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

Norihiro TOKITOH, Nami CHOI, and Wataru ANDO*
Department of Chemistry, University of Tsukuba,
Sakura-mura, Niihari-gun, Ibaraki 305

Kinetic studies on the thermal isomerization of 1,1-bis(tri-methylsilyl)-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.[1-3]   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)[4] and the thermal isomerization of 1,1-di-t-butyl-3,3-diphenylallene 2-episulfide(4) into 6 via 5[5] as shown below, and revealed that 2 and 5 have a biradical structure with some ionic character.
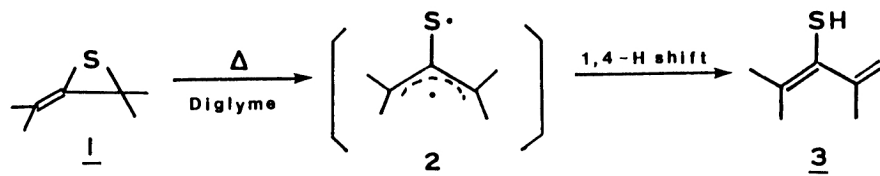
$$\Delta E_a = 26.5\ \text{kcal mol}^{-1},\ \Delta H^{\ddagger} = 26.2\ \text{kcal mol}^{-1},\ \Delta S^{\ddagger} = -12.1\ \text{e.u.}$$
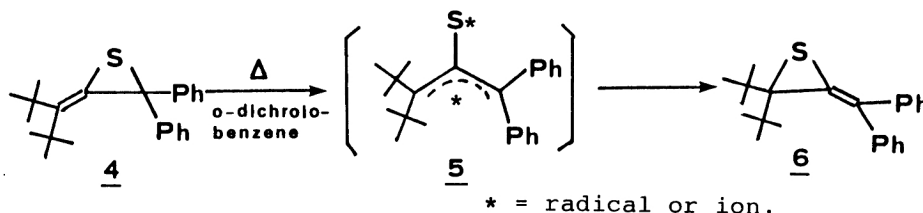

* = radical or ion.

$$\Delta E_a = 24.3\ \text{kcal mol}^{-1},\ \Delta H^{\ddagger} = 23.5\ \text{kcal mol}^{-1},\ \Delta S^{\ddagger} = -14.8\ \text{e.u.}$$
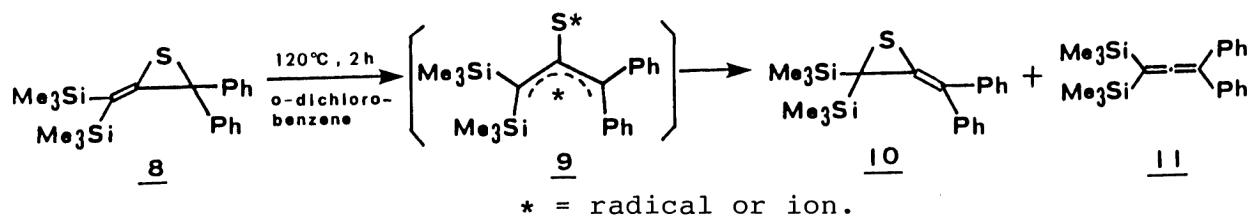
As for the structure of the thioxyallyl intermediate we have already reported its MCSCF calculation to show that $^1B_1$ state is more stable than $^1A_1$ state and it has some dipole moment,[6,7] however, there has been little

experimental arguments for its charge distribution.   Here, we present an inves-
tigation 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[8] in chloroform followed by the thermal denitrogen-
ation of the intermediary 2-alkylidene-1,3,4-thiadiazoline derivative(7)[9] to
give an allene episulfide(8) in 58% yield.[10]
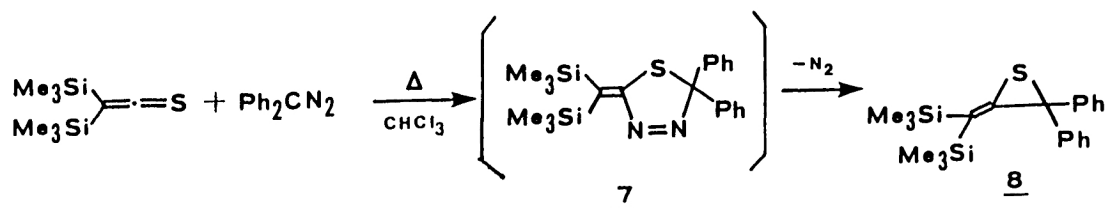
    When 8 was heated in o-dichlorobenzene at 120 °C for 2 h, 62% of isomerized
allene episulfide(10)[11] was obtained along with 33% of allene(11)[12] at 72%
conversion similarly to the thermolysis of 4.   Under the reaction conditions 10
gave only the allene (11) without any isomerization backward into 8.

* = radical or ion.

    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 ^{1}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[13] 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
preliminaly calculated charge distributed structure of thioxyallyl intermed-
iate.[7]

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

Temp/K	Solvent[a]	Rate const. k/s^{-1}	Activation parameters
411	A	62.5×10^{-5}	$E_a = 19.16 \pm 0.15$ kcal mol^{-1}
398	A	29.0×10^{-5}	
383	A	12.8×10^{-5}	$\Delta H^{\ddagger} = 18.39 \pm 0.14$ kcal mol^{-1}
373	A	5.85×10^{-5}	$\Delta S^{\ddagger} = -29.03 \pm 0.29$ e.u.
363	A	2.74×10^{-5}	
397	B	34.8×10^{-5}	$E_a = 14.54 \pm 0.31$ kcal mol^{-1}
387	B	24.0×10^{-5}	
363	B	6.35×10^{-5}	$\Delta H^{\ddagger} = 13.79 \pm 0.30$ kcal mol^{-1}
			$\Delta S^{\ddagger} = -40.10 \pm 0.75$ e.u.

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

It seems to us that the α-effect of the neighboring trimethylsilyl groups[14] 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.
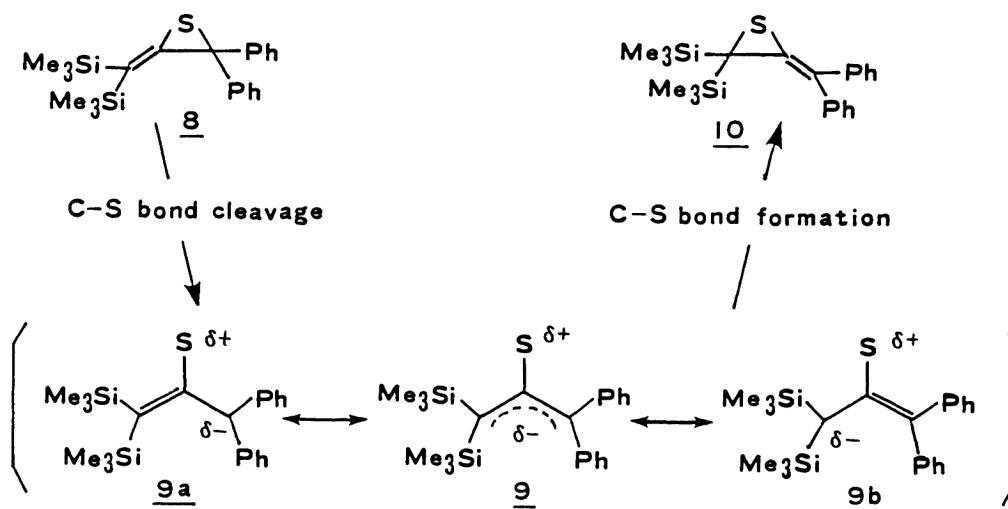
Scheme I .

Above results are in contrast to the analogous oxygen system, i.e. allene oxide-oxyallyl system,[15] 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-thioxy-allyl system will attract more attention from both experimental and theoretical standpoints.

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9) The lack of 8 from the reaction of bis(trimethylsilyl)thioketene with diphenylcarbene generated by metal catalyst and the isolation of 2-alkylidene-1,3,4-thiadiazoline intermediate in the reaction of t-butylthioketene with diphenyldiazomethane confirmed the intermediacy of 7.

10) 8; ^{1}H-NMR(CDCl$_3$) δ = -0.10(9H,s), 0.26(9H,s), and 7.0-7.4(10H,m); ^{13}C-NMR(CDCl$_3$) δ = 0.3(q), 1.2(q), 48.6(s), 116.7(s), 127.3(d), 128.0(d), 128.9(d), 140.8(s), and 158.9(s); UV(hexane) λ_{max} 272 nm (ε18200); MS, m/z 368(M$^+$,12%), 336(28), 248(90), 198(63), and 73(100); exact mass, found m/z 368.1432 calcd for C$_{21}$H$_{28}$Si$_2$S 368.1448.

11) 10; ^{1}H-NMR(CDCl$_3$) δ = -0.04(18H,s) and 7.0-7.5(10H,m);^{13}C-NMR(CDCl$_3$) δ = -1.3(q), 32.8(s), 122.4(s), 126.8(d), 126.9(d), 128.2(dx2), 128.3(dx2), 136.8(s), 140.4(s), and 140.9(s); MS, m/z 368(M$^+$,75%), 336(25), 263(100), and 73(88); exact mass, found m/z 368.1441 calcd for C$_{21}$H$_{28}$Si$_2$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}H-NMR(CDCl$_3$) δ = 0.08(18H,s) and 7.1-7.6(10H,s); ^{13}C-NMR(CDCl$_3$) δ = 0.45(q), 93.0(s), 96.7(s), 1215.6(d), 127.5(d), 128.3(d), 137.6(s), and 209.2(s);IR(CCl$_4$) 1895 cm^{-1}; MS, m/z 336(M$^+$, 29%), 263(6), 248(69), and 73(100); exact mass, found m/z 336.1726 calcd for C$_{21}$H$_{28}$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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