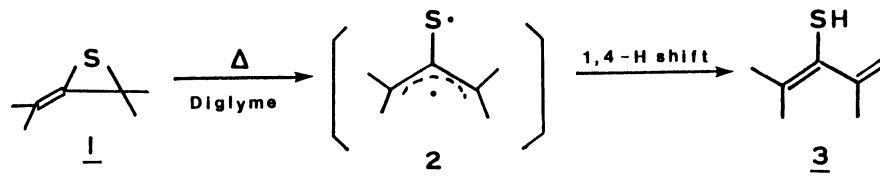


Effect of Silyl Substituent on Thermal Isomerization of  
Allene Episulfide. A New Aspect in Thioxyallyl Intermediate

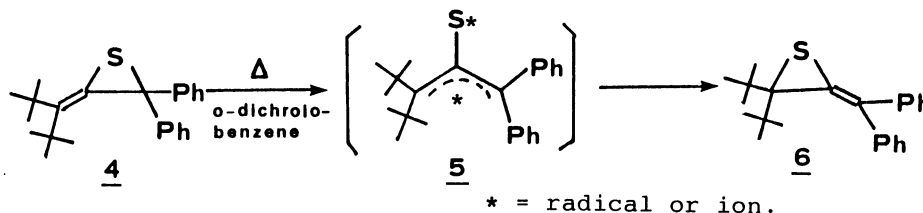
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Kinetic studies on the thermal isomerization of 1,1-bis(trimethylsilyl)-3,3-diphenylallene 2-episulfide showed an attractive accelerating effect of silyl substituents attributable to the partial ionic nature of thioxyallyl intermediate.

Allene episulfide, a novel strained small ring system, undergoes a variety of characteristic reactions which are well interpreted with an intermediacy of thioxyallyl, a sulfur analogue of trimethylenemethane intermediate in the case of methylenecyclopropane.<sup>1-3)</sup> Recently, we have described kinetic studies on the thermal C-S bond cleavage of tetramethylallene episulfide(1) followed by the 1,4-hydrogen shift through 2 to give the corresponding vinyl sulfide derivative(3)<sup>4)</sup> and the thermal isomerization of 1,1-di-t-butyl-3,3-diphenylallene 2-episulfide(4) into 6 via 5<sup>5)</sup> as shown below, and revealed that 2 and 5 have a biradical structure with some ionic character.



$$\Delta E_a = 26.5 \text{ kcal mol}^{-1}, \Delta H^\ddagger = 26.2 \text{ kcal mol}^{-1}, \Delta S^\ddagger = -12.1 \text{ e.u.}$$



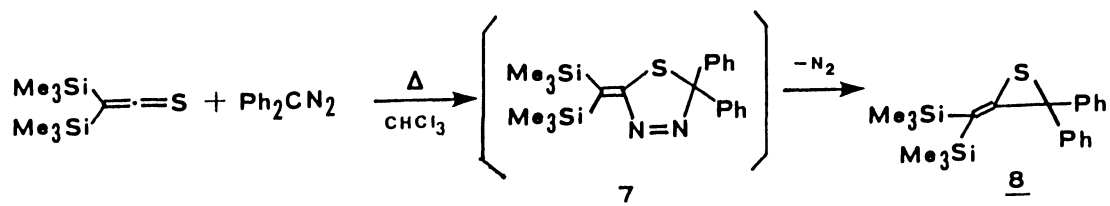
\* = radical or ion.

$$\Delta E_a = 24.3 \text{ kcal mol}^{-1}, \Delta H^\ddagger = 23.5 \text{ kcal mol}^{-1}, \Delta S^\ddagger = -14.8 \text{ e.u.}$$

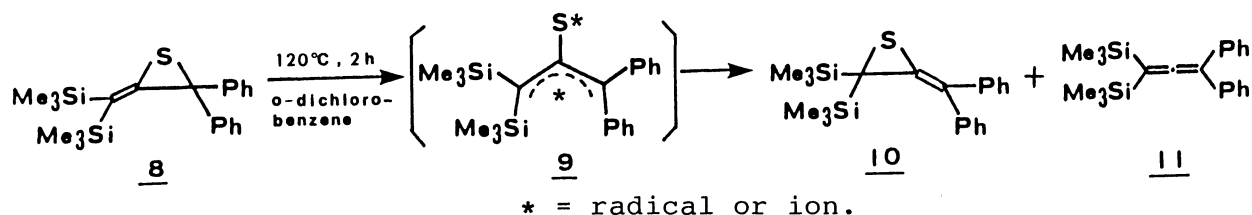
As for the structure of the thioxyallyl intermediate we have already reported its MCSCF calculation to show that  $^1B_1$  state is more stable than  $^1A_1$  state and it has some dipole moment,<sup>6,7)</sup> however, there has been little

experimental arguments for its charge distribution. Here, we present an investigation of thermal isomerization of 1,1-bis(trimethylsilyl)-3,3-diphenylallene 2-episulfide (**8**), the substituent effect of which enlightened us on the partial ionic character of the thioxyallyl intermediate.

The introduction of trimethylsilyl groups into an allene episulfide skeleton was achieved by the cycloaddition of diphenyldiazomethane with bis(trimethylsilyl)thioketene<sup>8)</sup> in chloroform followed by the thermal denitrogenation of the intermediary 2-alkylidene-1,3,4-thiadiazoline derivative (**7**)<sup>9)</sup> to give an allene episulfide (**8**) in 58% yield.<sup>10)</sup>



When **8** was heated in *o*-dichlorobenzene at 120 °C for 2 h, 62% of isomerized allene episulfide (**10**)<sup>11)</sup> was obtained along with 33% of allene (**11**)<sup>12)</sup> at 72% conversion similarly to the thermolysis of **4**. Under the reaction conditions **10** gave only the allene (**11**) without any isomerization backward into **8**.



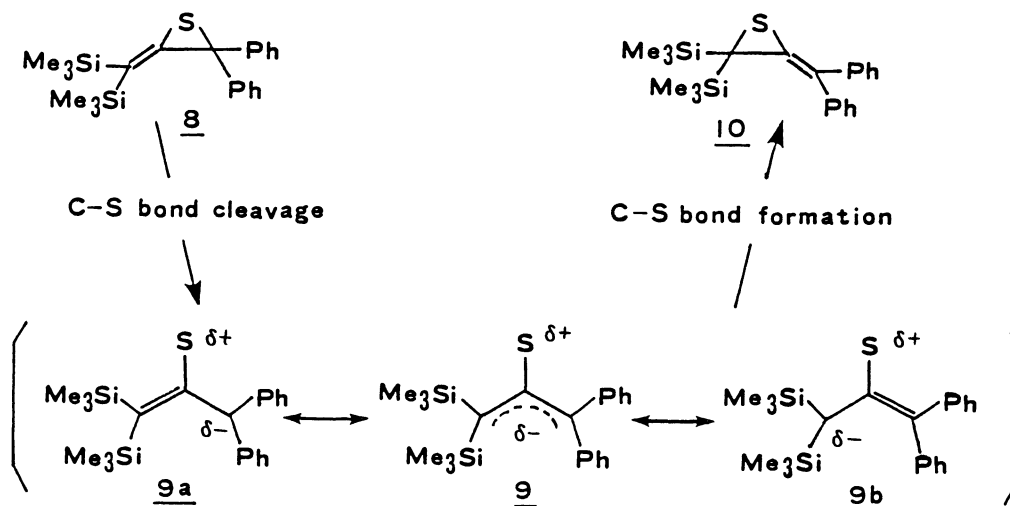
Then to examine the substituent effect of the silyl groups on the isomerization of allene episulfide and a nature of thioxyallyl intermediate, kinetic studies on the thermolysis of **8** were carried out in *o*-dichlorobenzene and diglyme by measuring the rate of decrease using <sup>1</sup>H-NMR spectroscopy. The first-order rate constants and the activation parameters thus obtained are listed in Table 1. Comparison of the rate constants and activation parameters for the isomerization of **8** and **4** shows that the replacing of the two *t*-butyl groups by the more electropositive trimethylsilyl groups resulted in a noticeable increase of the rate of isomerization. In a polar solvent such as diglyme, the thermolysis of **8** showed a slight acceleration similarly to that of **4**<sup>13)</sup> indicating the partial ionic nature of the possible transition states and/or intermediates due to the dipole moment of the C-S bond. These results imply that the mechanism of the valence isomerization of **8** involves thioxyallyl intermediate (**9**) with a positive charge on sulfur atom and a negative charge on the allylic part as shown in Scheme 1, which is in good agreement with the preliminarily calculated charge distributed structure of thioxyallyl intermediate.<sup>7)</sup>

Table 1. First-order Rate Constants and the Activation Parameters of the Thermolysis of Allene Episulfide(8)

Temp/K	Solvent <sup>a)</sup>	Rate const. k/s <sup>-1</sup>	Activation parameters
411	A	62.5 x 10 <sup>-5</sup>	E <sub>a</sub> = 19.16 ± 0.15 kcal mol <sup>-1</sup> ΔH <sup>‡</sup> = 18.39 ± 0.14 kcal mol <sup>-1</sup> ΔS <sup>‡</sup> = -29.03 ± 0.29 e.u.
398	A	29.0 x 10 <sup>-5</sup>	
383	A	12.8 x 10 <sup>-5</sup>	
373	A	5.85 x 10 <sup>-5</sup>	
363	A	2.74 x 10 <sup>-5</sup>	
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397	B	34.8 x 10 <sup>-5</sup>	E <sub>a</sub> = 14.54 ± 0.31 kcal mol <sup>-1</sup>
387	B	24.0 x 10 <sup>-5</sup>	ΔH <sup>‡</sup> = 13.79 ± 0.30 kcal mol <sup>-1</sup>
363	B	6.35 x 10 <sup>-5</sup>	ΔS <sup>‡</sup> = -40.10 ± 0.75 e.u.

a) A; o-dichlorobenzene, B; diglyme.

It seems to us that the α-effect of the neighboring trimethylsilyl groups<sup>14)</sup> contributed in cooperation with the resonance stabilization by the phenyl groups to the stabilization of the resonance structure(9b) which intervenes in the C-S bond forming step, though one cannot help abandon the possible stabilizing effect of silyl substituents to α-radical center at all.



Scheme 1.

Above results are in contrast to the analogous oxygen system, i.e. allene oxide-oxyallyl system,<sup>15)</sup> which has in general involved the zwitterionic oxyallyl intermediate possessing a negative charge on the oxygen atom and a positive charge on the allylic part, therefore, the chemistry of allene episulfide-thioxyallyl system will attract more attention from both experimental and theoretical standpoints.

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- 8) S. J. Harris and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1976, 1008.
- 9) The lack of **8** from the reaction of bis(trimethylsilyl)thioetene with diphenylcarbene generated by metal catalyst and the isolation of 2-alkylidene-1,3,4-thiadiazoline intermediate in the reaction of t-butylthioetene with diphenyldiazomethane confirmed the intermediacy of **7**.
- 10) **8**;  $^1\text{H-NMR}(\text{CDCl}_3)$   $\delta = -0.10(9\text{H},\text{s}), 0.26(9\text{H},\text{s}),$  and  $7.0-7.4(10\text{H},\text{m})$ ;  $^{13}\text{C-NMR}(\text{CDCl}_3)$   $\delta = 0.3(\text{q}), 1.2(\text{q}), 48.6(\text{s}), 116.7(\text{s}), 127.3(\text{d}), 128.0(\text{d}), 128.9(\text{d}), 140.8(\text{s}),$  and  $158.9(\text{s})$ ; UV(hexane)  $\lambda_{\text{max}}$  272 nm ( $\epsilon$  18200); MS,  $m/z$  368( $\text{M}^+$ , 12%), 336(28), 248(90), 198(63), and 73(100); exact mass, found  $m/z$  368.1432 calcd for  $\text{C}_{21}\text{H}_{28}\text{Si}_2\text{S}$  368.1448.
- 11) **10**;  $^1\text{H-NMR}(\text{CDCl}_3)$   $\delta = -0.04(18\text{H},\text{s})$  and  $7.0-7.5(10\text{H},\text{m})$ ;  $^{13}\text{C-NMR}(\text{CDCl}_3)$   $\delta = -1.3(\text{q}), 32.8(\text{s}), 122.4(\text{s}), 126.8(\text{d}), 126.9(\text{d}), 128.2(\text{dx}2), 128.3(\text{dx}2), 136.8(\text{s}), 140.4(\text{s}),$  and  $140.9(\text{s})$ ; MS,  $m/z$  368( $\text{M}^+$ , 75%), 336(25), 263(100), and 73(88); exact mass, found  $m/z$  368.1441 calcd for  $\text{C}_{21}\text{H}_{28}\text{Si}_2\text{S}$  368.1449e.
- 12) As judged by the very low formation rate of **11** in the early stage of thermolysis of **8**, **11** might be mainly derived from the isomer (**10**) and an alternative direct desulfurization of **8** into **11** seems unlikely to compete with the isomerization. **11**;  $^1\text{H-NMR}(\text{CDCl}_3)$   $\delta = 0.08(18\text{H},\text{s})$  and  $7.1-7.6(10\text{H},\text{s})$ ;  $^{13}\text{C-NMR}(\text{CDCl}_3)$   $\delta = 0.45(\text{q}), 93.0(\text{s}), 96.7(\text{s}), 1215.6(\text{d}), 127.5(\text{d}), 128.3(\text{d}), 137.6(\text{s}),$  and  $209.2(\text{s})$ ; IR( $\text{CCl}_4$ )  $1895\text{ cm}^{-1}$ ; MS,  $m/z$  336( $\text{M}^+$ , 29%), 263(6), 248(69), and 73(100); exact mass, found  $m/z$  336.1726 calcd for  $\text{C}_{21}\text{H}_{28}\text{Si}_2$  336.1728.
- 13) Both of the thermolysis of **4** and **8** in diglyme were accelerated about two times faster than that in o-dichlorobenzene; see Ref. 5.
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