC_6H_5CH_2S$); **25*Sb***: 242 (M^+, 54), 151 (15, M−$C_6H_5CH_2$), 118 (100, M−$C_6H_5CH_2S$), 91 (29).

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-4-methoxybenzylsulfonium Triflate (7*Sc*) with CsF (Entry 9 in Table 2) A solution of benzyl 4-methoxybenzyl sulfide[15] (**6*Sc***) (164 mg, 1.0 mmol) and (trimethylsilyl)-methyl triflate (260 mg, 1.1 mmol) in CH_2Cl_2 (10 ml) was treated in a manner similar to that described for entry 8 in Table 1, and a solution of **7*Sc*** in DMF was then allowed to react with CsF (460 mg, 3 mmol). The products were a complex mixture which was difficult to separate.

The structure of **7*Sc*** was confirmed by ^{1}H-NMR spectroscopic analysis after concentration of the reaction mixture of benzyl 4-methoxybenzyl sulfide and (trimethylsilyl)methyl triflate. a viscous oil, ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.02 (9H, s), 2.51 (2H, s), 3.80 (3H, s), 4.58—4.77 (4H, m), 6.91 (2H, d, *J*=8.9 Hz), 7.38—7.48 (7H, m).

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-4-cyanobenzylsulfonium Perchlorate (7*Sd*) with CsF (Entry 10 in Table 2) In a manner similar to that described for entry 11 in Table 1, **1** (4.8 g, 28 mmol), 4-cyanobenzyl bromide (5.9 g, 30 mmol) and triethylamine (2.8 g, 28 mmol) were allowed to react in CH_2Cl_2 (50 ml) to give benzyl 4-cyanobenzyl sulfide (**6*Sd***) (3.15 g, 47%), mp 59—61 °C. IR (KBr) cm^{-1} 2222, 1495, 1454. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 3.60 (4H, s), 7.23—7.38 (7H, m), 7.58 (2H, d, *J*=7.9 Hz). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 35.3, 35.8, 110.9, 118.8, 127.3 (2C), 128.6 (2C), 129.0, 129.7 (2C), 132.3 (2C), 137.4, 144.0. *Anal*. Calcd for $C_{15}H_{13}NS$: C, 75.28; H, 5.47; N, 5.85. Found: C, 75.21; H, 5.54; N, 5.63.

A solution of **6*Sd*** (1.21 g, 5 mmol) and (trimethylsilyl)methyl triflate (1.42 g, 6 mmol) in CH_2Cl_2 (30 ml) was allowed to react and then treated with saturated aqueous $NaClO_4$ (10 ml) to give **7*Sd*** (1.81 g, 83%), mp 101—103 °C (EtOH–Et_2O). IR (KBr) cm^{-1} 2231, 854. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 0.00 (9H, s), 2.57, 2.67 (2H, ABq, *J*=14.5 Hz), 4.68, 4.78 (2H, ABq, *J*=12.9 Hz), 4.88, 4.89 (2H, ABq, *J*=12.9 Hz), 7.34—7.47 (5H, m), 7.60—7.70 (4H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: −1.60 (3C), 23.2, 47.3, 48.5, 114.1, 117.6, 126.9, 129.9 (2C), 130.5 (2C), 130.7 (2C), 131.5, 132.9, 133.3 (2C). *Anal*. Calcd for $C_{19}H_{24}ClNO_4SSi$: C, 53.57; H, 5.68; N, 3.29. Found: C, 53.45; H, 5.59; N, 2.92.

Salt **7*Sd*** (426 mg, 1 mmol) and CsF (460 mg, 3 mmol) were treated in DMF (5 ml) and worked up in a manner similar to that described for entry 6 in Table 2. The residue was chromatographed on a silica gel column (hexane : Et_2O=9 : 1) to give benzyl 5-cyano-2-methylbenzyl sulfide (**25*Sd***) (205 mg, 81%) as a colorless oil, IR (film) cm^{-1} 2213. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 2.33 (3H, s), 3.56 (2H, s), 3.66 (2H, s), 7.21—7.44 (8H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 19.5, 32.9, 36.3, 109.6, 118.9, 127.2 (2C), 128.6 (2C), 128.9, 130.7, 131.2, 132.8, 137.4, 137.5, 142.7. MS (EI, 70 eV) *m/z* (rel. int. %) 253 (M^+, 100), 162 (10), 129 (49), 123 (19), 91 (99). *Anal*. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.56; H, 6.08; N, 5.57.

Reaction of *S*-Benzyl-*S*-[(trimethylsilyl)methyl]-4-nitrobenzylsulfonium Perchlorate (7*Se*) with CsF (Entry 11 in Table 2) In a manner similar to that described for entry 11 in Table 1, a solution of **6*Se***[16] (1.31 g, 5 mmol) and (trimethylsilyl)methyl triflate (1.42 g, 6 mmol) in CH_2Cl_2 (30 ml) was allowed to react and then treated with saturated aqueous $NaClO_4$ (10 ml) to give **7*Se*** (1.40 g, 65%), mp 146—149 °C. IR (KBr) cm^{-1} 1524, 1354, 1065, 853. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 0.02 (9H, s), 2.52, 2.64 (2H, ABq, *J*=14.2 Hz), 4.63, 4.74 (2H, ABq, *J*=13.5 Hz), 4.79, 4.82 (2H, ABq, *J*=12.9 Hz), 7.32—7.42 (5H, m), 7.62 (2H, d, *J*=8.5 Hz), 8.18 (2H, d, *J*=8.5 Hz). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: −1.6 (3C), 23.4, 46.9, 48.5, 124.6 (2C), 126.7, 129.9 (2C), 130.5 (2C), 130.6 (2C), 131.8, 134.7, 148.7. *Anal.* Calcd for $C_{18}H_{24}ClNO_6SSi$: C, 48.48; H, 5.42; N, 3.14. Found: C, 48.73; H, 5.36; N, 2.88.

Salt **7*Se*** (446 mg, 1 mmol) and CsF (460 mg, 3 mmol) were treated in DMF (5 ml) and the residue was chromatographed on a silica gel column (Et_2O) to give benzyl 2-methyl-5-nitrobenzyl sulfide (**25*Se***) (295 mg, 89%) as a colorless oil, IR (film) cm^{-1} 1520, 1348. ^{1}H-NMR (270 MHz; $CDCl_3$) δ: 2.38 (3H, s), 3.62 (2H, s), 3.68 (2H, s), 7.23—7.34 (6H, m), 7.48—8.01 (2H, m). ^{13}C-NMR (125 MHz; $CDCl_3$) δ: 19.4, 33.2, 36.3, 122.1, 124.3, 127.3, 128.6 (2C), 129.0 (2C), 131.2, 137.4, 137.6, 144.9, 146.2. MS (EI, 70 eV) *m/z* (rel. int. %) 273 (M^+, 96), 182 (5), 149 (15), 91 (100). *Anal*. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.75; H, 5.65; N, 5.00.

References

1) Markó I. E., in "Comprehensive Organic Synthesis," ed. by Trost B. M., Fleming I., Pergamon Press, Oxford, 1991, Vol. 3, p. 913; Lepley A. R., Giumanini A. G., in "Mechanisms of Molecular Migrations," ed. by Thyagarajan B. S., Wiley-Interscience, New York, 1971, Vol. 3, p. 297.
2) Nakano M., Sato Y., *J. Org. Chem*., **52**, 1844—1847 (1987); Okazaki S., Shirai N., Sato Y., *ibid*., **55**, 334—337 (1990); Shirai N., Watanabe Y., Sato Y., *ibid*., **55**, 2767—2770 (1990); Tanaka T., Shirai N., Sugimori J., Sato Y., *ibid*., **57**, 5034—5036 (1992).
3) Tanzawa T., Ichioka M., Shirai N., Sato Y., *J. Chem. Soc*., *Perkin Trans. 1*, **1995**, 431—435.
4) *a*) Hayashi Y., Oda R., *Tetrahedron Lett*., **1968**, 5381—5384; *b*) Schöllkopf U., Ostermann G., Schossig J., *ibid*., **1969**, 2619—2622; *c*) Ratts K. W., Yao A. N., *J. Org. Chem*., **33**, 70—75 (1968); *d*) Mitchell R. H., Boekelheide V., *J. Am. Chem. Soc*., **96**, 1547—1557 (1974).
5) Sugiyama H., Sato Y., Shirai N., *Synthesis*, **1988**, 988—990.
6) Zhang C., Maeda Y., Sato Y., *Chem. Pharm. Bull*., **46**, 572—576 (1998).

7) Tanaka T., Shirai N., Sato Y., *Chem. Pharm. Bull.,* **40**, 518—520 (1992).
8) Padwa A., Gasdaska R., *Tetrahedron*, **44**, 4147—4156 (1988).
9) Maeda Y., Sato Y., *J. Chem. Soc*., *Perkin Trans. 1*, **1997**, 1491—1493.
10) Kögl F., Verbeek J. H., Erxleben H., Borg W. A. J., *Z. Physiol. Chem*., **279**, 121—139 (1943).
11) Sih J. C., Graber D. R., *J. Org. Chem*., **49**, 5206—5213 (1984).
12) Huynh C., Ratovelomanana V., Julia S., *Bull. Soc. Chim. Fr*., **1977**, 710—716.
13) Eck D. L., Stacy G. W., *J. Heterocycl. Chem*., **6**, 147—151 (1969).
14) Birkofer L., Birkofer A., *Chem. Ber*., **89**, 1226—1229 (1956).
15) Tullen D. L., *J. Org. Chem*., **32**, 4006—4008 (1967).
16) Wakasaka M., Hatanaka, M., Nitta H., Hatamura M., *Synthesis*, **1980**, 67—68.