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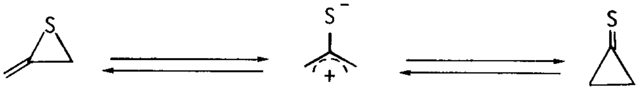
A NEW STRATEGY TO SULFUR HETEROCYCLES: REACTIONS OF AN ALLENE EPISULFIDE WITH ELECTROPHILES

Wataru Ando*, Toshiya Furuhata, Yukio Hanyu, and Toshikazu Takata

Department of Chemistry, The University of Tsukuba
Sakura, Ibaraki 305, Japan

Abstract: A variety of sulfur-containing five- and six-membered cyclic compounds was obtained by the acid-catalyzed and thermal reactions of an allene episulfide with various electrophiles.

Although many reactions of thiiranes with nucleophiles and electrophiles are documented to bring about ring opening,1) only a few examples are demonstrated for the ring opening reaction leading directly to heterocycles containig sulfur atom: reactions with nitriles2) and cyano acetates3) give thiazolines and iminothiophenes, respectively. Meanwhile, allene episulfide(1)4)5) is an unique thiirane having an exomethylene group, and thereby is suggested to participate a tautomerism5) involving thioxyallyl ion(2) and cyclopropanethione(3) due to its easy ring opening, like methylene cyclopropane6) or allene oxide.7) Since only two stable allene episulfides are known,8) no or little study has been done on the chemistry of 1 in comparison with its oxygen analogue.7) Recently, we have first obtained the spectroscopic evidence of protonated 2 by treatment of tetramethyl allene episulfide(4)8b) with super acid at -70°C,9) and at room temperature, several dimeric products were obtained probably via thioxyallyl ion. We now extend to the acid-catalyzed and thermal reactions of 1 in the presence of various electrophiles, and found that 4 can function as a reactive species toward various electrophiles to afford heterocycles.

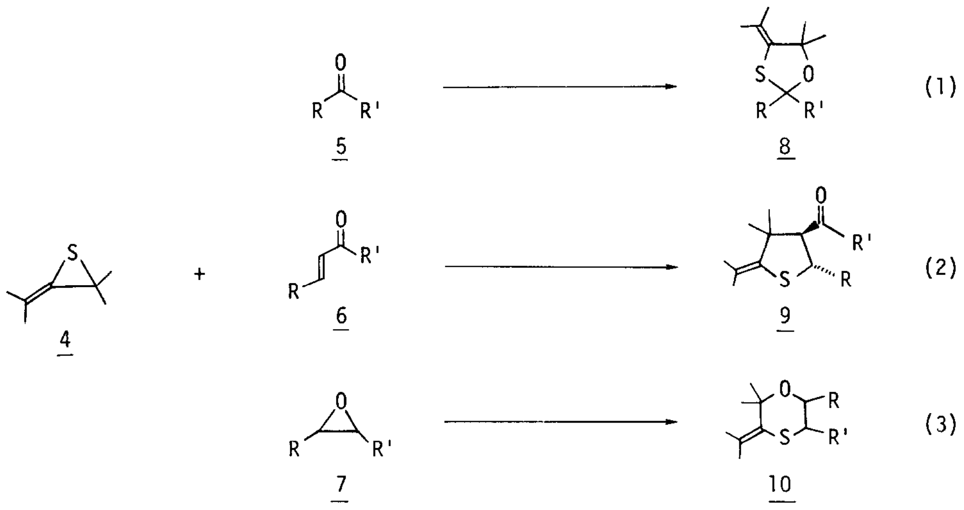


1 2 3

Method A. A mixture of 4(1 mmol) and benzaldehyde(5 mmol) dissolved in dry ether(5 mL) was treated with dimethyl sulfate(1 mmol) under nitrogen atmosphere. After complete consumption of 4 the mixture was subjected to silica gel chromatography to give 2,2-dimethyl-3-(2-propylidene)-5-phenyl-4-thioxolane(8, R=Ph, R'=H) in 48% yield.

Method B. The mixture of 4(1 mmol) and benzaldehyde(5 mmol) dissolved in dry diglyme(5 mL) was heated for 8h at 110-115°C under nitrogen. Removal of excess benzaldehyde and diglyme under reduced pressure gave the crude adduct(8) which was purified by the chromatography(yield 40%).

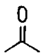
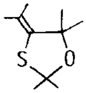
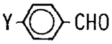
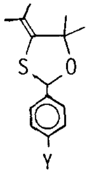
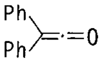
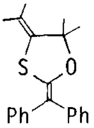
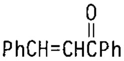
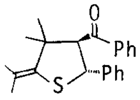
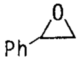
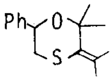
Thus, reaction of 4 with various electrophiles formed a variety of heterocycles containing sulfur atom(Eq.1-3), along with dimeric products of 4.10) The main product was same in both methods. The selected results are shown in Table 1. The all products were characterized by IR, NMR, MS and elemental analyses.



Surprisingly, diphenyl ketene also reacted at carbonyl part to produce diphenylmethylidene derivative in a high yield(Runs 6 and 7), since generally electrophilic reaction to ketene occurs at C-C double bond.11) trans-Chalcone as an α,β-unsaturated ketone(6) unexpectedly afforded thiolane(9) by a cycloaddition to C-C double bond with trans mode, but the yield was still low, and mesityl oxide was unreactive. Meanwhile, six-membered ring product (10) was obtained in the case of styrene oxide(7) in a moderate yield(Runs 10 and 11). The other regio-isomer, however, was not detected at all.

Dimethyl sulfate was used as an acid catalyst for aldehyde, ketene and oxirane which were unstable for BF_3 catalyst. Although the thermal reaction was pertinent for p-nitrobenzaldehyde, the gradual thermal decomposition of the products was often observed under the conditions.

Table 1 Formation of Sulfur Heterocycles in the Reaction of Tetramethyl Allene Episulfide(4) with Various Electrophiles.

Run	Substrate	Method[a]	Acid	Reaction Time(h)	Product	Isolated Yield(%)
1		A[b]	$BF_3 \cdot Et_2O$	0.75		64
2	 Y=H	A	Me_2SO_4	32		48
3	Y=H	B	none	8		40
4	$Y=NO_2$	B	none	0.25		70
5	$Y=CH_3$	B	none	21		7
6		A	Me_2SO_4	1[c]		64
7		B	none	1		86
8	 $PhCH=CHC(=O)Ph$	A	$BF_3 \cdot Et_2O$	1		23
9		B	none	11		15
10		A	Me_2SO_4	48		53
11		B	none	10		41

a) Method A: acid-catalyzed reaction in ether; Method B: thermal reaction at 110-115°C in diglyme. b) acetone solvent. c) in refluxing ether.

The reaction mechanism is rather complicated and it is not clear whether the thioxyallyl ion is always involved or not. Inspection of data in Table 1 (Runs 3-5) seems to show clear dependency on electrophilicity of the carbonyl groups in the thermal reactions, while the coordination of Lewis acid to the electrophiles as well as 4 may be intrinsic in the acid-catalyzed reactions. These results do not need the intermediacy of the thioxyallyl ion. However, the involvement of the thioxyallyl ion cannot be ruled out by the evidence that the formation of the dimeric products of 4 in every reactions.[9)10)]

Further synthetic applicability and detail reaction mechanism are under active investigation.

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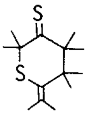
10) The following dimeric compounds9) were obtained as by-products in less than 10% total yield. These were easily removed by silica gel chromatography(eluent:hexane). In the thermal reaction, 13 and either of 11 and 12 were produced, while both 11 and 12 were formed in the acid-catalyzed reaction.



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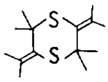

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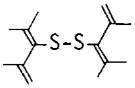

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