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A New Fragmentation Reaction of γ-Oxosulfonium Methylides

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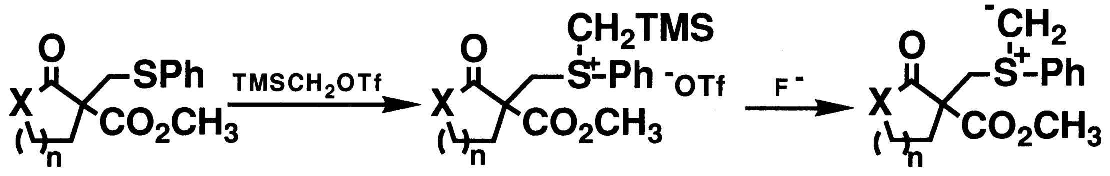
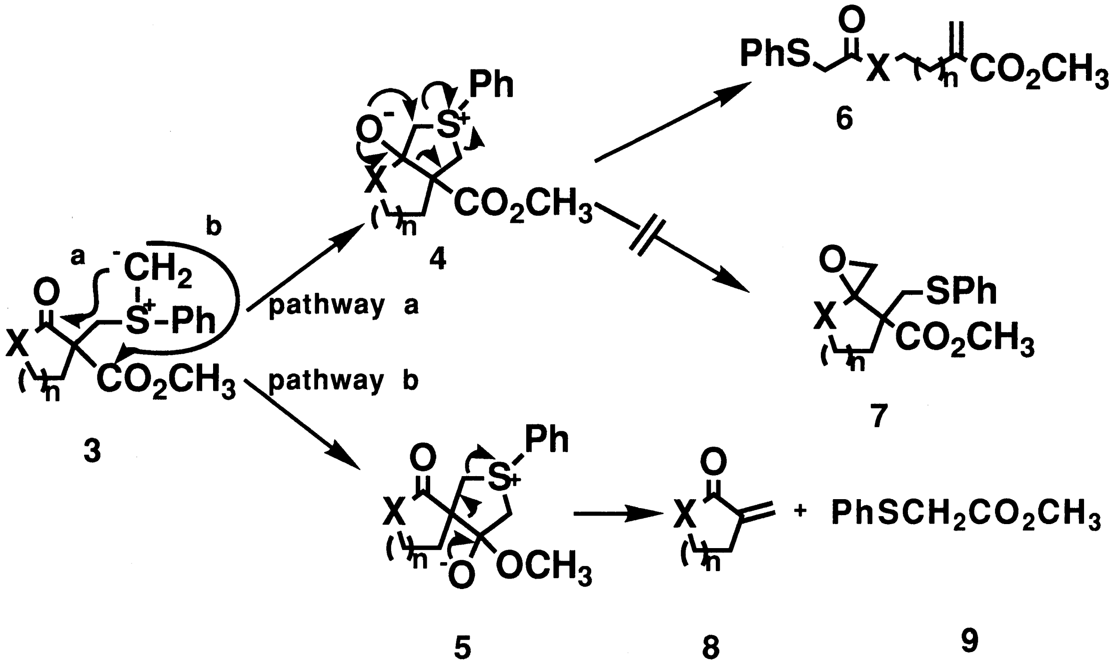
Reactions of sulfonium methylides attached to a 5- or 6-membered cycloalkanone undergo the ring-fission as a major reaction course to give α-methylene-ω-(phenylthio)carboxylates, whereas sulfonium methylides attached to a larger ring give α-methylenecycloalkanones predominantly. Reactions of the acyclic compounds are also examined.

Reactions of sulfonium ylides with ketones or aldehydes have been widely exploited for the construction of various epoxides,1) including annulation accompanied by concomitant formation of an epoxide ring.2) These ylides have been generally generated by the abstraction of a proton α to the sulfonium group with base. Recently the fluoride-induced desilylation of (trimethylsilyl)methylsulfonium salts has provided an easy access to the regiospecific generation of sulfonium methylides from sulfonium salts.3) We now report a novel reaction of sulfonium ylides generated from (trimethylsilyl)methylsulfonium salts of a variety of α-(phenylthio)methyl-β-ketoesters.



1 **2** **3**

In the reaction of the sulfonium ylide **3** it would be expected that **3** undergoes fragmentation through at least two pathways involving attack by the ylide carbanion at either the carbonyl carbon (pathway **a**) or the ester carbon (pathway **b**) as illustrated in Scheme 1. In fact, treatment of the (trimethylsilyl)methylsulfonium salt **2** (X=CH_2, n=2) with tetrabutylammonium fluoride gave the ring-fissioned α,β-unsaturated ester **6** (X=CH_2, n=2) via pathway **a** together with small amounts of α-methylenecyclohexanone **8** (X=CH_2, n=2) and methyl (phenylthio)acetate **9** both of which were obviously derived via pathway **b**. The results obtained in the reaction of various sulfonium ylides are shown in Table 1.

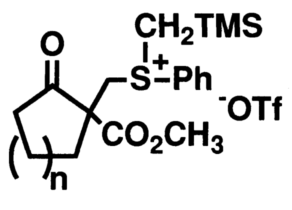
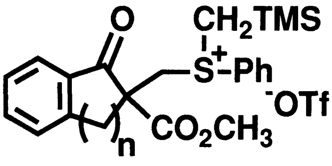
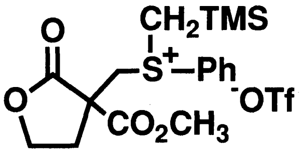
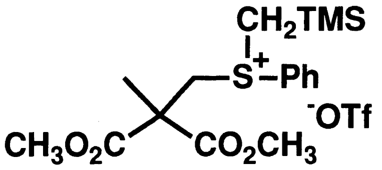
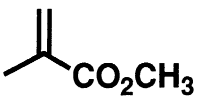
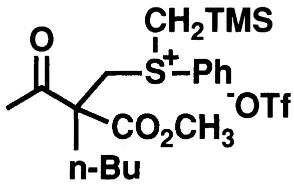
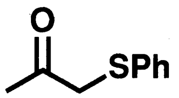
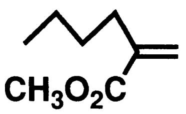


Scheme 1.

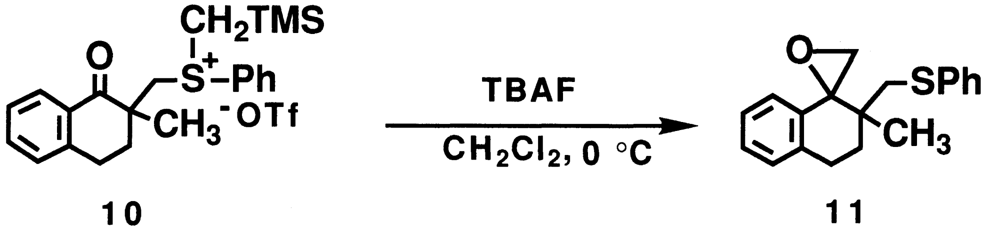
In the reaction of the ylides bearing a cycloalkanone it depends upon the ring size of the cycloalkanone whether the reaction proceeds via pathway **a** or **b**. The cyclopentanone sulfonium methylide afforded the ring-fissioned product **6** (X=CH$_2$, n=1, entry 1) predominantly as in the case of the cyclohexanone sulfonium methylide (entry 2), while the reaction of the ylides having a larger ring cycloalkanone such as cycloheptanone, cyclooctanone or cyclododecanone resulted in the predominant fragmentation via pathway **b** (entries 3-5), affording the α-methylenecycloalkanones4) **8** (X=CH$_2$, n=3, 4, or 8) and methyl (phenylthio)acetate **9** in high yields. The reaction of the ylides bearing an indanone or tetralone moiety proceeded predominantly via pathway **a** as being similar to that of the corresponding cyclopentanone and cyclohexanone ylides (entries 6 and 7). In the reaction of the γ-butyrolactone ylide (entry 8) attack by the ylide occurred predominantly at the ester carbon through pathway **b**. The ketone carbonyl was more susceptible than the ester carbonyl as shown in the reaction of the acyclic ylide (entry 10).

It should be noted that formation of the epoxide **7** could not be observed in the present reaction, because reactions of sulfonium ylides bearing a carbonyl group have been reported to give epoxides.1,2) Electron-withdrawing properties of the ester (pathway **a**) and carbonyl (pathway **b**) groups may cause the preferred cleavage of the bridged bond in the intermediate **4** and **5**, respectively. Indeed, 2-methyltetralone sulfonium salt **10** gave the epoxide **11** in 93% yield, wherein no ring-fissioned products via either pathway **a** or **b** were not formed. The present process provides a new ring cleavage reaction through sulfonium ylides, giving the α-methylene-ω-(phenylthio)carboxylate **6** which can be transformed to carbocycles.5)

Table 1. Fragmentation of sulfonium methylides

Entry	Sulfonium salt		Products, yield / %[a]		
	2		6	8	9
1		n = 1	65	—	5
2		n = 2	58	4	22
3		n = 3	23	13	75[b]
4		n = 4	3	75	90
5		n = 8	12	69	70
6		n = 1	66	5	14
7		n = 2	57	33	31
8			17	—	63
9			 80		84
10			 61  50	—	5

a) Isolated yield. b) When the sulfonium salt was treated with CsF (1.3 equiv.) in CH_2Cl_2 under reflux for 22 h, the yields of **6**, **8**, and **9** were 30, 35, and 48%, respectively.



10 **11**

A typical procedure is as follows: A mixture of sulfide **1** and (trimethylsilyl)methyl trifluoromethanesulfonate (1.2 equiv.) in CH_2Cl_2 was stirred at room temperature for 1 day. After removal of the solvent under reduced pressure the salt was washed with a mixture of hexane and ethyl acetate (9 : 1). The salt **2** was then treated with a THF solution of tetrabutylammonium fluoride (1.5 equiv.) at 0 °C for 3 h in the presence of powdered molecular sieves 4A.⁶⁾ Then the reaction was quenched with water. The mixture was extracted with ether. The combined extracts were washed with brine, dried with $MgSO_4$, filtrated and concentrated under reduced pressure. Purification of this crude product by silica gel chromatography (10% ethyl acetate in hexane) gave products.

References

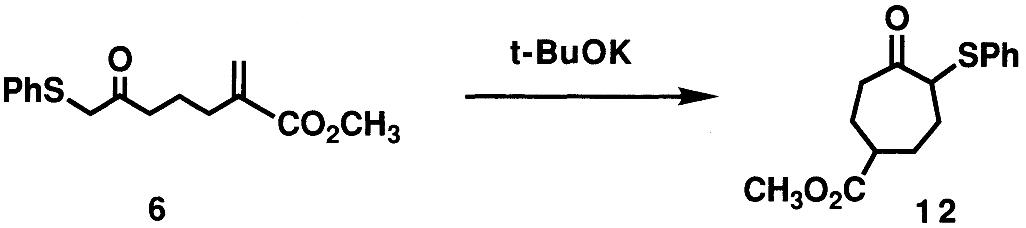
1) E. Block and M. Aslam, *Tetrahedron*, **44**, 281 (1988); "The Chemistry of the Sulfonium Group Part 1 and 2," ed by C. J. M. Stirling, John Wiley & Sons, New York (1981); E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York (1978); B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides," Academic Press, New York (1975).

2) J. K. Crandall, H. S. Magaha, R. K. Widener, and G. A. Tharp, *Tetrahedron Lett.*, **21**, 4807 (1980); M. E. Garst and A. T. Johnson, *ibid.*, **21**, 4812 (1980).

3) E. Vedejs and F. G. West, *Chem. Rev.*, **88**, 941 (1986); E. Vedejs and G. R. Martines, *J. Am. Chem. Soc.*, **101**, 6452 (1979).

4) In some reactions exo-methylene compounds **8** could not be obtained or otherwise isolated in lower yields compared with those of the (phenylthio)acetate **9** probably because of the instability of **8** under the reaction conditions.

5) The α-methylene-ω-(phenylthio)carboxylate **6** ($X=CH_2$, n=1) obtained from the cyclopentanone sulfonium methylide was cyclized to the α-(phenylthio)cycloheptanone **12** in 82% yield by treatment with potassium *t*-butoxide at 0 °C.



6 **12**

6) R. M. Hanson and K. B. Sharpless, *J. Org. Chem.*, **51**, 1922 (1986).

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