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NEW ASPECTS IN THE TAUTOMERISM OF 1,2,3-BUTATRIENE EPISULFIDES

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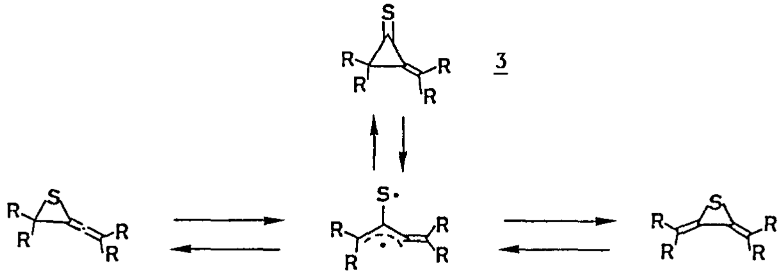
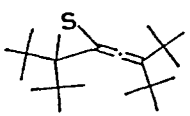
Summary; Facile formation of novel 1,2,3-butatriene episulfides by alkenylidene carbene addition to thioketone is described, and the relative stability of the 1,2,3-butatriene 1-episulfide and 2-episulfide is also discussed.

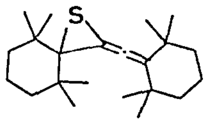
In contrast to the wide chemistry of the alkenylidenecyclopropane and bisalkylidenecyclopropane derivatives which has attracted considerable interest on account of the thermal interconversion via the trimethylenemethane type intermediate induced by the ring strain,[1)] the chemistry of sulfur analogous tautomeric system which consists of 1,2,3-butatriene 1-episulfide(**1**), 2-episulfide(**2**), and methylenecyclopropanethione(**3**) has not been fully investigated.



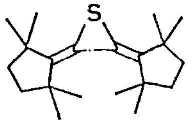
We have already reported an interesting isomerization of the sterically protected alkylidenecyclopropanethiones(**3**) leading to a novel formation of 1,2,3-butatriene 1-episulfides(**1a** and **1b**) and 2-episulfide(**2c**).[2)] Although in these reactions it was found that the direction of thiirane ring formation from the thioxyallyl type intermediate(**4**) was influenced by the nature of the substituents on the terminal carbons of 1,2,3-butatriene skeleton, we could not ascertain the intrinsic stability of the two types of 1,2,3-butatriene episulfides(**1** and **2**).[3)]



1a

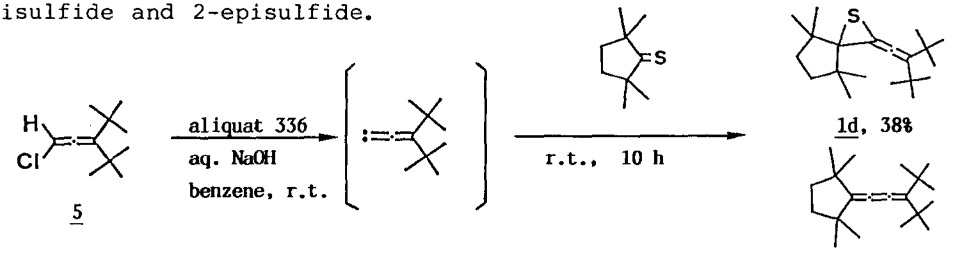


1b



2c

To elucidate their relative stability, we have established here a new and systematic synthetic route for 1,2,3-butatriene 1-episulfide by alkenylidene carbene addition to thioketone using several kinds of chloroallenes and/or chloroalkyne as the carbene sources under the phase-transfer reaction conditions$^{4)}$ and investigated the thermal equilibration between the 1,2,3-butatriene 1-episulfide and 2-episulfide.



5

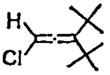
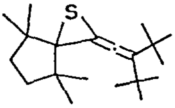
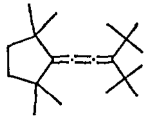
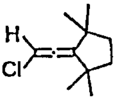
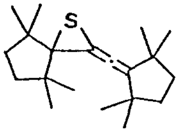
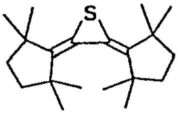
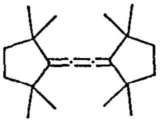
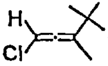
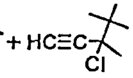
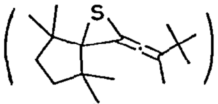
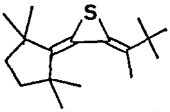
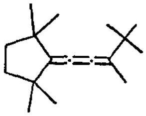
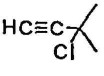
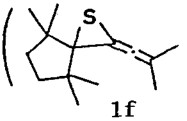
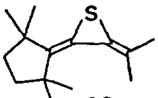
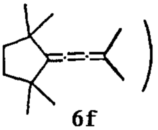
1d, 38%

6d, 13%

When the benzene solution(0.6 ml) of 2,2,5,5-tetramethylcyclopentanethione(1.2 mmol, 187 mg) and 1,1-di-t-butyl-3-chloroallene(5; 1.0 mmol, 187 mg) was added to the suspension of methyltrioctylammonium chloride (aliquat 336; 50 mg, 0.12 mmol) and 2 ml of 50% aq. NaOH solution by means of a syringe at room temperature and the mixture was stirred vigorously for 10h, 1,2,3-butatriene 1-episulfide(**1d**; 91 mg, 38%) was obtained as white crystals along with the butatriene(**6d**; 29 mg, 13%) and recovered chloroallene(**5**; 48 mg, 23%). The results using the other carbene sources(**7**-**9**) are listed in Table 1.

In the case of chloroallene(**7**), besides the desired 1,2,3-butatriene 1-episulfide(**1c**, 35%) the corresponding 2-episulfide(**2c**, 8%) was isolated toge-

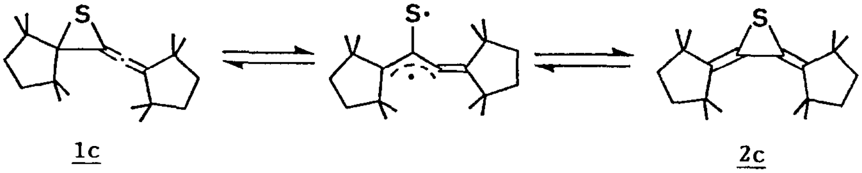
Table 1. Alkenylidene Carbene Addition to Tioketone.

Entry	Carbene Sources	Products and Yields(%)		
1	 5	 1d, 38%	—	 6d, 13%
2	 7	 1c, 35%	 2c, 8%	 6c, 3%
3	 +  8 8'	 1e	 2e, 39%	 6e, 15%
4	 9	 and/or 1f	 + 2f	 6f

ther with the butatriene(**6c**, 3%) as by-products. Furthermore, the reaction with the sterically less hindered carbene source(**8** and/or **8'**) afforded mainly the 2-episulfide(**2e**) in 39% yield along with the butatriene(**6e**, 15%) after silica gel chromatography and the reaction with the alkenylidene carbene derived from 3-chloro-3-methyl-1-butyne(**9**) resulted in a formation of an unstable mixture of the 1,2,3-butatriene episulfides(**1f** and/or **2f**) and the butatriene(**6f**). The structures of the episulfides and butatrienes obtained here were confirmed by ^{1}H-NMR, ^{13}C-NMR, IR, and MS spectra and elemental analysis.[5)]

The 1,2,3-butatrienes(**6c** and **6d**) are probably formed by the desulfurization of once produced 1,2,3-butatriene episulfides(**1c**, **1d**, and **2c**) with the alkenylidene carbene, since the isolated episulfides(**1c**, **1d**, and **2c**) are very stable at room temperature. The formation of 1,2,3-butatriene 2-episulfides(**2c** and **2e**) and the lack of 1-episulfide derivative in the case of **2e** might be interpreted with the acid-catalyzed isomerization of initially generated 1-episulfides on silica gel suggesting the higher thermodynamic stability of 2-episulfide skeleton over the 1-episulfide. By HPLC purification no 2-episulfide(**2e**) but an unseparable mixture of the 1-episulfide(**1e**) and **6e** was obtained from the crude mixture of the reaction using **8** and/or **8'**, where the steric repulsion is avoidable between the substituents facing each other in the 2-episulfide structure. **1e** was rather unstable and readily isomerized into **2e** by TLC separation on silica gel.

Next, we investigated the thermal interconversion of **1c** and **2c** to prove their relative stability. Heating of the o-dichlorobenzene solution of 2-episulfide(**2c**) at 120°C for 40 min resulted in a formation of equilibrated mixture with the 1-episulfide(**1c**) which was ascertained by the ^{1}H-NMR and HPLC monitoring and the characteristic IR absorption of the allenic carbon-carbon stretching at 1980 cm^{-1}. As for **1c**, the similar thermal equilibration with **2c** was observed within the temperature range from 90 to 120 °C, and the equilibrium ratio of **2c** to **1c** became smaller at the higher reaction temperature. This conflicting thermal instability of **2c** with the essential stability of the 2-episulfide skeleton relative to the 1-episulfide one might be attributable to the increasing steric repulsion of the inner methyl groups on the cisoid butadiene unit of **2c** caused by the augmentative molecular vibration at higher temperature.[6)] The other 1,2,3-butatriene 1-episulfides such as **1a**, **1b**, and **1d** were readily desulfurized at 120 °C showing the quantitative formation of



[**2c**]/[**1c**]; 1.52(90 °C) and 1.16(120 °C)

the corresponding 1,2,3-butatrienes without any evidence for thermal isomerization into 2-episulfides.[7] Furthermore, the equilibrated mixture of **1c** and **2c** was also thoroughly desulfurized to afford the 1,2,3-butatriene(**6c**) by heating at 120 °C for 5 h.

Among the results of our successful synthesis and reactions of 1,2,3-butatriene episulfides we were lucky enough to come by both type of episulfides (**1c** and **2c**) as stable crystals in the case of 2,2,5,5-tetramethylcyclopentane ring substituted system, and the thermal interconversion between **1c** and **2c** is worthy of attention as the first example of the sulfur-analogous tautomeric system of alkenylidenecyclopropane and bisalkylidenecyclopropane.

References and Notes

1. a) J. K. Crandall and D. R. Paulson, J. Am. Chem. Soc., **88**, 4320 (1966); b) D. R. Paulson, J. K. Crandall, and C. A. Bunnel, J. Org. Chem., **35**, 3708 (1970); c) R. Bloch, P. Le Perchec, and J. -M. Conia, Angew. Chem., Int. Ed. Engl., **9**, 798 (1970); d) M. E. Hendrick, J. A. Haride, and M. Jones, Jr., J. Org. Chem., **36**, 3061 (1971); e) G. Kobrick and B. Bosner, Tetrahedron Lett., **1973**, 2031; f) D. H. Aue and M. J. Meshishnek, J. Am. Chem. Soc., **99**, 223 (1977); g) J. Belzner and G. Szeimies, Tetrahedron Lett., **27**, 5839 (1986).
2. W. Ando, H. Hayakawa, and N. Tokitoh, Tetrahedron Lett., **28**, 1803 (1987).
3. We have also reported a novel formation of 1,1,4,4-tetramethyl-1,2,3-butatriene 2-episulfide(thiiranoradialene) by an intramolecular carbene addition reaction, however, no 1-episulfide derivative was obtained implying its relative instability; W. Ando, Y. Hanyu, and T. Takata, Tetrahedron Lett., **22**, 4815 (1981).
4. P. J. Stang, Chem. Rev., **78**, 383 (1978) and references cited therein.
5. The spectral data of the newly obtained compounds are as follows: **1c**; White crystals, mp. 87 °C; ^{1}H-NMR($CDCl_3$) δ 1.08(s,6H), 1.13(s,6H), 1.17(s,6H), 1.19(s,6H), 1.40-1.66(m,8H); ^{13}C-NMR($CDCl_3$) δ 28.32(q), 29.60(qx2),30.36(q), 38.90(t), 39.49(t), 43.12(s), 44.87(s), 70.44(s), 101.79(s), 138.36(s), 179.90(s); IR($CHCl_3$) 1980 cm^{-1}; MS, m/z 304(M^+); Exact mass, found m/z 304.2235 (calcd for $C_{20}H_{32}S$ 304.2225): **1d**; White crystals, mp. 86-7 °C; ^{1}H-NMR($CDCl_3$) δ 1.03(s,6H), 1.11(s,6H), 1.25(s,18H), 1.75(s,4H); ^{13}C-NMR($CDCl_3$) δ 28.73(q), 30.85(q), 32.15(q), 37.33(s), 39.18(t), 44.23(s), 72.62(s), 97.87(s), 134.93(s), 186.53(s); IR($CHCl_3$) 1965 cm^{-1}; MS, m/z 306 (M^+), E. A., Found C; 78.47, H; 11.34% (Calcd for $C_{20}H_{34}S$ C; 78.36, H; 11.17%): **2e**; White crystals, mp. 110-2 °C; ^{1}H-NMR($CDCl_3$) δ 1.24(s,6H), 1.27(s,9H), 1.28(s,6H), 1.68(brs,4H), 2.12(s,3H); ^{13}C-NMR($CDCl_3$) δ 19.39(q), 26.62(q), 28.75(q), 30.13(q), 37.00(s), 40.31(t), 40.83(t), 45.72(s), 46.30(s), 104.46(s), 104.98(s), 125.49(s), 140.76(s); MS, m/z 266(M^+); E. A., Found C; 77.29, H; 10.90% (Calcd for $C_{18}H_{28}S$, C; 77.21, H; 10.67%): **6d**; White crystals, mp. 131-2 °C; ^{1}H-NMR($CDCl_3$) δ 1.15(s,12H), 1.28(s,18H), 1.67(s,4H); ^{13}C-NMR($CDCl_3$) δ 29.66(q), 32.35(q), 37.38(s), 39.49(t), 45.75(s), 132.45(s), 139.18(s), 151.41(s), 159.83(s); MS, m/z 274 (M^+); E.A., Found C; 87.68, H; 12.69%(Calcd for $C_{20}H_{34}$ C; 87.51, H; 12.48%): **6e**; Colorless oil, ^{1}H-NMR($CDCl_3$) δ 1.13(s,6H), 1.14(s,6H), 1.15(s,9H), 1/67(s,4H), 1.92(s,3H); ^{13}C-NMR($CDCl_3$) δ 19.31(q), 29.28(q), 29.42(q), 29.57(q), 35.93(s), 39.21(d), 39.46(d), 45.34(s), 45.50(s), 120.39(s), 138.86(s), 148.57(s), 158.51(s); MS, m/z 234(M^+).
   The formation of the episulfides(**1f** and/or **2f**) and the butatriene(**6f**) was confirmed by the GC-MS and ^{1}H-NMR spectra of the crude mixture.
6. The steric conjestion between the inner methyl groups of **2c** has been certainly confirmed by the X-ray molecular structure analysis; N. Tokitoh, H. Hayakawa, M. Goto, and W. Ando, Chem. Lett., **1988**, in press.
7. Although the thermolysis of these episulfides in o-dichlorobenzene was performed with monitoring by ^{1}H-NMR and HPLC at the temperature range from 70-120 °C, only the desulfurization into the corresponding butatrienes was observed.

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