

- (4) (a) E. P. Kyba, *J. Am. Chem. Soc.*, **98**, 4805 (1976), reports no evidence for such intermediates in a careful stereochemical study of nucleophilic displacement by *tert*-butyllithium at *tert*-phosphine phosphorus. (b) Phosphoranide intermediates had earlier been suggested by G. Wittig and A. Maercker, *J. Organomet. Chem.*, **8**, 491 (1967). (c) An equilibrium between a phosphoranide and a phosphine carbanion has been suggested by D. Hellwinkel, *Chem. Ber.*, **102**, 528 (1969). (d) Ph. Savignac, B. Richard, Y. Leroux, and R. Burgada, *J. Organomet. Chem.*, **93**, 331 (1975). (e) A P-H phosphorane with an interesting tetradentate tetraamino ligand has been reported by J. E. Richman, U.S. Patent 3 987 128 (*Chem. Abstr.*, **86**, 122897u (1977)), and private communication, to give some reactions similar to those reported here for **10**.
- (5) (a) K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam, *Top. Phosphorus Chem.*, **1**, 17 (1964); (b) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, New York, 1967, Chapter 8.
- (6) I. Granoth and J. C. Martin, *J. Am. Chem. Soc.*, **100**, 5229 (1978).
- (7) L. J. Adzima and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 1657 (1977).
- (8) L. J. Adzima and J. C. Martin, *J. Org. Chem.*, **42**, 4006 (1977).
- (9) Elemental analyses of new compounds are within 0.4% of calculated values. Chemical shifts for  $^{31}\text{P}$  and  $^1\text{H}$  are given in parts per million downfield from 85%  $\text{H}_3\text{PO}_4$  in THF and  $\text{Me}_4\text{Si}$  in  $\text{CDCl}_3$ , respectively, unless otherwise stated.  $^1\text{H}$  NMR (THF- $d_6$ ) of **6**:  $\delta$  1.52 (6 H, s, Me), 1.83 (6 H, s, Me), 6.75–7.60 (8 H, m, H-Ar).  $^1\text{H}$  NMR of **10**:  $\delta$  1.56 (6 H, s, Me), 1.62 (6 H, s, Me), 7.22–7.48 (6 H, m, H-Ar), 8.08–8.28 (2 H, m, H ortho to P), 8.48 (1 H, d,  $^1J_{\text{HP}} = 680$  Hz, HP).
- (10) K. S. Colle and E. S. Lewis, *J. Org. Chem.*, **43**, 571 (1978).
- (11) This deprotonation of P-H phosphorane **10** by  $\text{LiAlH}_4$  is to be contrasted with failure of sodium methoxide to act as a base toward an apical proton of a P-H phosphorane: D. S. Milbrath and J. G. Verkade, *J. Am. Chem. Soc.*, **99**, 6607 (1977).
- (12) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974).
- (13) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).
- (14) Prepared from phenylphosphonous dichloride and the Grignard reagent prepared from 2-(2-bromophenyl)-2-propanol, in analogy to the preparation of **7**.<sup>6</sup>
- (15) Two additional lines of evidence can be cited favoring the closed-ring tautomeric structures **6** and **10**. Benzylation of **6** with excess benzyl bromide occurs only at P to give a phosphorane. It is perhaps even more significant that 30% hydrogen peroxide fails to oxidize **10** under a variety of conditions which lead to oxidation of phosphorus(III) compounds which are models for the open-chain tautomer of **10**, the conjugate acid of **11**.
- (16) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 236 (1967).
- (17) On leave from Israel Institute for Biological Research, Ness Ziona, Israel.

Itshak Granoth,\*<sup>17</sup> J. C. Martin\*

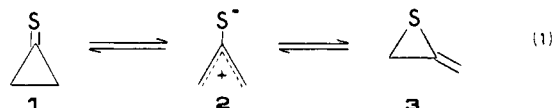
Roger Adams Laboratory, University of Illinois  
Urbana, Illinois 61801

Received July 11, 1978

## Allene Episulfide<sup>1</sup>

Sir:

In view of the fascinating chemistry associated with the cyclopropanone-allene oxide tautomeric system,<sup>2</sup> we have initiated an investigation of the analogous, little studied, cyclopropanethione-allene episulfide system (eq 1).<sup>3</sup> Anticipating that the parent compounds **1** and **3** would be highly reactive we have employed a flash vacuum pyrolysis-micro-



wave (FVP-MW) spectroscopic approach that has previously proven successful in the characterization of other reactive organosulfur molecules.<sup>4</sup> We report herein the generation and microwave structure of allene episulfide (methylenethiirane, **3**). We also provide data relevant to the processes depicted in eq 1.

Compounds **4**<sup>5</sup> and **5** (prepared in 54% yield from 5-norbornene using the lithio-2-(methylthio)-2-oxazoline reagent<sup>6,7</sup> (**6**)) seemed likely thermal precursors of **1** and **3**, respectively.<sup>8</sup> However, using the FVP-MW procedure we find that both **4** and **5** cleanly decompose to allene episulfide (**3**) at pyrolysis temperatures of 600–700 °C, with no detectable amounts of cyclopropanethione being formed.<sup>9</sup> Pyrolysis of **5**

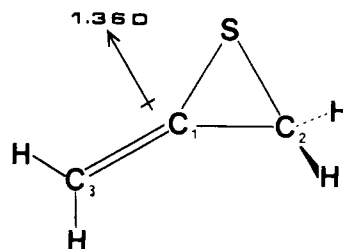
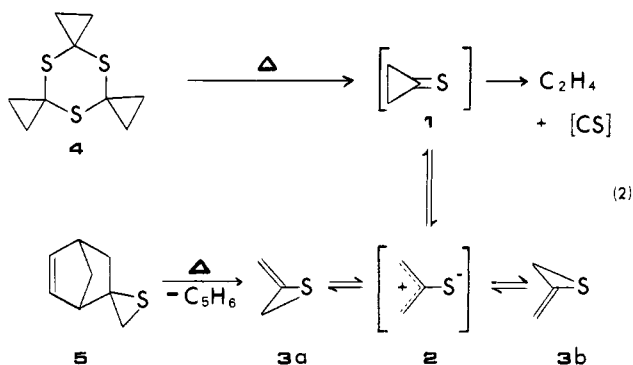


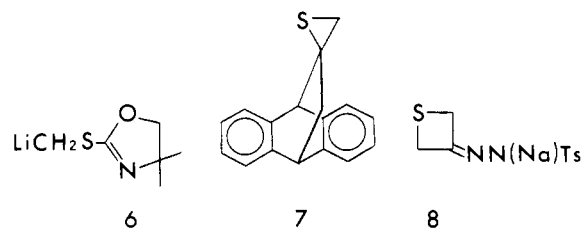
Figure 1.

$^{13}\text{C}$  or  $d_2$  labeled on the thiirane ring<sup>10</sup> afforded allene episulfide with labeling equally distributed ( $\pm 5\%$ ) between the ring and exocyclic methylene groups ( $\text{C}_2$  and  $\text{C}_3$  in Figure 1), as indicated by microwave analysis. These observations are consistent with the mechanistic picture presented in eq 2 in which it is suggested that the  $^{13}\text{C}$  and deuterium scrambling in allene episulfide (**3**), the formation of **3** from cyclopropanethione trimer **4**, and the formation of ethylene in both of these pyrolyses proceed by way of a thioxyallyl ion (**2**) (or a related diradical resonance structure) as a common interme-

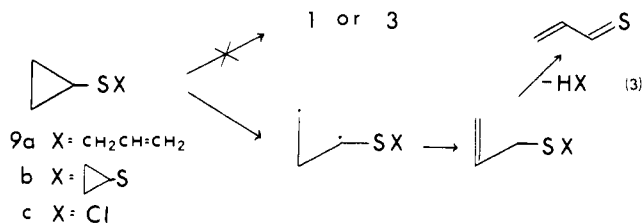


diate.<sup>11,13</sup> We further interpret these results to indicate that allene episulfide is thermodynamically *more stable* than cyclopropanethione, in apparent contrast to the order of stability in the allene oxide-cyclopropanone system.<sup>2,14</sup>

Allene episulfide is also formed on pyrolysis (520 °C) of anthracene adduct **7**<sup>16</sup> and on heating tosylhydrazide salt **8**.<sup>3b,18</sup> Efforts to generate  $\text{C}_3\text{H}_4\text{S}$  isomers **1** or **3** by pyrolysis of cyclopropyl precursors of type **9a-c**<sup>19</sup> lead instead to the



formation of another  $\text{C}_3\text{H}_4\text{S}$  isomer, identified by its microwave spectrum as thioacrolein.<sup>21</sup> We postulate that this latter compound arises from a ring-opening process such as that depicted in eq 3.



The identity of allene episulfide (**3**) has been established unambiguously by a microwave substitution structure determination. Spectral assignments of the normal isotopic species, along with the four  $^{34}\text{S}$  and  $^{13}\text{C}$  singly-substituted species and

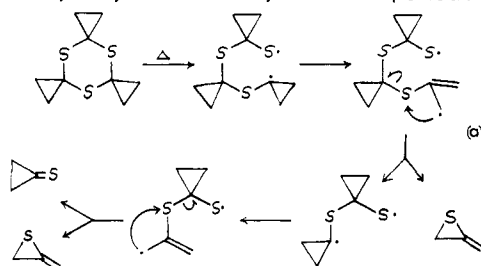
the two CD<sub>2</sub> species, give the following structural parameters (see Figure 1): C<sub>1</sub>—S, 1.732 (2), C<sub>2</sub>—S, 1.849 (1), C<sub>1</sub>—C<sub>2</sub>, 1.454 (5), C<sub>1</sub>=C<sub>3</sub>, 1.333 (2), C<sub>2</sub>—H, 1.084 (1) Å; ∠C<sub>1</sub>SC<sub>2</sub>, 47.8 (1), ∠SC<sub>1</sub>C<sub>2</sub>, 70.3 (1), ∠SC<sub>2</sub>C<sub>1</sub>, 61.9 (1), ∠C<sub>3</sub>C<sub>1</sub>C<sub>2</sub>, 146.2 (3), ∠HC<sub>2</sub>H, 116.4 (1)°, and (assuming a symmetrical HC<sub>2</sub>H groups), C<sub>3</sub>—H, 1.081 (1) Å and ∠C<sub>1</sub>C<sub>3</sub>H, 120.5 (2)°. The HC<sub>2</sub>H plane is displaced from the SC<sub>2</sub>C<sub>1</sub> angle bisector plane by an angle of 7.2° bringing these hydrogens closer to the S atom. The dipole moment of **3** is 1.36 (2) D.

The mechanism proposed in eq 2 to account for the scrambling of <sup>13</sup>C and deuterium labeling in **3** is consistent with the long, and presumably weakened, C<sub>2</sub>—S bond in **3**.<sup>23,24</sup> Allene episulfide has a gas-phase lifetime varying from ~3 min (room temperature) to ~20 min (dry ice temperature) at ~0.05 Torr and may be revitalized after condensation at -196 °C. Efforts are currently underway to define more precisely the equilibrium of eq 1 by experimental as well as theoretical methods and to synthesize cyclopropanethiones by nonpyrolytic routes.<sup>26</sup>

**Acknowledgment.** We gratefully acknowledge support for this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society (E.B.), the North Atlantic Treaty Organization (E.B.), the Research Corporation (R.E.P.), the National Science Foundation under its Undergraduate Research Participation program, and the University of Missouri—St. Louis. We thank Professor A. G. Hortmann for samples and helpful discussions.

## References and Notes

- (1) (a) Flash Vacuum Pyrolysis Studies. 6. (b) Part 5: R. E. Penn, E. Block, and L. K. Reville, *J. Am. Chem. Soc.*, **100**, 3622 (1978). (c) Presented at the 12th Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., Oct 31, 1976, at the 174th ACS National Meeting of the American Chemical Society, Chicago, Ill., Aug 31, 1977, Abstracts ORGN 90, and at the 8th International Symposium on Organic Sulfur Chemistry, Portoroz, Yugoslavia, June 18–23, 1978.
- (2) For leading references, see (a) N. J. Turro, *Acc. Chem. Res.*, **2**, 25 (1969); (b) H. H. Wasserman, G. M. Clark, and P. Turley, *Fortschr. Chem. Forsch.*, **47**, 73 (1974); (c) T. H. Chan and B. S. Ong, *J. Org. Chem.*, **43**, 2994 (1978).
- (3) Tetrasubstituted allene episulfides have been previously described: (a) W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969); (b) A. G. Hortmann and A. Bhattacharjya, *J. Am. Chem. Soc.*, **98**, 7081 (1976).
- (4) (a) Methanesulfenic acid: ref 1b. (b) Thioformaldehyde: H. Bock, B. Solouki, S. Mohmand, E. Block, and L. K. Reville, *J. Chem. Soc., Chem. Commun.*, 287 (1977). (c) Sulfine: E. Block, R. E. Penn, R. J. Olsen, and P. F. Sherwin, *J. Am. Chem. Soc.*, **98**, 1264 (1976); E. Block, H. Bock, S. Mohmand, P. Rosmus, and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, **15**, 383 (1976).
- (5) C. C. Price and J. Vittimberga, *J. Org. Chem.*, **27**, 3736 (1962).
- (6) (a) A. I. Meyers and M. E. Ford, *J. Org. Chem.*, **41**, 1735 (1976). (b) The exo–endo stereochemistry of the thirane ring has not been assigned; mechanistic considerations suggest that sulfur should be in the exo position.
- (7) All new compounds have been fully characterized.
- (8) (a) Trithianes are known to be thermal precursors of thiocarbonyl compounds: D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectrosc.*, **39**, 136 (1971); P. S. Fraser, L. V. Robbins, and W. S. Chilton, *J. Org. Chem.*, **39**, 2509 (1974). (b) For a recent review of retro-Diels–Alder reactions of compounds related to **5**, see J. L. Ripoll, A. Rouessac, and F. Rouessac, *Tetrahedron*, **34**, 19 (1978).
- (9) Although the microwave spectrum of **1** is now unknown, the reasonable range within which spectral absorption should occur can be confidently predicted from the microwave spectral and structural data on cyclopropanone (J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 1896 (1969)) and the assumption that the C=S distance in **1** is greater than the C=O distance in cyclopropanone by 0.40 ± 0.05 Å.
- (10) Prepared using the lithio-2-(methyl-<sup>13</sup>C-thio)- or lithio 2-(methyl-*d*<sub>2</sub>-thio)-2-oxazoline reagent **6** prepared by using methyl-<sup>13</sup>C- or -*d*<sub>2</sub> iodide and the procedure of Meyers.<sup>6a</sup>
- (11) Alternatively **3** may be formed directly from **4** via sequence a through ring



- opening of intermediate cyclopropyl radicals to allyl radicals (a process known to be very facile<sup>12</sup>), followed by homolytic displacement at sulfur. The last step of this sequence affords **1**.
- (12) K. S. Chen, D. J. Edge, and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 7036 (1973).
  - (13) The pyrolysis of **4**, **5**, **7**, and **8** also affords CS<sub>2</sub> which we suggest may arise from CS via a sulfur-abstraction step.
  - (14) Assuming bond strengths of 129 kcal mol<sup>-1</sup> for C=S,<sup>15</sup> 146 kcal mol<sup>-1</sup> for C=C, 74 kcal mol<sup>-1</sup> for C—S,<sup>15</sup> and 83 kcal mol<sup>-1</sup> for C—C, and assuming that the value for the difference in strain energy between cyclopropane and thirane (8 kcal mol<sup>-1</sup>)<sup>15</sup> is a good approximation of the difference in strain energy between **1** and **3**, it is found that **3** is 7 kcal mol<sup>-1</sup> more stable than **1**. Applying the same analysis to cyclopropanone–allene oxide, one finds that cyclopropanone is 22 kcal mol<sup>-1</sup> more stable than allene oxide.
  - (15) S. W. Benson, *Chem. Rev.*, **78**, 23 (1978).
  - (16) Prepared in 52% yield from the anthracene–ketene adduct<sup>17</sup> and **6**.
  - (17) P. F. Hudrik, A. M. Hudrik, and C.-N. Wan, *J. Org. Chem.*, **40**, 1116 (1975).
  - (18) Kindly supplied by A. G. Hortmann and A. Bhattacharjya. See A. Bhattacharjya, Ph.D. Thesis, Washington University, 1976. Bhattacharjya was unsuccessful in isolating allene episulfide on bulk pyrolysis of **8**.
  - (19) Prepared by reaction of cyclopropanethiol<sup>20</sup> with allyl bromide (**9a**<sup>7</sup>), oxidation of cyclopropanethiol with I<sub>2</sub> (**9b**<sup>7</sup>), and reaction of dicyclopropyl disulfide (**9b**) with chlorine (**9c**<sup>7</sup>).
  - (20) L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **89**, 593 (1970).
  - (21) A microwave study of thioacrolein has been briefly reported (H. W. Kroto, "Sixth Austin Symposium on Gas Phase Molecular Structure," Austin, Texas, 1976, Paper MA4) but detailed results have not yet reached print. Independent assignment in this laboratory of the normal isotopic species (A = 45.8 × 10<sup>3</sup>, B = 2796.0, and C = 2635.3 MHz) as well as several isotopic modifications serve to identify thioacrolein beyond question.
  - (22) Twice the standard deviations are given throughout as a measure of the uncertainty in the structural parameters. Owing to the proximity of the central carbon to a principal inertial axis, the C<sub>1</sub>—C<sub>2</sub> distance has a systematic uncertainty which could be as large as ±0.015 Å.
  - (23) The C—S bond distance in thirane is 1.819 Å: R. L. Shoemaker and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 6263 (1968).
  - (24) A similar lengthening of the S—C (saturated) distance is seen in α-thio-lactones<sup>25a</sup> and thiranimines.<sup>25b</sup>
  - (25) (a) E. Schaumann and V. Behrens, *Angew. Chem., Int. Ed. Engl.*, **16**, 722 (1977); (b) G. L'abbe, J.-P. Dekerk, J.-P. Declercq, G. Germain, and M. Van Meerse, *ibid.*, **17**, 195 (1978).
  - (26) Following submission of this work a report appeared (E. Jongejan, Th. S. V. Buys, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **97**, 214 (1978)) describing the formation of allene episulfide by pyrolysis of 8,9-dioxo-4-thiadispiro[2.1.2.3]decan-9-one. Allene episulfide, characterized by its <sup>1</sup>H and <sup>13</sup>C NMR, IR, UV, and mass spectra, is reported to be stable in dilute solution at -30 °C for several hours. Byproducts of the pyrolysis include allene, carbon disulfide, and ethylene, which products are suggested (as we have) to arise from fragmentation of cyclopropanethione.
  - (27) National Science Foundation Undergraduate Research Participant, 1976.

Eric Block,\* Robert E. Penn,\* Michael D. Ennis<sup>27</sup>  
Terry A. Owens,<sup>27</sup> Shin-Liang Yu

Department of Chemistry, University of Missouri—St. Louis  
St. Louis, Missouri 63121

Received July 13, 1978

## Lychnopholic Acid, a Novel Trioxxygenated Caryophyllene Derivative from *Lychnophora affinis* Gardn.<sup>1</sup>

Sir:

Intense interest during the past 10 years in cytotoxic, potentially antitumor-active natural products has led to the isolation and characterization of many sesquiterpenoids having, very frequently, multiple oxygenated functional groups in chemically interesting contiguous arrays.<sup>2</sup> These compounds generally belong to the eudesmane, germacrane, guaiane, and pseudoguaiane subfamilies of sesquiterpenoids. Other classes of sesquiterpenoids, however, seem for unknown reasons to have very few oxygenated representatives; in particular, the only oxygenated caryophyllenes hitherto known appear to be caryophyllene oxide (**1**), caryophyllenol I and II (**2** and **3**, respectively),<sup>3</sup> α-multijugenol, which is isomeric with **2** and **3**,<sup>4</sup> and the nor derivatives kobusone (**4**) and isokobusone (**5**).<sup>5</sup> We now report the novel structure **6** (relative configuration) for lychnopholic acid, a noncytotoxic constituent of *Lychnophora affinis* Gardn. (Compositae), a plant originally under investigation in our laboratory<sup>6</sup> for its cytotoxic constituents.