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Molecular Structure of Novel 1,2,3-Butatriene Episulfides

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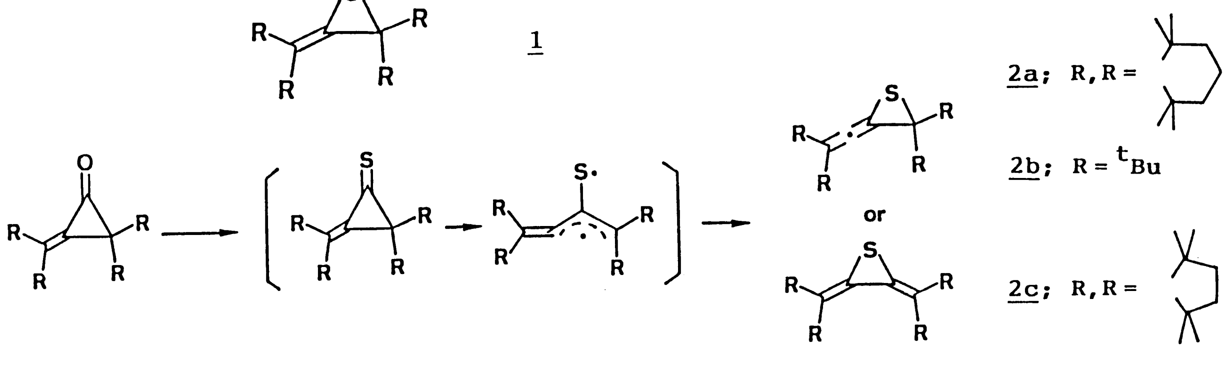
Molecular structures of novel 1,2,3-butatriene 1-episulfide and 2-episulfide derivatives have been determined by X-ray crystallographical analysis, and the structure of the 1-episulfide is in good agreement with the optimized geometries of the parent allene episulfide skeleton obtained from the RHF Closed-Shell SCF calculation.

Although the synthesis and reactivities of allene episulfide (**1**), the sulfur analogue of methylenecyclopropane, have been of great interest from a standpoint of strained small ring system,$^{1)}$ only a few reports have dealt with its molecular structure which should be closely related to the ring strain and reactivity.$^{2)}$ Most of the known allene episulfides were characterized in a gas phase or isolated as an oil and few examples have been synthesized in a crystalline form so far as we know.

Recently, we have reported a novel formation of 1,2,3-butatriene 1-episulfides(**2a** and **2b**) and 2-episulfide (**2c**), the methylene homologues of allene episulfide, in a very stable crystalline form by the thionation of the corresponding sterically protected methylenecyclopropanones via the intermediary cyclopropanethiones.$^{3)}$ In this paper we present the X-ray crystal structure analysis of the 1,2,3-butatriene episulfides (**2**)$^{4)}$ and make a comparative study of them with the theoretically optimized molecular structure of the parent allene episulfide.$^{5)}$



Among the three kinds of new 1,2,3-butatriene episulfides, **2a** and **2c** were subjected to recrystallization from ethanol-dichloromethane to give the samples for crystallographical analysis, and the X-ray diffraction of **2a** afforded the following crystal data and the refined molecular structure as shown in Fig. 1 together with the selected bond lengths and angles; crystal data of **2a**: $C_{22}H_{36}S$, MW 332.25, monoclinic, space group $P2_1/c$, a=10.837(1), b=12.027(1), c=16.398(1) Å, β=103.65(2)°, V=2076.9(2) $Å^3$, D_c=1.06 g cm^{-3}, μ(Mo-K_α)=1.55 cm^{-1}, Z=4, R=0.055.$^{6)}$

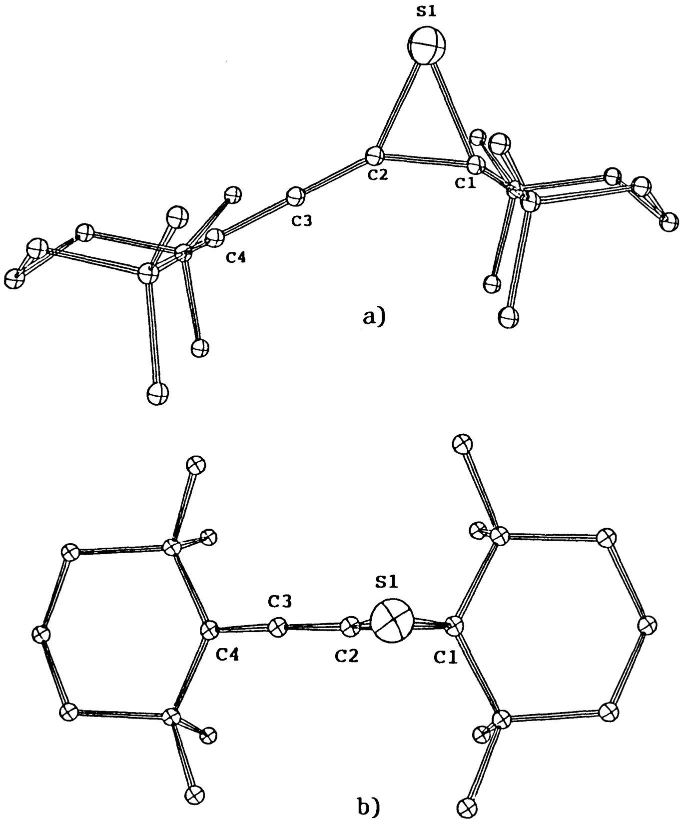


Fig. 1. Molecular structure of 1,2,3-butatriene 1-episulfide (2a) (a) side view, b) top view) and selected bond lengths (Å) and angles (degree).

C(1)-S(1), 1.887(2); C(2)-S(1), 1.772(2); C(1)-C(2), 1.464(3); C(2)-C(3), 1.283(3); C(3)-C(4), 1.307(3); ∠C(1)-S(1)-C(2), 47.0(1); C(2)-C(1)-S(1), 62.4(1); C(1)-C(2)-S(1), 70.6(1); C(1)-C(2)-C(3), 147.8(2); S(1)-C(2)-C(3), 141.5(2); C(2)-C(3)-C(4), 178.3(2).

The analysis of **2a** is worthy of attention from the viewpoint of not only confirming the alkenylidene thiirane ring structure whose allene unit was well preserved despite the ring strain and steric congestion but also the first example of the crystallographical structure analysis of allene episulfide derivative. Of particular notes among the results obtained from the crystallographical analysis of **2a** having an unsymmetrically substituted thiirane ring structure are the marked elongation of C(1)-S(1) bond (1.887(2) Å) and the expansion of C(1)-C(2)-S(1) bond angle (70.6(1)°) evidently due to the strained allene episulfide structure, which are in good agreement with the optimized geometries of the parent allene episulfide skeleton (**1**) determined by RHF Closed-Shell SCF calculation with STO-3G basis set as shown in Fig. 2. Furthermore, the X-ray structure of **2a** is consistent with that observed in the case of **1** using microwave spectroscopy by Block.$^{2a)}$

Meanwhile, **2c** was proved to have the nearly symmetrical thiiranoradialene structure with a characteristic shortening of the C(2)-C(3) bond (1.427(7) Å),

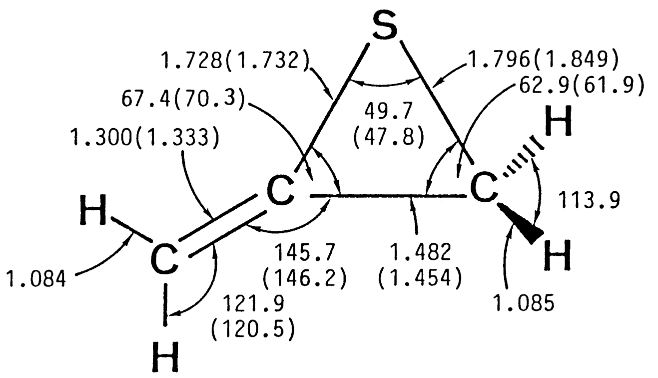


Fig. 2. Optimized geometries of allene episulfide (1).

Values are determined with the STO-3G basis set (in angstroms and degrees) by RHF Closed-Shell calculations. Values in parentheses are the observed ones with microwave analysis by Block.

the value of which is slightly shorter than that of common episulfide derivative (ca. 1.49 Å)7) or 1,3-butadiene derivative (ca. 1.46 Å),8) as well as in the case of previously reported 1,1,4,4-tetramethyl-1,2,3-butatriene 2-episulfide.9) The bond angles of C(1)-C(2)-C(3) and C(2)-C(3)-C(4) in **2c** were found to be almost equal to each other (158.1(6)° and 158.7(6)°) indicating the greater separation in distance of the termini of the diene chromophore than that of normal cisoid diene in solid state (Fig. 3).10) Crystal data for **2c** are as follows; $C_{20}H_{32}S$, MW 304.22, monoclinic, space group $P2_1$, a=8.136(3), b=10.247(3), c=12.128(5) Å, β=112.71(4)°, V=932.7(5) Å^3, D_c=1.08 g cm^{-3}, μ(Mo-Kα)=1.54 cm^{-1}, Z=2, R=0.087.6)

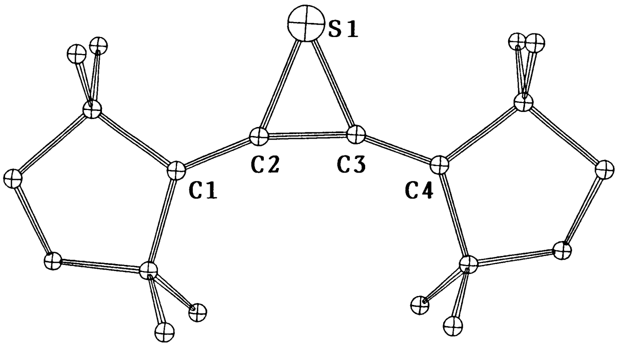


Fig. 3. Molecular structure of 1,2,3-butatriene 2-episulfide (2c) and selected bond lengths(Å) and angles (degree).

S(1)-C(2), 1.799(4); S(1)-C(3), 1.799(4); C(2)-C(3), 1.427(7); C(1)-C(2), 1.317(9); C(3)-C(4), 1.316(6); ∠C(2)-S(1)-C(3), 46.7(2); S(1)-C(2)-C(3), 66.6(3); S(1)-C(3)-C(2), 66.6(3); S(1)-C(2)-C(1), 134.7(4); S(1)-C(3)-C(4), 134.7(5); C(1)-C(2)-C(3), 158.1(6); C(2)-C(3)-C(4), 158.7(6).

These results suggest that the bulky substituents on the terminal carbons of the 1,2,3-butatriene episulfides **2a** and **2c** did not affect the intrinsic nature of these novel skeletons but effectively protected the reactive and strained molecules, since the symmetricity of the thiiranoradialene structure is more perfectly reflected in **2c** than in the aforementioned tetramethyl derivatives.

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4) The newly obtained 1,2,3-butatriene episulfides afforded satisfactory spectral data and their compositions were ascertained by the elemental analysis and high resolution mass spectroscopy.

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6) Crystal dimension; **2a** 0.2×0.3×0.3 mm^3, **2c** 0.5×0.5×0.1 mm^3. Data collection; Rigaku four-circle diffractometer, graphite monochromated Mo-K radiation (λ=0.71069 Å). For **2a** 5171 (including systematically absent) reflections were collected and 3209 with $|F_o|>3\sigma(|F_o|)$ were used and 1723 reflections were used for **2c** among 2273 collected ones. Their structures were solved by direct methods using MULTAN 78.[11] In the case of **2a** all hydrogen atoms were found in D-Fourier map and included in full matrix least-square refinement using anisotropic factors for non-H atoms and isotropic ones for H, however, the methyl hydrogen atoms were excluded from the refinement of **2c** since they were not found in the D-Fourier map of **2c**. Calculations were carried out on a Facom M-380 with UNICS III.[12]

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