

GENERATION OF SULFUR YLIDES BY THE DESILYLATION OF α -TRIMETHYLSILYLBENZYL SULFONIUM SALTS

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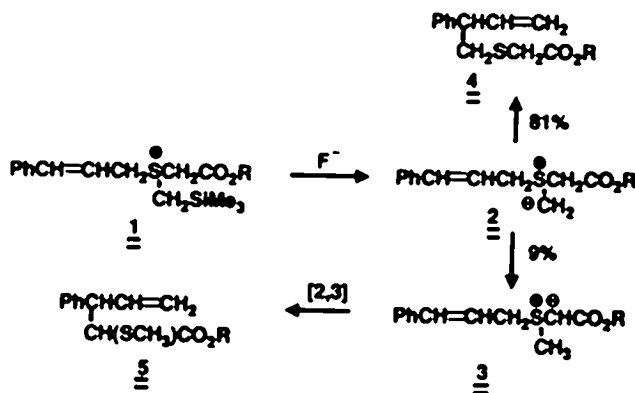
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Abstract: The [2,3]-sigmatropic rearrangement of sulfur ylides derived via the desilylation of several α -trimethylsilylbenzyl sulfonium salts has been studied. The initially formed ylide was found to rapidly equilibrate with the thermodynamically more stable ylide. In the absence of trapping reagents, a Sommelet-Hauser type rearrangement occurs.

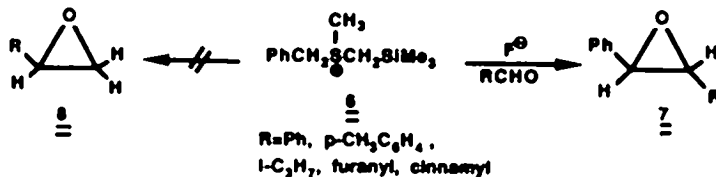
Since Wittig's pioneering studies on phosphonium ylides,¹ ylides have attracted considerable attention.² Stable ylides of phosphorous, nitrogen, sulfur and other heteroatoms have been prepared and used in synthetic chemistry. Generation of these ylides is achieved either via α -deprotonation of the corresponding onium salts^{3,4} or electrophilic carbene attack on the corresponding heteroatom compounds.⁵ More recently, the desilylation of α -trimethylsilyl onium salts by fluoride ion has been used as a convenient method for preparing sulfur and nitrogen ylides.⁶⁻¹⁵ The chemistry of sulfur ylides has been the subject of extensive investigation, largely because of the synthetic challenge of making stable molecules of this kind and because of the interesting rearrangements which they often undergo.¹⁶ Relatively little work has been done, however, using the trimethylsilyl functionality as a leaving group in the generation of ylides for [2,3]-sigmatropic rearrangements.¹⁷⁻¹⁹ In searching for new ways to utilize sulfur ylides in organic synthesis, we investigated the fluoride-induced desilylation reaction of several benzyl α -trimethylsilylsulfonium salts.²⁰ We report here the results of these studies

Results and Discussion

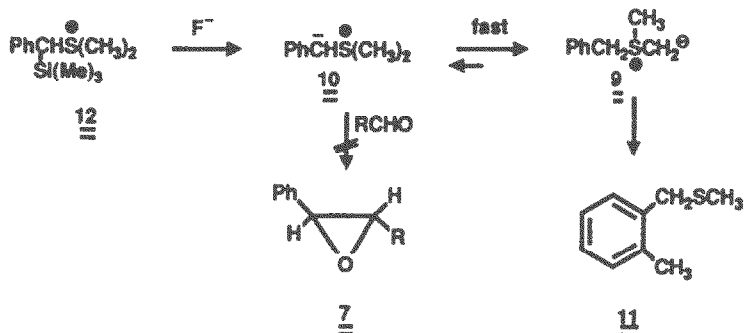
In 1979, Vedejs and Martinez reported that the fluoride induced desilylation of sulfonium salt 1 afforded 81% of the 2,3-sigmatropic shift product derived from the kinetic ylide 2 even though a more stabilized ester ylide 3 could have been produced by proton transfer.⁶ Thus, we were



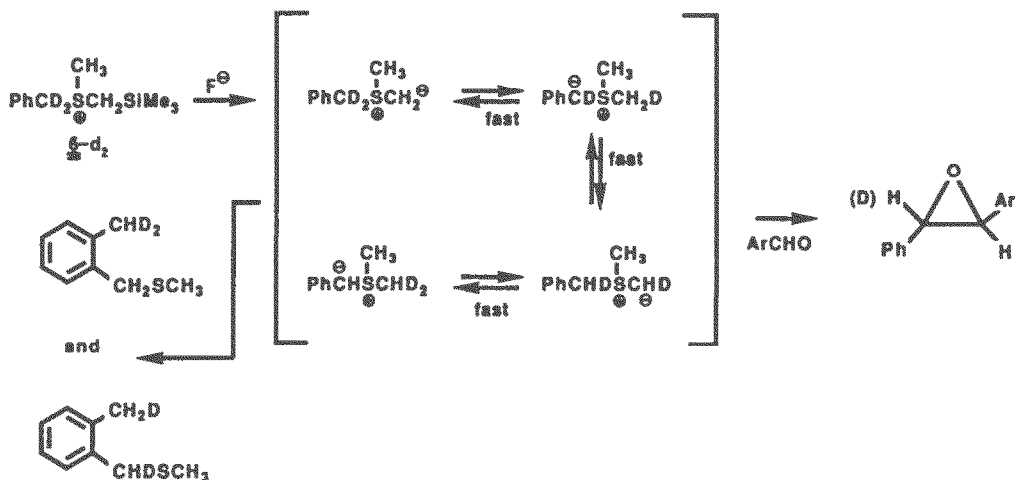
somewhat surprised to find that treatment of sulfonium salt 6 with fluoride ion in the presence of an aldehyde produced only the disubstituted *trans*-epoxide 7. No signs of the mono-substituted epoxide 8 could be found in the crude reaction mixture. Evidently, the initially formed sulfur ylide 9 rapidly rearranged to the more stable ylide 10 which reacted with the aldehyde to give the observed epoxide. This result contrasts with Vedejs' earlier observations wherein the predominant



product is that obtained from the thermodynamically less stable ylide.⁶ Attempts to trap ylide 10 with ketones or imines failed. The only material isolated in high yield corresponded to the 2,3-sigmatropic rearranged product 11. These results are understandable if one assumes that the initially formed ylide 9 undergoes a proton shift to give 10 at a faster rate than addition to the aldehyde carbonyl group.

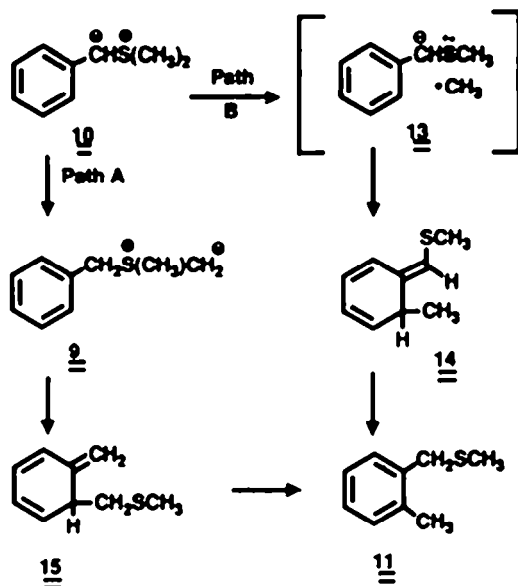


This postulate was tested by a desilylation study of the dideuterated benzylium salt **6-d₂**. Treatment of **6-d₂** with cesium fluoride gave **11** with significant deuterium scrambling (>50%) onto the benzylic positions. Furthermore, in the presence of an aromatic aldehyde, the reaction of **6-d₂** with fluoride ion gave rise to an epoxide which had lost (~50%) a significant amount of the deuterium label. These results are perfectly consistent with an extremely facile proton transfer which occurs within the ylide and which is competitive with both the 2,3-sigmatropic rearrangement and epoxide formation.

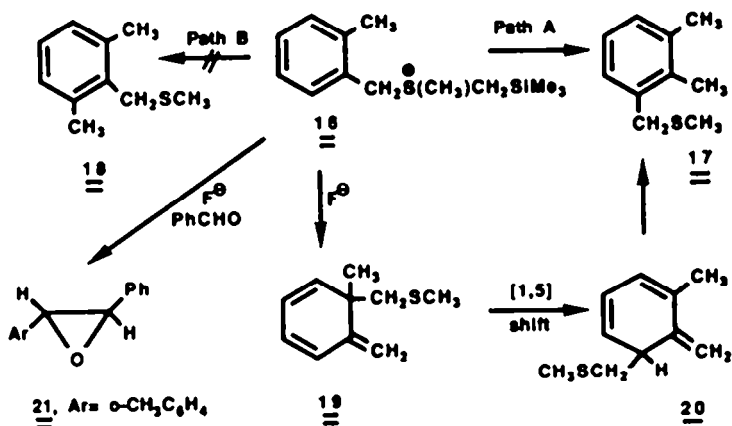


The fact that *o*-methylthiomethyltoluene (**11**) is isolated in the absence of a trapping agent is of considerable mechanistic interest. One possibility (path A) to account for this observation is that the thermodynamically more stable sulfur ylide **10** is in partial equilibrium with the less stable ylide **9**. In the absence of aldehyde, the small amount of **9** present in equilibrium rearranges via a 2,3-sigmatropic shift thereby driving the reaction to completion.²¹ In fact, we have found that treatment of trimethylsilyl substituted sulfonium salt **12** with cesium fluoride produced **11** in 78% yield thereby providing support for this postulate.

A more mechanistically intriguing possibility is that benzyl ylide **10** rearranges via a radical-pair mechanism (Path B). It is well known that the 2,3-sigmatropic rearrangement of ylides can be accompanied by a second pathway of higher activation energy, shown to be a radical dissociation-recombination route, whose importance depends on the structural environment and temperature.²²⁻²⁴ In order to distinguish between these two possibilities we studied the reaction of silylsulfonium salt **16** with fluoride ion. According to Path A (proton shift-[2,3]-rearrangement), the product formed should correspond to structure **17**. Mechanism B, on the other hand, would give

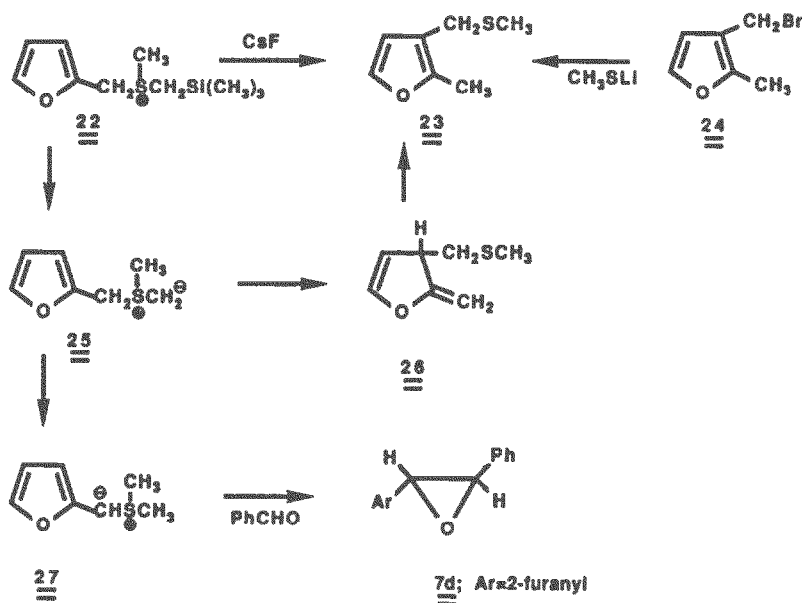


rise to the isomeric compound 18. We found that treatment of 16 with cesium fluoride in dimethoxyethane ultimately produced structure 17. However, the initially formed products corresponded to a 1:2 mixture of cyclohexadienes 19 and 20. Chromatography of the mixture on

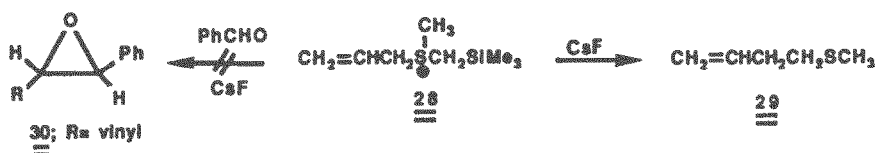


silica gel afforded 17 in 90% yield. The structure of 17 was established by comparison with an independently synthesized sample prepared by treating the Grignard reagent derived from 1-bromo-2,3-dimethylbenzene with chloromethyl methyl sulfide. The formation of 19 and 20 from 16 can be attributed to a 2,3-sigmatropic rearrangement of the initially formed sulfur ylide onto both ortho positions (Path A).^{25,26} The conversion of 19 to 17 probably occurs via a 1,5-sigmatropic shift of the methyl or methylthiomethyl group to give 20 followed by an aromatization step. The fact that cyclohexadienes 19 and 20 can be isolated clearly demonstrates the mildness of the desilylation procedure for sulfonium ylide generation as compared to the α -deprotonation method. We also found that treatment of 16 with fluoride ion in the presence of benzaldehyde gave epoxide 21 as the major product (78%). This finding is similar to the earlier observations made with sulfonium salt 8.

We also examined the reaction of the 2-furanyl sulfonium salt 22 with cesium fluoride. The major product isolated here corresponded to furan 23. This assignment was verified by comparison with an independently synthesized sample prepared by treating 2-methyl-3-(bromomethyl)furan (24) with thiomethyl lithium. The exo-methylene species 26, presumed to be an intermediate in this reaction, could actually be detected by NMR spectroscopy (NMR ($CDCl_3$, 360 MHz) δ 2.16 (s, 3H), 2.58 (dd, 1H, $J=12.9$ and 8.5 Hz), 2.74 (dd, 1H, $J=12.9$ and 8.5 Hz), 3.71 (m, 1H), 4.28 (m, 1H), 4.63



(m, 1H), 5.30 (m, 1H) and 6.50 (m, 1H). This material readily rearranged to furan 23 upon standing at room temperature. Interestingly, the reaction of 22 with cesium fluoride in the presence of a 2.0 mole excess of benzaldehyde afforded a 2:1 mixture of furan 23 and epoxide 7d. Under the same experimental conditions, the 2,3-sigmatropic rearrangement of the closely related sulfonium salt 6 could be completely suppressed in the presence of benzaldehyde. Although proton transfer from ylide 25 to 27 still occurs rapidly, the isolation of 23 as the major product indicates that the 2,3-sigmatropic shift is proceeding at a faster rate than bimolecular trapping. Replacement of a phenyl group with the less aromatic furan ring enhances the rearrangement rate. In fact, treatment of the much simpler allyl sulfonium salt 28 with cesium fluoride in the presence of a 10 mole excess of benzaldehyde only afforded 4-(methylthio)-1-butene (29). No trace of epoxide 30 was detected in



the crude reaction mixture. In this case, the 2,3-sigmatropic shift is extremely facile since the process does not involve any loss of aromaticity.

In conclusion, sulfur ylides can be readily prepared from the desilylation of (trimethylsilyl-methyl)sulfonium salts. The initially formed ylide rapidly equilibrates with the thermodynamically more stable ylide. In the absence of trapping reagents, a Sommelet-Hauser type rearrangement occurs.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on a Varian EM-390 and Nicolet NMC-360 MHz spectrometer. ¹³C-NMR spectra were recorded on an IBM NB 200 SY FT spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, Ga. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Alkylation of Trimethyl[[(phenyl)methylthio]methyl]silane with Methyl Triflate Followed by Reaction with Cesium Fluoride. A solution containing 0.96 g of trimethylsilylmethyl mercaptan²⁷ in 30 ml of ether at -200°C was treated with 6 ml of a 1.45 M solution of *n*-butyllithium in hexane and the mixture was stirred for 1 h. At the end of this time, 1.0 ml of benzyl bromide was added and the solution was allowed to stir overnight, poured into water and extracted with ether. The ether layer was washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give 1.65 g (98%) of trimethyl[[(phenyl)methyl]thiomethyl]silane as a colorless oil (lit.²⁷ bp 124°C (8 mm)); IR (neat) 2960, 1500, 1455, 1245, 850 and 700 cm⁻¹; NMR (CCl₄, 90 MHz) δ 0.02 (s, 9H), 1.47 (s, 2H), 3.52 (s, 2H) and 7.1 (s, 5H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.86, 17.64, 40.22, 126.59, 128.17, 128.78 and 138.30; m/e 210 (M⁺), 195, 119, 104, 91 and 73 (base); Anal. Calcd. for C₁₁H₁₈SSi: C, 62.79; H, 8.62; S, 15.24. Found: C, 62.88; H, 8.63; S, 15.30.

A solution containing 1.0 g of the above material in 1 ml of anhydrous benzene at 0°C was treated dropwise with a solution containing 0.54 ml of methyl trifluoromethanesulfonate in 1 ml of anhydrous benzene. The reaction was stirred overnight and was then concentrated to give 1.78 g (100%) of methyl (phenylmethyl){(trimethylsilyl)methyl}sulfonium trifluoromethanesulfonate (**6**) as a white solid; mp 79-80°C; IR (KBr) 1505, 1465, 1435, 1260, 1160, 1035 and 860 cm⁻¹; NMR (CDCl₃, 360 MHz) δ 0.24 (s, 9H), 2.63 (AB quartet, 2H, J=13.7 Hz); 2.82 (s, 3H), 4.78 (AB quartet, 2H, J=12.6 Hz) and 7.4-7.5 (m, 5H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.44, 24.16, 25.04, 49.37, 127.00, 129.44, 130.00 and 130.73; Anal. Calcd. for C₁₃H₂₁F₃O₃S₂Si: C, 41.69; H, 5.65; S, 17.12. Found: C, 41.59; H, 5.66; N, 17.21. The deuterated sulfonium salt **6-d**₂ was prepared in an analogous fashion using benzyl-d₂ bromide and was devoid of the signal at 4.78 ppm.

A suspension containing 250 mg of dried cesium fluoride in 2 ml of anhydrous dimethoxyethane was treated with 250 mg of the above salt and the mixture was heated for 14 h at 50°C. At the end of this time the solution was poured into water and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and concentrated under reduced pressure to give 76 mg (75%) of 1-methyl-2-[(methylthio)methyl]benzene (**11**) as a colorless oil; IR (neat) 2970, 2915, 1495, 1465, 1430, 1030, 770, 750 and 735 cm⁻¹; NMR (CDCl₃, 90 MHz) δ 1.97 (s, 3H), 2.35 (s, 3H), 3.63 (s, 2H) and 7.10 (s, 4H); m/e 152 (M⁺), 105 (base), 104, 103, 79 and 77; Anal. Calcd. for C₉H₁₂S: C, 71.02; H, 7.95; S, 21.03. Found: C, 70.96; H, 7.83; S, 20.92.

General Procedure for the Reaction of Methyl(phenylmethyl){(trimethylsilyl)methyl}sulfonium Triflate (6**) with Cesium Fluoride in the Presence of Various Aldehydes.** A stirred suspension containing 400 mg of flame-dried cesium fluoride in 3 ml of

anhydrous dimethoxyethane was treated with 1.1 equiv of the appropriate aldehyde and then 500 mg of the triflate salt. The mixture was heated at 40°C for 12 h, poured into water and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and concentrated under reduced pressure. The following aldehydes were used to trap the sulfonium ylide.

Benzaldehyde: The only product obtained in 80% yield was *trans*-stilbene oxide (**71**);²⁸ NMR (CDCl₃, 90 MHz) δ 3.82 (s, 2H) and 7.31 (s, 10H).

***p*-Tolualdehyde:** The only product obtained in 73% yield was *trans*-2-(4-methylphenyl)-3-phenyloxirane (**7b**);²⁹ NMR (CDCl₃, 360 MHz) δ 2.34 (s, 3H), 3.81 (d, 1H, J=1.9 Hz), 3.83 (d, 1H, J=.9 Hz) and 7.1-7.4 (m, 9H).

Isobutyraldehyde: The major product obtained in an 80% yield was identified as a 4:1 mixture of *trans* and *cis* 2-(1-methylethyl)-3-phenyloxirane (**7c**); NMR (CDCl₃, 360 MHz) δ 1.02 (d, 3H, J=6.9 Hz), 1.09 (d, 3H, J=6.7 Hz), 1.63-1.73 (m, 1H), 2.75 (dd, 1H, J=6.9 and 2.1 Hz) (*trans* isomer), 2.85

(dd, 1H, J=9.2 and 4.2 Hz) (*cis* isomer), 3.65 (d, 1H, J=2.1 Hz) (*trans* isomer), 4.09 (d, 1H, J=4.2 Hz) (*cis* isomer) and 7.0-7.3 (m, 5H).

2-Furaldehyde: The major product obtained in 83% yield was identified as *trans*-2-(2-furyl)-3-phenyloxirane (**7d**); NMR (CDCl₃, 360 MHz) δ 3.89 (d, 1H, J=2.1 Hz), 4.36 (d, 1H, J=2.1 Hz), 6.39 (dd, 1H, J=3.2 and 1.9 Hz), 6.48 (d, 1H, J=3.2 Hz) and 7.2-7.5 (m, 6H).

Cinnamaldehyde: The major product obtained in 70% yield was identified as *trans*-2-(*trans*-2-phenylethylene)-3-phenyloxirane (**7e**);³⁰ NMR (CDCl₃, 360 MHz) δ 3.52 (dd, 1H, J=7.6 and 1.9 Hz), 3.88 (d, 1H, J=1.9 Hz), 6.06 (dd, 1H, J=16.1 and 7.6 Hz), 6.72 (d, 1H, J=16.1 Hz) and 7.1-7.6 (m, 10H).

Preparation of (Trimethyl)(methylthio)phenylmethylsilane Followed by Reaction of the Methyl Triflate Salt with Cesium Fluoride. The above silane was prepared according to the procedure of Seebach and Geiss.³¹ A solution containing 1.0 g of the silane in 3 ml of anhydrous benzene at 0°C was treated dropwise with a solution containing 0.55 ml of methyl trifluoromethanesulfonate in 1 ml of benzene. The reaction was stirred overnight and was then concentrated under reduced pressure to give 1.75 g (98%) of dimethyl[(phenyl)trimethylsilylmethyl]sulfoniumtrifluoromethanesulfonate (**12**) as a viscous yellow oil; IR (neat) 3030, 1435, 1260 (b), 1165, 1030 and 855 cm⁻¹; NMR (CDCl₃, 360 MHz) δ 0.26 (s, 9H), 2.72 (s, 3H), 3.07 (s, 3H), 4.51 (s, 1H) and 7.25-7.5 (m, 5H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.76, 24.94, 25.51, 47.29, 128.76, 129.09, 129.68 and 131.02.

A suspension containing 300 mg of dried cesium fluoride in 3 ml of anhydrous dimethoxyethane was treated with 305 mg of the above salt and the mixture was stirred for 18 h at 450°C. At the end of this time, the solution was poured into water and extracted with methylene chloride. The methylene chloride layer was dried over magnesium sulfate and concentrated under reduced pressure. Analysis of the crude residue by NMR spectroscopy showed the presence of 1-methyl-2-[(methylthio)methyl]benzene (**11**) in 88% yield. When the reaction of **12** with cesium fluoride was performed in the presence of benzaldehyde, the only isolable product (98%) was identified as *trans*-stilbene oxide (**7a**).

Alkylation of Trimethyl[(2-methylphenyl)methylthio]methylsilane with Methyl Triflate Followed by Reaction with Cesium Fluoride. A solution containing 5.0 g of trimethylsilylmethyl mercaptan in 150 ml of anhydrous ether at -200°C was treated with 34 ml of a 1.38 M solution of *n*-butyllithium in hexane and the mixture was stirred for 90 min. At the end of this time, 5.6 ml of bromo-*o*-xylene was added and the reaction mixture was allowed to stir overnight. The solution was poured into water and extracted with ether. The ethereal layer was washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give 8.96 g (96%) of trimethyl[(2-methylphenyl)methylthio]methylsilane as a colorless oil (bp 810°C, 0.08 mm); IR (neat) 2950, 2910, 2900, 2880, 1495, 1465, 1390, 1245, 845, 765 and 730 cm⁻¹; NMR (CCl₄, 90 MHz) δ 0.03 (s, 9H), 1.56 (s, 2H), 2.53 (s, 3H), 3.58 (s, 2H) and 7.01 (s, 4H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.83, 18.00, 18.97, 38.31, 125.47, 126.87, 129.82, 130.35, 135.97 and 136.47; Anal. Calcd. for C₁₂H₂₀SSi: C, 64.22; H, 8.98; S, 14.29. Found: C, 64.07; H, 9.05; S, 14.19.

A solution containing 1.0 g of this material in 3 ml of anhydrous benzene at 0°C was treated dropwise with a solution containing 0.54 ml of methyl triflate in 1 ml of anhydrous benzene. The reaction was stirred overnight and was then concentrated under reduced pressure to give a crude brown solid. Recrystallization from carbon tetrachloride gave 1.6 g (90%) of methyl [(2-methylphenyl)methyl][(trimethylsilyl)methyl]sulfonium trifluoromethanesulfonate (**16**) as a white solid; mp 79-80°C; IR (KBr) 2970, 1435, 1265, 1230, 1165, 1035 and 860 cm⁻¹; NMR (CDCl₃, 360 MHz) δ 0.25 (s, 9H), 2.43 (s, 3H), 2.61 (d, 1H, J=13.7 Hz), 2.90 (s, 3H), 2.91 (d, 1H, J=13.7 Hz), 4.70 (d, 1H, J=12.6 Hz), 4.82 (d, 1H, J=12.6 Hz) and 7.2-7.5 (m, 4H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.46, 19.15, 24.65, 25.57, 48.13, 125.59, 126.87, 130.30, 131.31, 132.12 and 137.98; Anal. Calcd. for C₁₄H₂₃F₃O₃S₂Si: C, 43.28; H, 5.97; S, 16.50. Found: C, 42.38; H, 5.90; S, 16.23.

A suspension containing 500 mg of dried cesium fluoride in 3 ml of dimethoxyethane was treated with 455 mg of the above salt and the mixture was heated for 12 h at 450°C. At the end of this time the reaction mixture was poured into water and extracted with chloroform. The organic

layer was dried over magnesium sulfate and concentrated under reduced pressure to give 125 mg (64%) of a mixture of two compounds. The major compound (44%) isolated by silica gel chromatography was identified as 1,2-dimethyl-3-[(methylthio)methyl]benzene (17) on the basis of its spectral data and by comparison with an independently synthesized sample; IR (neat) 3020, 2980, 2920, 2860, 1470, 1440, 1390, 795 and 745 cm^{-1} ; NMR (CDCl_3 , 360 MHz) δ 2.03 (s, 3H), 2.28 (s, 3H), 2.29 (s, 3H), 3.70 (s, 2H) and 7.0-7.15 (m, 3H); Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{S}$: C, 72.23; H, 8.49. Found: C, 72.19; H, 8.51.

An authentic sample of 17 was prepared by treating a solution containing 730 mg of chloromethyl methyl sulfide in 50 ml of anhydrous ether at 00C with 50 ml of a 0.15 M solution of freshly prepared (2,3-dimethyl)phenyl magnesium bromide in ether. The mixture was allowed to stir at room temperature overnight. At the end of this time, the solution was poured into water and the organic phase was washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Silica gel chromatography of the crude residue using a 5% ethyl acetate-hexane mixture as the eluent gave 660 mg (54%) of 1,2-dimethyl-3-[(methylthio)methyl]benzene (17) which was identical in all respects to the material isolated from the reaction of 16 with cesium fluoride.

The minor component (20%) isolated from the column was assigned as 5-methylene-6-methyl-6-[(methylthio)methyl]-1,3-cyclohexadiene (19); NMR (CDCl_3 , 360 MHz) δ 2.03 (s, 3H), 2.10 (s, 3H), 2.55 (d, 1H, $J=12.5$ Hz), 2.69 (d, 1H, $J=12.5$ Hz), 5.10 (s, 1H), 5.15 (s, 1H), 5.71 (d, 1H, $J=9.5$ Hz) 5.87 (m, 1H), 5.99 (m, 1H) and 6.16 (d, 1H, $J=9.5$ Hz). This compound readily isomerized to 17 when subjected to silica gel chromatography.

When the reaction of 16 with cesium fluoride was allowed to stir at 250C for only 45 min, the crude NMR spectrum showed the presence of two products in a 2:1 ratio. The major component was identified as 4-methyl-5-methylene-6-[(methylthio)methyl]-1,3-cyclohexadiene (20); NMR (CDCl_3 , 360 MHz) δ 2.12 (s, 3H), 2.51 (dd, 1H, $J=12.9$ and 6.3 Hz), 2.67 (dd, 1H, $J=12.9$ and 8.1 Hz), 3.2 (m, 1H), 4.99 (s, 1H), 5.23 (s, 1H), 5.72-5.85 (m, 1H) and 5.9-6.0 (m, 2H). The minor component was identified as cyclohexadiene 19.

When the reaction of 16 with cesium fluoride was stirred for 13 h at 450C in the presence of benzaldehyde, the major product (78%) that was isolated after silica gel chromatography was identified as *trans*-1-(*o*-methylphenyl)-2-phenyloxirane (21) on the basis of its spectral properties; IR (neat) 3070, 3040, 2990, 1620, 1545, 1495, 1460, 1345, 1290, 1035, 900, 870, 760, 725 and 700 cm^{-1} ; NMR (CDCl_3 , 360 MHz) δ 2.35 (s, 3H), 3.76 (d, 1H, $J=1.9$ Hz), 3.99 (d, 1H, $J=1.9$ Hz) and 7.1-7.5 (m, 9H); ^{13}C -NMR (CDCl_3 , 50 MHz) δ 18.73, 60.79, 61.74, 124.01, 125.41, 126.09, 127.66, 128.18, 128.50, 129.73, 135.51, 135.80 and 137.29; HRMS Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}$: 210.1045. Found: 210.1044.

Alkylation of Trimethyl[(2-furyl)methylthio]methylsilane with Methyl Triflate Followed by Reaction with Cesium Fluoride. A solution containing 5.0 ml of furfuryl mercaptan in 200 ml of anhydrous tetrahydrofuran at -230C was treated with 45 ml of a 1.24 M solution of *n*-butyllithium in hexane. The reaction mixture was stirred for 2.5 h at -200C and was then treated with 7.35 ml of (iodomethyl)*n*methylsilane and stirred overnight. The solution was poured into water and extracted with ether. The ethereal layer was washed with a 10% sodium hydroxide solution, brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude oil was distilled to give 4.8 g (48%) of trimethyl[(2-furyl)methylthio]methylsilane as a colorless oil (bp 530C, 1.0 mm); IR (neat) 2955, 1505, 1245, 1150, 1010, 940, 850 and 735 cm^{-1} ; NMR (CCl_4 , 90 MHz) δ 0.07 (s, 9H), 1.67 (s, 2H), 3.60 (s, 2H), 6.05 (m, 1H), 6.17 (m, 1H) and 7.22 (m, 1H); ^{13}C -NMR (CDCl_3 , 20 MHz) δ -1.84, 18.11, 32.21, 107.22, 110.09, 141.85 and 151.71; UV (95% ethanol) 224 nm (ϵ 10900); Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{OSSi}$: C, 53.95; H, 8.05; S, 16.00. Found: C, 54.16; H, 8.30; S, 15.72.

A solution containing 1.0 g of the above material in 5 ml of anhydrous benzene at 00C was treated dropwise with a solution containing 0.57 ml of methyl triflate in 2 ml of anhydrous benzene. The reaction was stirred overnight and the resulting solution was concentrated to give a thick oil. Analysis of the oil by NMR spectroscopy showed the presence of methyl [(2-furyl)methyl] [(trimethylsilyl)methyl]sulfonium trifluoromethanesulfonate (22) in 85% yield; NMR (CDCl_3 , 90 MHz) δ 0.24 (s, 9H), 2.47 (s, 2H), 2.78 (s, 3H), 4.77 (s, 2H), 6.45 (m, 1H), 6.60 (d,

1H, $J=4.0$ Hz) and 7.50 (m, 1H). This material was dissolved in 5.0 ml of anhydrous dimethoxyethane and was stored at -100°C .

A suspension containing 300 mg of flame-dried cesium fluoride in 3 ml of anhydrous dimethoxyethane was treated with 1 ml of a 0.44 M solution of the above salt in dimethoxyethane and the mixture was stirred for 12 h at 400°C . At the end of this time, the solution was poured into water and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was subjected to silica gel column chromatography using chloroform as the eluent to give 31 mg (50%) of an oil which was identified as 2-methyl-3-(methylthio)methylfuran (23) on the basis of its spectral properties and by an independent synthesis; IR (CHCl_3) 2990, 2815, 1625, 1520, 1440, 1425, 1215, 1185, 1135, 1090, 950, 910 and 900 cm^{-1} ; NMR (CDCl_3 , 360 MHz) δ 2.00 (s, 3H), 2.25 (s, 3H), 2.45 (s, 2H), 6.29 (d, 1H, $J=1.8$ Hz) and 7.22 (d, 1H, $J=1.8$ Hz).

When the reaction of 22 with cesium fluoride was allowed to stir for only 2 h at 400°C and worked up in the usual fashion, the crude material showed the presence of 2-methylene-3-thiomethyl-4,5-dihydrofuran (26). The structure of this material was assigned on the basis of its spectral properties; NMR (CDCl_3 , 360 MHz) δ 2.16 (s, 3H), 2.58 (dd, 1H, $J=12.9$ and 8.5 Hz), 2.74 (dd, 1H, $J=12.9$ and 8.5 Hz), 3.71 (m, 1H), 4.28 (m, 1H), 4.63 (m, 1H), 5.30 (m, 1H) and 6.50 (m, 1H). This material readily isomerized to 23 upon standing. When the reaction of 22 with cesium fluoride was carried out in the presence of a 2 mole excess of benzaldehyde, the crude reaction mixture contained a 2:1 mixture (62%) of 2-methyl-3-(methylthio)methylfuran (23) and trans-2-(2-furyl)-1-phenyloxirane (7d).

Independent Synthesis of 2-Methyl-3-(methylthio)methylfuran (23). A solution containing 150 ml of pyridine and 70.2 g of ethyl acetoacetate was treated dropwise with 100 g of a 45% aqueous chloroacetaldehyde solution over a period of 15 min. The mixture was allowed to stir for 4 h during which time the temperature rose to 500°C and then slowly subsided. After stirring overnight, the reaction mixture was poured into water and extracted with ether. The ether layer was treated with a 10% aqueous hydrochloric acid solution to wash out the remaining pyridine, dried over magnesium sulfate and concentrated under reduced pressure. Distillation gave 68 g (86%) of 2-methyl-3-carboethoxyfuran³² as a colorless oil (bp $72\text{--}75^{\circ}\text{C}$, (7.0 mm)); IR (neat) 2980, 1720, 1605, 1430, 1415, 1300, 1235, 1190, 1160, 1130, 995, 945 and 740 cm^{-1} ; NMR (CDCl_3 , 360 MHz) δ 1.35 (t, 3H, $J=7.1$ Hz), 2.56 (s, 3H), 4.29 (q, 2H, $J=7.1$ Hz), 6.64 (d, 1H, $J=1.9$ Hz) and 7.22 (d, 1H, $J=1.9$ Hz).

A suspension containing 11.5 g of lithium aluminum hydride in 500 ml of anhydrous ether was treated dropwise with a solution containing 67.5 g of the above compound in 500 ml of ether over a period of 2.5 h. After the addition was complete, the mixture was heated at reflux for an additional 2 h, cooled to 00°C and treated with 11.5 ml of water and 11.5 ml of a 15% sodium hydroxide solution. The thick slurry was slowly treated with 20 ml of water until a fine grey precipitate had formed. The suspension was filtered and the filtrate was dried over magnesium sulfate and concentrated under reduced pressure to give 45 g (91%) of 3-hydroxymethyl-2-methylfuran as a colorless oil; IR (neat) 3320 (b), 2920, 2880, 1515, 1210, 1140, 1045, 1000 and 895 cm^{-1} ; NMR (CDCl_3 , 360 MHz) δ 1.78 (bs, 1H), 2.28 (s, 3H), 4.45 (d, 2H, $J=4.8$ Hz), 6.35 (d, 1H, $J=1.7$ Hz) and 7.25 (d, 1H, $J=1.7$ Hz).

A solution containing 10 g of the above furan in 100 ml of anhydrous ether at 00°C was treated with a solution containing 3.1 ml of phosphorous tribromide in 10 ml of ether. The ether solution was washed with two 50 ml portions of a 50% sodium hydroxide solution and dried over magnesium sulfate. The stock solution of 3-bromomethyl-2-methylfuran (24) prepared in this manner was used without further purification.

A solution containing 5.3 ml of methyl disulfide in 50 ml of anhydrous ether at 00°C was treated with 45 ml of a 1.2 M solution of methyl lithium in ether and stirred for 1 h. At the end of this time the solution was treated with 8.5 ml of hexamethylphosphoramide, cooled to -78°C and cannulated into the freshly prepared solution of the above bromide at -78°C . The reaction mixture was stirred for 4 h at -78°C and was allowed to slowly warm to room temperature. The reaction mixture was poured into water and the organic phase was washed with brine, dried over magnesium

sulfate and concentrated under reduced pressure. Silica gel chromatography of the crude residue using a 10% ethyl acetate-hexane mixture as the eluent gave 2.5 g of 23 which was identical in all respects to the material isolated from the reaction of 22 with cesium fluoride.

Preparation of Trimethyl[(1-propenyl)thio]methylsilane Followed by Reaction of its Methyl Triflate Salt with Cesium Fluoride. A solution containing 5.0 g of trimethylsilylmethyl mercaptan in 150 ml of anhydrous tetrahydrofuran at -23°C was treated with 34 ml of a 1.38 M solution of *n*-butyllithium in hexane and the mixture was stirred for 90 min. At the end of this time, 3.6 ml of allyl bromide was added and the reaction mixture was allowed to stir overnight. The solution was then poured into water and extracted with ether. The ethereal layer was washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give 6.1 g (91%) of trimethyl[(1-propenyl)thio]methylsilane as a colorless oil (bp 35°C, 3.5 mm); IR (neat) 3080, 2950, 2900, 2870, 1635, 1425, 1400, 1390, 1245, 1225, 1130, 990, 910 and 850 cm⁻¹; NMR (CCl₄, 90 MHz) δ 0.08 (s, 9H), 1.56 (s, 2H), 3.0 (d, 2H, J=7.0 Hz), 4.93 (m, 2H) and 5.4-5.9 (m, 1H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.83, 16.83, 38.62, 116.62 and 134.02; Anal. Calcd. for C₇H₁₆SSi: C, 52.43; H, 10.06; S, 20.00. Found: C, 52.62; H, 10.11; S, 19.87.

A solution containing 1.0 g of the above compound in 3 ml of anhydrous benzene at 0°C was treated dropwise with a solution containing 0.75 ml of methyl triflate in 1 ml of anhydrous benzene. The reaction was stirred overnight and then concentrated under reduced pressure to give 2.0 g (99%) of methyl (1-propenyl)[(trimethylsilyl)methyl]sulfonium trifluoromethanesulfonate (28) as a thick yellow oil; IR (neat) 3020, 2960, 2910, 1430, 1260 (b), 1160, 1030, 995, 965, 850 and 760 cm⁻¹; NMR (CDCl₃, 360 MHz) δ 0.28 (s, 9H), 2.60 (AB quartet, 2H, J=13.8 Hz), 2.87 (s, 3H), 4.12 (d, 2H, J=7.1 Hz) and 5.65-5.9 (m, 3H); ¹³C-NMR (CDCl₃, 20 MHz) δ -1.53, 24.03, 24.62, 46.96, 122.98 and 128.46.

A suspension containing 300 mg of anhydrous cesium fluoride in 2 ml of anhydrous dimethoxyethane was treated with a solution containing 270 mg of the above compound in 1 ml of dimethoxyethane and the mixture was heated for 24 h at 40°C. At the end of this time the reaction mixture was poured into water and extracted with methylene chloride. The methylene chloride layer was dried over magnesium sulfate and concentrated under reduced pressure to give 55 mg (72%) of 4-(methylthio)-1-butene (29) (lit³³ bp 124°C); NMR (CDCl₃, 360 MHz) δ 2.02 (s, 3H), 2.26 (m, 2H), 2.47 (t, 2H, J=7.4 Hz), 4.9-5.05 (m, 2H) and 5.65-5.8 (m, 1H).

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