

carboxyl-assisted<sup>17</sup> transformation of acyclic olefins will facilitate further functionalization of intermediates such as 18, enabling us to rapidly develop the polyketide-derived acyclic systems of biologically important macrolides. Efforts to further define the scope of the iterative scheme and applications of this strategy to the synthesis of complex, naturally occurring acyclic systems are in progress.

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**Registry No.** ( $\pm$ )-1, 87247-04-9; ( $\pm$ )-2, 102680-34-2; ( $\pm$ )-3, 64727-70-4; ( $\pm$ )-4, 102616-10-4; ( $\pm$ )-5, 102616-11-5; ( $\pm$ )-6, 102616-12-6; ( $\pm$ )-7, 102616-13-7; ( $\pm$ )-8, 102616-14-8; ( $\pm$ )-9, 102616-15-9; ( $\pm$ )-10, 102616-16-0; ( $\pm$ )-11, 102616-17-1; ( $\pm$ )-12, 102616-18-2; ( $\pm$ )-13, 102616-19-3; ( $\pm$ )-14, 102616-20-6; ( $\pm$ )-15, 102616-21-7; ( $\pm$ )-16, 102616-22-8; ( $\pm$ )-17, 102616-23-9; ( $\pm$ )-18, 102616-24-0; ( $\pm$ )-19, 102616-25-1; PhCH<sub>2</sub>OCH<sub>2</sub>C(O)Cl, 19810-31-2; ((E)-CH<sub>3</sub>CH=CH)<sub>2</sub>CuLi, 33462-38-3; MeOCH<sub>2</sub>C(O)Cl, 38870-89-2.

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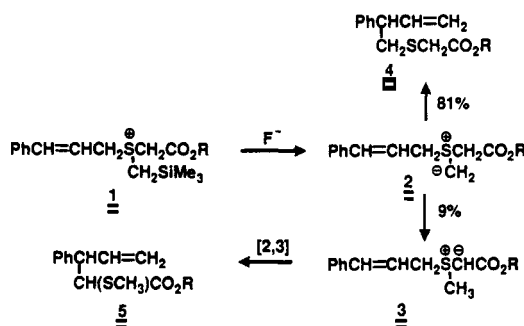
### [2,3]-Sigmatropic Rearrangement of Sulfur Ylides Derived from Trimethylsilyl Sulfonium Salts

**Summary:** The [2,3]-sigmatropic rearrangement of sulfur ylides derived via the desilylation of several  $\alpha$ -trimethylsilyl benzylsulfonium 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.

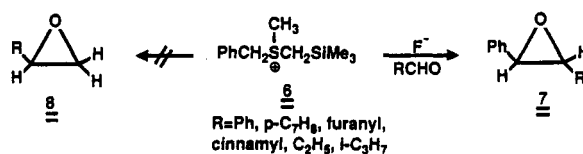
**Sir:** Desilylation of  $\alpha$ -trimethylsilyl onium salts by fluoride ion has been widely utilized in recent years as a convenient method for preparing nitrogen and sulfur ylides.<sup>1-10</sup> Relatively little work has been done, however, using the trimethylsilyl functionality as a leaving group in the generation of ylides for [2,3]-sigmatropic rearrangements.<sup>1,2,11-13</sup> In searching for new ways to utilize sulfur

ylides in organic synthesis, we investigated the fluoride-induced desilylation reaction of several benzyl  $\alpha$ -trimethylsilyl sulfonium salts. We report here the results of this study.

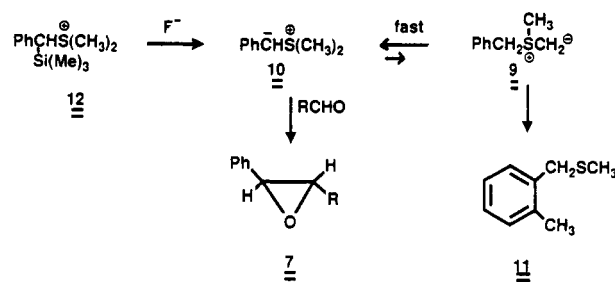
In 1979, Vedejs and Martinez reported that the fluoride-induced desilylation of 1 afforded 81% of the 2,3-sigmatropic shift product derived from the kinetic ylide 2 even though a more stabilized ester ylide 3 could have been produced by proton transfer.<sup>1</sup> Thus, we were somewhat



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.<sup>14</sup> No signs of the monosubstituted 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.<sup>1</sup> 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.



The fact that *o*-[(methylthio)methyl]toluene (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

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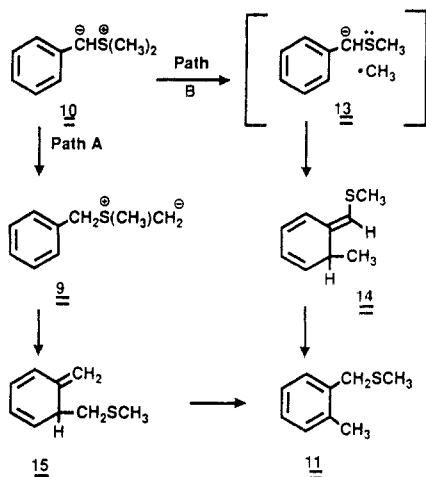
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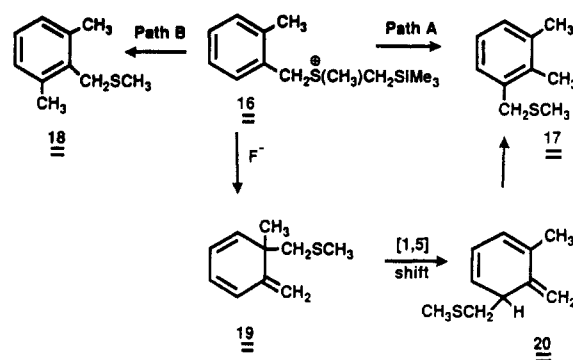
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(14) Yields ranged from (80-95%), and the structure of the epoxides were established by comparison with authentic samples.



completion.<sup>15</sup> 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.<sup>16-18</sup> 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 major product formed (80%) corresponded to cyclohexadiene **19**: NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  2.03 (s, 3 H), 2.10 (s, 3 H), 2.56 (d, 1 H,  $J = 12.5$  Hz), 2.70 (d, 1 H,  $J = 12.5$  Hz), 5.11 (br s, 1 H), 5.17 (br s, 1 H), 5.73 (d, 1 H,  $J = 9.5$  Hz), 5.88 (dd, 1 H,  $J = 9.5$  and 5.7 Hz), 6.02 (dd, 1 H,  $J = 9.5$  and 5.7 Hz),



and 6.18 (d, 1 H,  $J = 9.5$  Hz). Chromatography of this material on silica gel gave rise to **17**.<sup>19</sup> 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 conversion of **19** to **20** probably occurs either via a [1,5]-sigmatropic shift of the methyl or (methylthio)methyl group to give **20** followed by an aromatization step. The formation of **19** from **16** can be attributed to a [2,3]-sigmatropic rearrangement of the initially formed sulfur ylide (path A) onto the more substituted ortho position. The reason for this selectivity is not so obvious but may be related to the nonsynchronous nature of the sigmatropic rearrangement in which partial positive charge is developed in the transition state at the ortho position of the aromatic ring.

We are continuing to explore the desilylation of trimethylsilyl sulfonium salts as a method for generating ylides for [2,3]-sigmatropic rearrangements.

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**Registry No.** **16**, 102696-63-9; **17**, 102696-64-0; **18**, 102696-65-1; 1-bromo-2,3-dimethylbenzene, 576-23-8; chloromethyl methyl sulfide, 2373-51-5.

(19) **17**: NMR (CDCl<sub>3</sub>, 360 MHz)  $\delta$  2.03 (s, 3 H), 2.28 (s, 3 H), 2.30 (s, 3 H), 3.70 (s, 2 H), and 7-7.1 (m, 5 H).

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