Relationship between the Configurations of 2-Phenyltetrahydrothiophenium 1-Methylides and Their Rearrangement Products

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Received May 15, 2000

trans-2-Phenyltetrahydrothiophenium 1-methylide (*trans*-**3**), which is generated by fluoride ion-induced desilylation of *trans*-2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiophenium salt (*trans*-**2**), gave a mixture of 1,4,5,10a-tetrahydro-3*H*-2-benzothiocine (**4**) ([2,3]sigmatropic rearrangement product) and 4-methylsulfanyl-1-phenyl-1-butene (**5**) (Hofmann elimination product). Ylide *trans*-**3** cannot undergo [2,3]sigmatropic rearrangement because the ylide-carbon is too far from the phenyl group, and *trans*-**3** would instead isomerize to *cis*-**3**. In this paper, we discuss the mechanism of the isomerization of *trans*-**3** to *cis*-**3**.

Introduction

Sommelet−Hauser rearrangement of 2-arylcycloammonium or -sulfonium 1-methylides is a convenient route for three-carbon enlargement of the starting cyclic compounds.[1] Fluoride ion-induced desilylation of [(trimethylsilyl)methyl]ammonium or -sulfonium salts is superior for such ring enlargement because the methylides generate regioselectively in high yields under nonbasic reaction conditions. For example, nine- or 10-membered heterocyclic compounds have been conveniently prepared by reacting 2-aryl-1-[(trimethylsilyl)methyl]substituted six- or seven-membered ammonium or sulfonium salts with cesium fluoride.[2,3] However, synthesis of eight-membered amines from five-membered ammonium 1-methylides is limited because cis-configurational isomers of the 2-aryl and 1-(trimethylsilyl)methyl groups give [2,3]sigmatropic rearrangement products, whereas the trans-isomers give Stevens rearrangement products.[4] We report here the ring-enlargement of 2-phenyltetrahydrothiophenium 1-methylide (**3**) to 2-benzothiocine (**4**).

Results and Discussion

Reaction of 2-phenyltetrahydrothiophene (**1**) with (trimethylsilyl)methyl triflate gave a 44:56 mixture of *cis*- and *trans*-2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiophenium salts (**2**). The trans-isomer was isolated by recrystallization of the mixture, and the configuration was confirmed by measurement of an NOE spectrum. However, isolation of the cis-isomer failed. After isolated sulfonium salt *trans*-**2** was suspended in DME due to the poor solubility of salt **2** at room temperature, cesium fluoride was added to the suspension. 1,4,5,10a-Tetrahydro-3*H*-2-benzothiocine (**4**) ([2,3]sigmatropic rearrangement product) and 4-methylsulfanyl-1-phenyl-1-butene (**5**) (Hofmann elimination product) were obtained in a ratio of 77:23 (Scheme 1, Table 1, entry 1). The reaction of a mixture of *cis*-**2** and *trans*-**2** (44:56) under the same conditions gave a mixture of **4** and **5** in a ratio of 80:20 (entry 2). The product ratio was independent of the configuration of the starting sulfonium salts. The product ratio changed to 29:69 by heating the reaction mixture at 70 °C, and 3,4,5,6-tetrahydro-1*H*-2-benzothiocine (**6**) (Sommelet−Hauser rearrangement product) was formed (entry 3). The [2,3]sigmatropic rearrangement product **4** could only be synthesized from the cis ylide *cis*-**3**, since the ylide-carbon in *trans*-**3** is too far from the 2-phenyl group, and *trans*-**3** would give Hofmann elimination product **5**. This idea is inconsistent with the product ratio of **4** and **5** in entries 1 and 2. Therefore, we thought that there would be an equilibrium state between *cis*-**3** and *trans*-**3**, and *cis*-**3** would isomerize from *trans*-**3** to give [2,3] sigmatropic rearrangement. Heating the reaction mixture might shift the equilibrium to *trans*-**3**, and the product ratio of **5** increased. Since **2** is more soluble in DMF or DMSO than in DME, we expected that **4** would be produced in high yield in the reaction of **2** with cesium fluoride in these solvents without heating. The reaction of *trans*-**2** with cesium fluoride in DMF at room temperature for 1 h gave **4** selectively (entry 4); however, the product ratio of **5** and **6** increased by allowing the reaction to proceed for 24 h (entry 5). In the reaction using DMSO for 1h, the yield and selectivity of **4** were low, in contrast to our prediction (entry 6). The total yield increased by allowing the reaction to proceed for 24 h

(1) (a) Hesse, M. *Ring Enlargement in Organic Chemistry*; VCH: New York, 1991; p 83. (b) Vedejs, E. *Acc. Chem. Res.* **1984**, *17*, 358. (c) Markó, I. E. In *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 913. (d) Brückner, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 6, p 873.

(2) (a) Shirai, N.; Sumiya, F.; Sato, Y.; Hori, M. *J. Org. Chem.* **1989**, *54*, 836. (b) Sumiya, F.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1991**, *39*, 36. (c) Kitano, T.; Shirai, N.; Sato, Y. *Synthesis* **1991**, 996. (d) Kitano, T.; Shirai, N.; Motoi, M.; Sato, Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2851. (e) Kawanishi, N.; Shirai, N.; Sato, Y.; Hatano, K.; Kurono, Y. *J. Org. Chem.* **1995**, *60*, 4272.

(3) (a) Tanzawa, T.; Shirai, N.; Sato, Y.; Hatano, K.; Kurono, K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 413. (b) Kitano, T.; Shirai, N.; Sato, Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 715.

(4) (a) Sakuragi, A.; Shirai, N.; Sato, Y.; Kurono, Y.; Hatano, K. *J. Org. Chem.* **1994**, *59*, 148. (b) Kawanishi, N.; Fujiwara, K.; Shirai, N.; Sato, Y.; Hatano, K.; Kurono, Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3013.

10.1021/jo0007377 CCC: $19.00
Published on Web 09/13/2000

Scheme 1

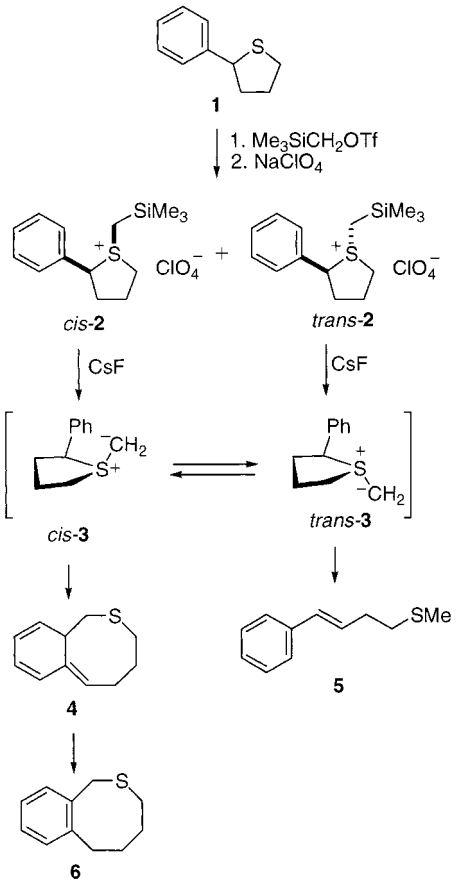


Table 1. Reaction of *cis*- and *trans*-2-Phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiophenium Perchlorates *cis*-2 and *trans*-2 with CsF

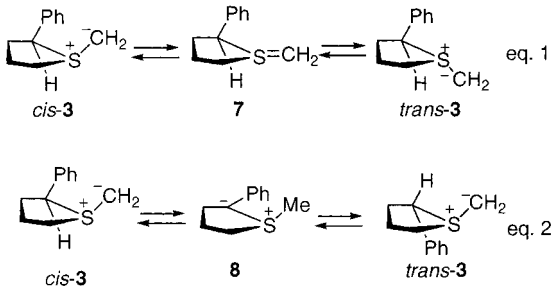
entry	ratio of cis to trans	solvent	time (h)	*T* (°C)	total yield (%)	product ratio[a] 4	5	6
1	0:100	DME	24	rt	97	77	23	0
2	44:56	DME	24	rt	95	80	20	0
3	0:100	DME	24	70	96	29	69	2
4	0:100	DMF	1	rt	69	93	7	0
5	0:100	DMF	24	rt	90	70	19	11
6	0:100	DMSO	1	rt	53	47	43	10
7	0:100	DMSO	24	rt	80	4	52	44

[a] Ratio of the products as determined by integration of the ^{1}H signals in 400-MHz NMR.

(entry 7). The rearrangement of ylide **3** in DMSO was slower than that in DME or DMF, but aromatization of **4** proceeded more rapidly in DMSO. The isomerization of *trans*-**3** to *cis*-**3** also occurred in DMF or DMSO.

While the inversion of configuration in a sulfonium ylide by elimination and recombination of an α-proton under basic conditions has been reported,[5] such an inversion of configuration under nonbasic conditions has not been reported, and the mechanism is interesting. We considered that the isomerization of *trans*-**3** to *cis*-**3** may occur via one of three processes: (a) pyramidal inversion on the sulfur atom,[6] (b) inversion on the sulfur atom by way of a sulfuran intermediate **7** (Scheme 2, eq 1),[7] and

Scheme 2



(c) inversion of a 2-phenyl group on a carbon atom via ylide **8** by [1,3]migration of a 2-proton (eq 2).[8]

To investigate the mechanism of the isomerization of *trans*-**3** to *cis*-**3**, we examined the chemical behavior of 2-methyl-2-phenyltetrahydrothiophenium 1-methylide (**11**), in which the ylide *cis*-**11** cannot isomerize to ylide *trans*-**11** by [1,3]-α-proton migration. *cis*- and *trans*-2-methyl-2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiophenium salts (**10**) were prepared by reacting 2-methyl-2-phenyltetrahydrothiophene (**9**) with (trimethylsilyl)methyl triflate. The ratio of cis to trans was 65:35. One isomer was isolated by recrystallization, but isolation of the other was not successful. No NOE enhancement was observed upon irradiation of S^+-CH_2-Si (δ 1.03 and 3.41) and 2-Me (δ 2.03) in the isolated salt. The chemical shifts in ^{1}H NMR of S^+-CH_2-Si were observed at 2.82 and 3.07 ppm for *trans*-**2** and at 1.10 and 2.49 ppm for *cis*-**2**. Since the chemical shifts of S^+-CH_2-Si were observed at 1.03 and 3.41 ppm in the isolated salt and at 2.60 and 3.45 ppm in the other salt, the stereochemistry of the isolated salt was considered to cis. The reaction of *cis*-**10** with cesium fluoride in DMSO gave a mixture of 1,3,4,9a-tetrahydro-1*H*-6-methyl-2-benzothiocine (**12**) ([2,3] sigmatropic rearrangement product) and 5-methylsulfanyl-2-phenyl-1-pentene (**13**) (Hofmann elimination product) in a ratio of 97:3 (Scheme 3, Table 2, entry 1). The reaction of a mixture of *cis*-**10** and *trans*-**10** (65:35) gave a mixture of **12** and **13** in a ratio of 60:40 (entry 2). Thus, the ratio of *cis*-**10** to *trans*-**10** and the ratio of the products **12** and **13** almost coincide. The [2,3]sigmatropic rearrangement product **12** would be obtained from *cis*-**10**, and the Hofmann elimination product **13** would be obtained from *trans*-**10**. Equilibrium between *cis*-**11** and *trans*-**11** was not observed, and pyramidal inversion on the sulfur atom and isomerization through a sulfurane intermediate did not occur. Therefore, isomerization of the trans sulfonium ylide *trans*-**3** to cis sulfonium ylide *cis*-**3** would proceed via ylide **8** by [1,3]proton migration. The chemical behavior of 2-phenyltetrahydrothiophenium 1-methylide-*1′,1′-d*$_2$ (**15**) was studied to confirm [1,3] proton migration. A mixture of *cis*- and *trans*-2-phenyl-1-[(trimethylsilyl)-methyl] tetrahydrothiophenium-*1′,1′-d*$_2$ salts (**14**, cis/trans = 41:59) was prepared by reacting **1** with (trimethylsilyl)methyl-*d*$_2$ triflate. The trans isomer *trans*-**14** was isolated by recrystallization from ethyl acetate. The reaction of this labeled salt *trans*-**14** with cesium fluoride in DMF at room temperature for 1 h gave a mixture of 1,4,5,10a-tetrahydro-3*H*-2-benzothiocine-*1,1-d*$_2$ (**17**), 1,4,5,-10a-tetrahydro-3*H*-2-benzothiocine-*1,6-d*$_2$ (**17′**), 4-meth-

(5) Coré, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1978**, *43*, 4826.
(6) Darwish, D.; Tomilson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5938.
(7) (a) Yoshida, Z.; Iwata, K.; Yoneda, S. *Tetrahedron Lett.* **1971**, 1519. (b) Trost, B. M.; Melvin Jr., L. S. *Sulfur Ylides*; Academic Press: New York, **1975**.
(8) (a) Padwa, A.; Gasdaska, J. R. *Tetrahedron* **1988**, *44*, 4147. (b) Nishimura, T.; Zhang, C.; Maeda, Y.; Shirai, N.; Ikeda, S.; Sato, Y. *Chem. Pharm. Bull.* **1999**, *47*, 267.

Scheme 3

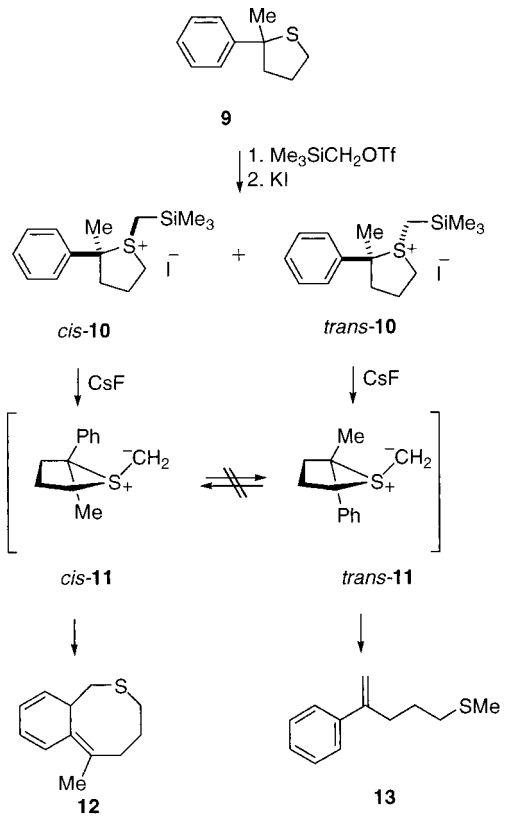


Table 2. Reaction of *cis*- and *trans*-2-Methyl-2-phenyl-1-[(trimethylsilyl)methyl]-tetrahydrothiophenium Iodides *cis*-10 and *trans*-10 with CsF at Room Temperature for 1 h in DMSO

			product ratio[a]	
entry	ratio of cis to trans	yield (%)	**12**	**13**
1	100:0	90	97	3
2	65:35	80	60	40

[a] Ratio of the products as determined by integration of the ^{1}H signals in 400-MHz NMR.

ylsulfanyl-1-phenyl-1-butene-*1′,1′-d*$_2$ (**18**) and 4-methylsulfanyl-1-phenyl-1-butene-*1,1′-d*$_2$ (**18′**) (Scheme 4). These products were separated into a mixture of **17** and **17′** (56%, 65:35) and a mixture of **18** and **18′** (6%, 65:35) by column chromatography on silica gel. The ratio was determined from integrated values in the ^{1}H NMR spectrum. (Integration value of 6-H (δ 5.60−5.65) is 0.65 and that of 1-H and one proton of 3-H (δ 2.43−2.57) is 1.35 in the mixture of **17** and **17′**. Integration value of 1-H (δ 6.45) is 0.65 and that of SMe (δ 2.14) is 1.35 in the mixture of **18** and **18′**). These results indicate that the isomerization between *cis*-**2** and *trans*-**2** was caused by [1,3]proton migration.

Experimental Section

DMF was dried by distillation under reduced pressure from BaO. DMSO was dried by distillation under reduced pressure from CaH_2. DME and chloroform were dried by distillation from CaH_2. CsF was dried over P_2O_5 at 180 °C. All melting and boiling points are uncorrected.

***cis*- and *trans*-2-Phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiophenium perchlorates (*cis*-2, *trans*-2).** A solution of 2-phenyltetrahydrothiophene[9] (**1**) (5.5 g, 33 mmol) and (trimethylsilyl)methyl triflate (10.3 g, 44 mmol) was stirred in $CHCl_3$ (40 mL) at room temperature for 3 h. The solvent was evaporated under reduced pressure. The residue was washed with Et_2O, dissolved in MeOH (5 mL) and stirred with aqueous 5 m $NaClO_4$ (30 mL) for 0.5 h. The mixture was extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$) and concentrated to give a mixture of *cis*-**2**, *trans*-**2** (44:56, 10.9 g, 94%). The trans isomer was isolated by recrystallization from ethyl acetate.

trans-**2**: mp 109−110 °C; IR (KBr) 846, 760 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) δ 0.19 (s, 9 H), 2.27−2.37 (m, 1 H), 2.56−2.66 (m, 1 H), 2.75−2.86 (m, 1 H), 2.82 (d, J = 13.7 Hz, 1 H), 2.87−2.96 (m, 1 H), 3.07 (d, J = 13.7 Hz,1 H), 3.69−3.74 (m, 1 H), 3.82−3.90 (m, 1 H), 5.25 (dd, J = 10.6, 6.4 Hz, 1 H) 7.49−7.53 (m, 5 H). NOE enhancement of 2-H (19% or 25%, δ 3.82−3.90) was observed upon irradiation of S^+-CH_2-Si (δ 2.82 and 3.07). ^{13}C NMR (100 MHz; $CDCl_3$) δ −1.4, 28.0, 28.4, 39.0, 47.0, 71.2, 128.0, 129.6, 129.7, 133.3. Anal. Calcd for $C_{14}H_{23}ClOSSi$: C, 47.91; H, 6.61. Found: C, 47.74; H, 6.47.

cis-**2**: ^{1}H NMR (500 MHz; $CDCl_3$) δ 0.16 (s, 9 H), 1.10 (d, J = 13.4 Hz, 1 H), 2.47−2.51 (m, 1 H), 2.49 (d, J = 13.4 Hz 1 H), 2.56−2.66 (m, 1 H), 2.75−2.86 (m, 1 H), 2.87−2.96 (m, 1 H), 3.54−3.61 (m, 1 H), 4.03−4.07 (m, 1 H), 5.43−5.47 (m, 1 H), 7.48−7.50 (m, 5 H).

Reaction of 2 with CsF. General Procedure. Sulfonium salt *trans*-**2** or a mixture of *cis*-**2** and *trans*-**2** (44:56) (700 mg, 2 mmol) was placed in a 30-mL 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 (304 mg, 2 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with N_2. The salt was dissolved in DME, DMF, or DMSO (10 mL) at room temperature or 70 °C and CsF was added from the test tube. The mixture was stirred for 1 or 24 h, poured into water and extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on an HPLC column (Nakarai Cosmosil 5NH_2 10 × 250 mm, hexane) to give 1,4,5,10a-tetrahydro-3*H*-2-benzothiocine (**4**), 4-methylsulfanyl-1-phenyl-1-butene (**5**) and 3,4,5,6-tetrahydro-1*H*-2-benzothiocine (**6**). The ratio was determined from integrated values in the ^{1}H NMR spectrum. The results are listed in Table 1.

4: oil; IR (film) 2920, 1248 cm^{-1}; UV λ_{max} (hexane) 318 (log ϵ 3.69), 306 nm (log ϵ 3.67); ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.84−1.90 (m, 2 H), 2.21−2.32 (m, 1 H), 2.44−2.54 (m, 3 H), 2.63−2.73 (m, 1 H), 2.85 (dt, J = 3.6, 15.5 Hz, 1 H), 3.58 (br s, 1 H), 5.70−5.76 (m, 1 H), 5.73 (ddd, J = 1.0, 6.3, 11.5 Hz 2 H), 5.89−5.94 (m, 1 H), 6.02 (dd, J = 0.7, 9.3 Hz, 1 H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 24.8, 31.9, 32.1, 38.8, 42.1, 121.3, 122.9, 129.3, 130.5, 132.5 139.1. Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 74.25; H, 8.01.

5: oil; IR (film) 2917, 1442 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) δ 2.14 (s, 3 H), 2.49−2.53 (m, 2 H), 2.61−2.66 (m, 2 H), 6.24 (dt, J = 6.9, 15.9 Hz, 1 H), 6.45 (d, J = 15.9 Hz, 1 H), 7.17−7.36 (m, 5 H). Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 74.03; H, 7.76.

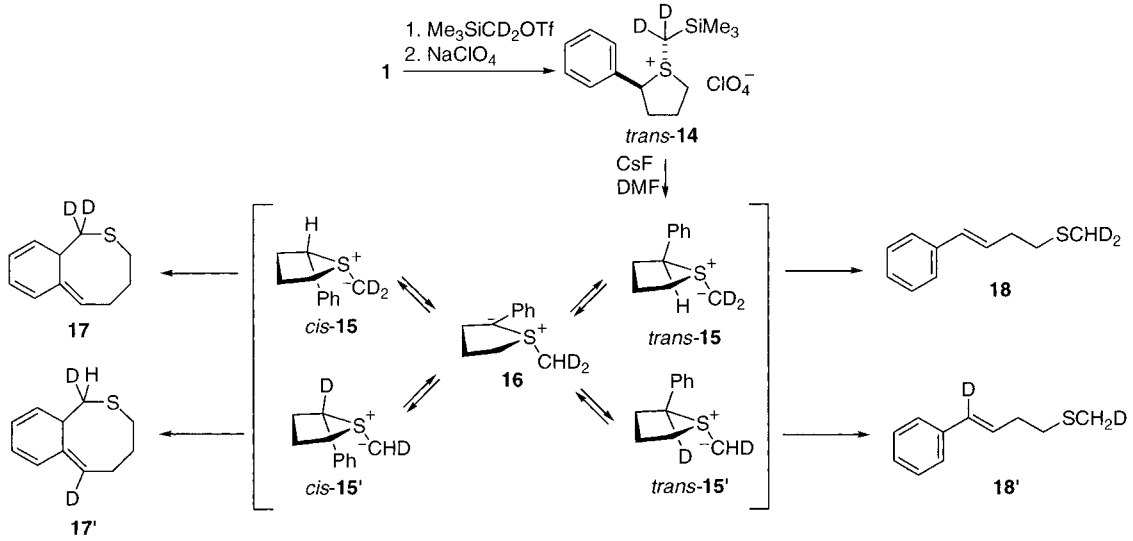
6: oil; IR (film) 3027, 1491 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) δ 1.75−1.77 (m, 2 H), 1.85−1.88 (m, 2 H), 2.35−2.37 (m, 2 H), 2.75−2.78 (m, 2 H), 3.81 (s, 2 H), 7.17−7.36 (m, 4 H). Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 73.85; H, 8.02.

***cis*- and *trans*-2-Methyl-2-phenyl-1-[(trimethylsilyl)-methyl]tetrahydrothiophenium Iodides (*cis*-10, *trans*-10).** A solution of 2-methyl-2-phenyltetrahydrothiophene[10] (**9**) (4.2 g, 24 mmol) and (trimethylsilyl)methyl triflate (6.0 g, 25 mmol) was stirred in $CHCl_3$ (20 mL) at room temperature for 3 h. The solvent was evaporated under reduced pressure. The residue was washed with Et_2O, dissolved in MeOH (5 mL), and stirred with aqueous 5 m KI (20 mL) for 0.5 h. The mixture was extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated to give a mixture of *cis*-**10** and *trans*-**10** (65:35, 8.8 g, 95%). The mixture of *cis*-**10** and

(9) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1997**, *53*, 5563.

(10) Truce, W. E.; Hollister, K. R.; Lindy, L. B.; Parr, J. E. *J. Org. Chem.* **1968**, *33*, 43.

Scheme 4



trans-**10** was recrystallized from AcOEt, and *cis*-**10** was isolated but *trans*-**10** was not.

cis-**10**: mp 137−139 °C; IR (KBr) 3000, 860 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 0.24 (s, 9 H), 1.03 (d, J = 13.4 Hz, 1 H), 2.03 (s, 3 H), 2.50 (dd, J = 6.0, 13.2 Hz, 1 H), 2.54−2.66 (m, 1 H), 3.16−3.23 (m, 1 H), 3.32−3.41 (m, 1 H), 3.41 (d, J = 13.4 Hz, 1 H), 4.10−4.16 (m, 1 H), 4.33−4.40 (m, 1 H), 7.41−7.47 (m, 5 H); ^{13}C NMR (100 MHz; $CDCl_3$) δ −0.6 (3 C), 24.4, 27.7, 28.4, 38.0, 44.5, 77.5, 127.2, 128.3, 130.4, 135.7. Anal. Calcd for $C_{15}H_{25}ISSi$: C, 45.91; H, 6.42. Found: C, 45.83; H, 6.25.

trans-**10**: ^1H NMR (400 MHz; $CDCl_3$) δ 0.37 (s, 9 H), 2.04 (s, 2 H), 2.60 (d, J = 13.1 Hz, 1 H), 2.31−2.38 (m, 1 H), 2.77−2.87 (m, 2 H), 2.96−3.01 (m, 1 H), 3.45 (d, J = 13.1 Hz, 1 H), 3.63−3.69 (m, 1 H), 3.83−3.90 (m, 1 H), 7.38−7.55 (m, 5 H); ^{13}C NMR (67.8 MHz; $CDCl_3$) δ −0.1 (3 C), 23.7, 26.0, 40.1, 44.7, 78.0, 128.4, 130.1, 130.7, 138.7.

Reaction of 10 with CsF. General Procedure. In a manner similar to that described for **2**, a solution of *cis*-**10** or a mixture of *cis*-**10** and *trans*-**10** (65:35) (784 mg, 1 mmol) and CsF (304 mg, 2 mmol) in DMSO (10 mL) was stirred at room temperature for 1 h, after which it was quenched with water and extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on an HPLC column (Nakarai Cosmosil 5NH_2 10 × 250 mm, hexane) to give 1,3,4,9a-tetrahydro-1*H*-6-methyl-2-benzothiocine (**12**) and 5-methylsulfanyl-2-phenyl-1-pentene (**13**). The ratio was determined from integrated values in the ^1H NMR spectrum. The results are listed in Table 2.

12: oil; IR (film) 2953, 740 cm^{-1}; UV λ_{max} (hexane) 326 nm (log ϵ 4.94); ^1H NMR (400 MHz; $CDCl_3$) δ 1.81 (s, 3 H), 1.83−1.88 (m, 1 H), 2.00−2.14 (m, 2 H), 2.36−2.54 (m, 3 H), 2.71−2.77 (m, 1 H), 2.85−2.93 (m, 1 H), 3.60 (br s, 1 H), 5.77−5.82 (m, 2 H), 5.94−5.98 (m, 1 H), 6.37 (d, J = 10.2 Hz, 1 H); ^{13}C NMR (67.8 MHz; $CDCl_3$) δ 17.7, 30.8, 31.1, 34.0, 38.5, 42.0, 121.1, 122.5, 123.6, 130.9, 131.1, 136.8. Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.54; H, 8.58.

13: oil; IR (film) 2953, 800 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.74−1.77 (m, 2 H), 2.06 (s, 3 H), 2.51 (t, J = 7.6 Hz, 2 H), 2.62 (t, J = 7.6 Hz, 2 H), 5.06 (d, J = 1.5 Hz, 1 H), 5.28 (d, J = 1.5 Hz, 1 H) 7.27−7.41 (m, 5 H); ^{13}C NMR (67.8 MHz; $CDCl_3$) δ 15.4, 27.4, 33.7, 34.2, 112.7, 126.1, 127.4, 128.2, 140.9, 147.6. Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.71; H, 8.53.

(Trimethylsilyl)methyl-d_2 Trifluoromethanesulfonate. This compound was synthesized according to Lee and Ha.[11] A mixture of trimethylsilyl triflate (3.0 g, 14 mmol) and diazomethane-d_2[12] (24 mmol) was stirred in ether for 1 h at 0 °C. The solvent was removed under reduced pressure, and the residue was distilled to give (trimethylsilyl)methyl-d_2 triflate (2.5 g, 75%); bp 100 °C/40 mmHg.

***trans*-2-Phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiophenium Perchlorate-*1′,1′-d*$_2$ (*trans*-14).** This compound was prepared by the same reaction conditions as for **2** to give a mixture of *cis*-**14** and *trans*-**14** (41:59, 90%). The trans isomer was isolated by recrystallization from ethyl acetate (40%): mp 114−115 °C; IR (KBr) 2980, 760 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 0.20 (s, 9 H), 2.29−2.40 (m, 1 H), 2.60−2.68 (m, 1 H), 2.70−2.81 (m, 1 H), 2.90−3.00 (m, 1 H), 3.62−3.66 (m, 1 H), 3.96 (ddd, J = 17.3, 10.2, 7.1 Hz, 1 H), 5.18 (dd, J = 10.7, 6.6 Hz, 1 H) 7.39−7.47 (m, 5 H); ^{13}C NMR (100 MHz; $CDCl_3$) δ −1.4, 28.4, 39.0, 46.9, 71.2, 128.0, 129.6, 129.7, 133.3.

Reaction of *trans*-14 with CsF. In a manner similar to that described for **2**, a solution of *trans*-**14** (674 mg, 2 mmol) and CsF (304 mg, 2 mmol) in DMF (10 mL) was stirred at room temperature for 1 h. The solution was worked up to give a mixture of 1,4,5,10a-tetrahydro-3*H*-2-benzothiocine-*1,1-d*$_2$ (**17**), 1,4,5,10a-tetrahydro-3*H*-2-benzothiocine-*1,6-d*$_2$ (**17′**), 4-methylsulfanyl-1-phenyl-1-butene-*1′,1′-d*$_2$ (**18**), and 4-methylsulfanyl-1-phenyl-1-butene-*1,1′-d*$_2$ (**18′**). These products were separated into a mixture of **17** and **17′** (200 mg, 56%, 65:35) and a mixture of **18** and **18′** (22 mg, 6%, 65:35) by column chromatography on silica gel. The ratio was determined from integrated values in the ^1H NMR spectrum.

17 and **17′**: ^1H NMR (400 MHz; $CDCl_3$) δ 1.83−1.90 (m, 2 H), 2.18−2.26 (m, 1 H), 2.43−2.57 (m, 1.35 H), 2.62−2.72 (m, 1 H), 2.81−2.90 (m, 1 H), 3.56 (br s, 1 H), 5.60−5.65 (m, 0.65 H), 5.67−5.75 (m, 2 H), 5.88−5.93 (m, 1 H), 6.02 (d, J = 9.3 Hz, 1 H).

18 and **18′**: ^1H NMR (400 MHz; $CDCl_3$) δ 2.14 (s, 1.35 H), 2.49−2.53 (m, 2 H), 2.61−2.66 (m, 2 H), 6.24 (dt, J = 6.9, 15.9 Hz, 1 H), 6.45 (d, J = 15.9 Hz, 0.65 H), 7.17−7.36 (m, 5 H).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Reserch (No. 11771390) provided by the Ministry of Education, Science and Culture, Japan.

JO0007377

(11) Lee, J. G.; Ha, D. S. *Synthesis* **1988**, 318.
(12) Aldrich Technical Information Bulletin No. AL-180.