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# ISOMERIZATION AND DESULFURIZATION OF ALLENE EPISULFIDES

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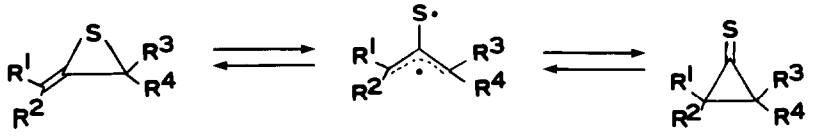
Abstract: Allene episulfides unevenly substituted underwent a thermal and acid catalyzed isomerization and a desulfurization, which were rationalized by the tautomeric recyclization and sulfur elimination of thioxyallyl intermediate.

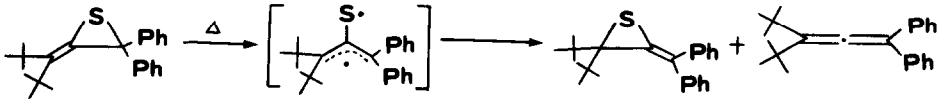
In the tautomerism of allene episulfide(1) with cyclopropanethione(3), thioxyallyl intermediate(2) has played a well-fitting and very important role, and has been attracting much current interest.[1,2] Previously we have reported the generation and reactions of thioxyallyl intermediate by the unimolecular thermal C-S bond cleavage of tetramethylallene episulfide.[3,4] However, very little is known for the possible recyclization route of thioxyallyl intermediate(2) derived from 1 backward into the allene episulfide skeleton.



1 2 3

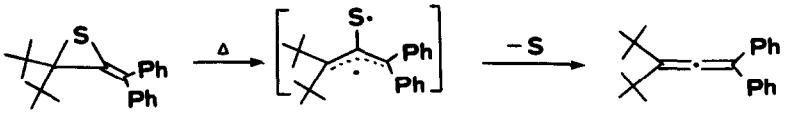
From this point of view, we now delineate the characteristic thermal and acid catalyzed valence isomerization of allene episulfides, the substituents of which were different on the S-α ring carbon and the terminal olefinic carbon each other.

When an allene episulfide(1a)[5] was heated in o-dichlorobenzene at 150°C for 2h, 69% of isomerized allene episulfide(4a) was obtained along with 31% of allene(5) at 40% of conversion.



1a 2a 4a 5

It was recognized that 4a and 5 were formed via common intermediate such as thioxyallyl intermediate(2a), since the thermolysis of 4a thus obtained did not afford the original allene episulfide(1a) but gave the allene(5) about eight times slower even at 180°C than that of 1a.




4a 2a 5

Then to ascertain the intermediacy of 2a we examined the kinetic studies on the thermolysis of 1a and 4a by measuring their rates of decrease using $^1$H-NMR spectroscopy. The first-order rate constants are listed in Table 1 along with the activation parameters which were in fairly good accordance with those obtained from the thermolysis of tetramethylallene episulfide leading to thioxyallyl intermediate.[4] The thermolysis of 1a and 4a accelerated in a polar solvent probably because of the dipole moment of C-S bond in thioxyallyl intermediate. These results are interpreted with thioxyallyl intermediate(2a) for the valence isomerization of 1a and for the desulfurization of 4a, respectively. However, small solvent effects can be regarded as a biradical character of 2a with a small contribution of zwitterionic structure.[8]

Table 1. First-order Rate Constants and the Activation Parameters on the Thermolysis of Allene Episulfides.

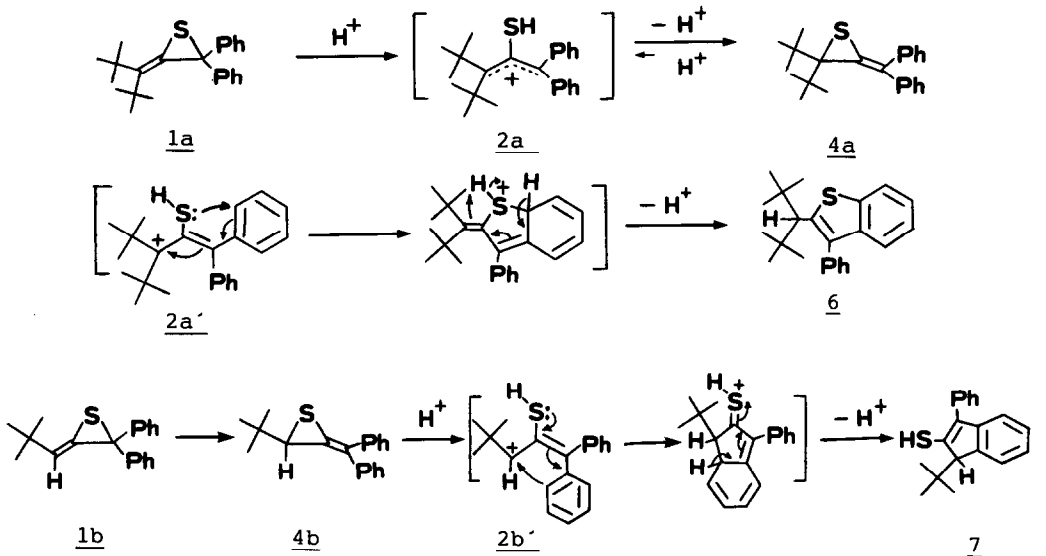
| | Temp.(K) | Solvent[a] | Rate Constant $k(s^{-1})$ | Activation Parameters |
|---|---|---|---|---|
| 1a | 453 | A | $46.2 \times 10^{-5}$ | Ea = 24.3 kcal mol$^{-1}$ |
| | 443 | A | $23.3 \times 10^{-5}$ | |
| | 433 | A | $12.5 \times 10^{-5}$ | $\Delta H^{\ddagger}$ = 23.5 kcal mol$^{-1}$ |
| | 423 | A | $6.80 \times 10^{-5}$ | |
| | 423 | B | $11.1 \times 10^{-5}$ | $\Delta S^{\ddagger}$ = -14.8 e.u. |
| 4a | 453 | A | $5.66 \times 10^{-5}$ | Ea = 28.5 kcal mol$^{-1}$ |
| | 443 | A | $2.34 \times 10^{-5}$ | |
| | 433 | A | $1.30 \times 10^{-5}$ | $\Delta H^{\ddagger}$ = 27.6 kcal mol$^{-1}$ |
| | 423 | A | $5.60 \times 10^{-6}$ | |
| | 423 | B | $1.26 \times 10^{-5}$ | $\Delta S^{\ddagger}$ = -9.8 e.u. |

a) A: o-dichlorobenzene, B: diglyme

An analogous valence isomerization of allene episulfides does take place readily with acid catalysts.[7] When 1a was treated with a catalytic amount of trifluoroacetic acid in chloroform at room temperature, the $^1$H-NMR spectrum monitored immediately after the addition showed a quantitative valence isomerization into 4a and the formation of the benzothiophene derivative(6) with slow intramolecular cyclization. 6 was obtained quantitatively after 20h.[10]

Similarly, allene episulfide(1b) isomerised into 4b completely even on silica gel column, however, the treatment of 4b with trifluoroacetic acid resulted in the exclusive formation of the indene derivative(7) in an excellent yield.[11]

Acid catalyzed isomerization might be interpreted with the intermediacy of the thioxyallyl ion as illustrated in the scheme, and the direction of the subsequent intramolecular cyclization leading to 6 or 7 seems to be controlled by the steric hindrance around the cationic reaction center.




References and Notes

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4. T. Furuhata and W. Ando, Tetrahedron, 1986, 42, 5301.