of the formyl and amide protons. In an effort to simplify the spectra so that the rate constant for intermolecular exchange could be more conveniently determined, the N–H proton was replaced with deuterium. The rate constant at the coalescence point for *N*-deuteriodiformamide was determined using complete line-shape analysis[13] ($k_c(EZ \rightarrow EE) = 45$ sec^{-1}, $T_c = -23°$, ΔG^* $(EZ \rightarrow EE) = 12.6$ kcal/mol). It is interesting to note the fairly wide range of barriers (8.2–12.6 kcal/mol) that is evident even within this small group of compounds.

Acknowledgment. We thank the National Science Foundation and the Edmond de Rothschild Foundation for support of this work.

(13) We thank Professor Martin Saunders for providing the multisite complete line-shape analysis computer program used.

(14) Alfred P. Sloan Fellow, 1972–1974.

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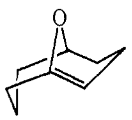
Received May 31, 1973

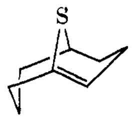
9-Thiabicyclo[3.3.1]non-1-ene[1,2]

Sir:

Previous studies of bridgehead alkenes have resulted in the synthesis of several representatives of this class of compounds.[3,4] We have initiated a program for the study of the chemical properties of some bridgehead alkenes substituted with heteroatoms within the bicyclic framework,[5] and we recently reported the synthesis of the unusual enol ether **1**. We now report of synthesis of the sulfur congener, 9-thiabicyclo[3.3.1]non-1-ene (**2**).

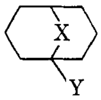


1

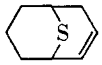


2

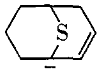
An acid-catalyzed reaction of hemiketal **3** with hydrogen sulfide in aqueous solution at 100° for 3 days in an autoclave produced 45% of 9-thiabicyclo[3.3.1]nonan-1-ol (**4**), mp 151–152°, and 45% of 9-thiabicyclo[3.3.1]nonane-1-thiol (**5**),[6] mp 83–85°. Reaction of hydroxy sulfide **4** with methanesulfonyl chloride and triethylamine in benzene–petroleum ether yielded 60% of methanesulfonate **6**, a stable white crystalline compound melting sharply at 66.5–68°. Elimination of methanesulfonic acid from **6** occurred smoothly with potassium *tert*-butoxide to give olefins **2** (65%) and **7** (1%). Evidently **7** is formed from **2** since the amount of **7** produced is proportional to the reaction time. The isomerization possibly proceeds through the allylic anion **8**.[7] Distillation attempts resulted in decomposition of **2**, and pure samples were obtained by preparative vpc.[6] Olefin **2** is a colorless liquid with a powerful penetrating odor. It is stable at ordinary temperatures in the absence of oxygen with which it reacts slowly.



3, X = O; Y = OH
4, X = S; Y = OH
5, X = S; Y = SH
6, X = S; Y = OSO_2CH_3
9, X = S; Y = H

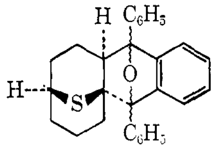


7

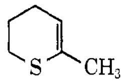


8

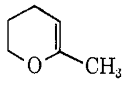
Reduction of **2** with aluminum hydride[8] produced known **9**[9] in 52% yield along with four unidentified products, and hydrogenation of **2** using a large excess of 5% palladium on carbon[10] gave **9** in 85% yield. Reaction of **2** with 1,3-diphenylisobenzofuran produces the adduct **10**, mp 225–228°. Since **2** is a stable entity we assign it the zusammen[11] stereochemistry.[3d] Consequently we assign partial stereochemistry to Diels–Alder adduct **10** as shown. The orientation of the oxygen bridge with respect to the sulfur bridge is presently unknown.



10



11



12

The spectroscopic properties of **2** provide some interesting comparisons. The infrared frequency for stretching of the carbon double bond occurs at 1600 cm^{-1}, whereas the band for 6-methyl-2,3-dihydrothiapyran (**11**) falls at 1640 cm^{-1}. Both bands are weak, as is typical of vinyl sulfides.

Table I lists the nmr chemical shifts of the vinyl protons of several vinyl sulfides. Some vinyl ethers and cyclohexene are included for comparison.

In normal untwisted vinyl ethers mixing of the nonbonding orbitals of oxygen with the π and π^* orbitals results in increased electron density at the β carbon and

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(1) Paper VII in the Bredt's rule series. For previous papers see ref 3 and 5.

(2) From the Ph.D. dissertation of C. B. Quinn, University of Michigan, 1973.

(3) (a) J. A. Chong and J. R. Wiseman, *J. Amer. Chem. Soc.*, **94**, 8627 (1972); (b) J. R. Wiseman and J. A. Chong, *ibid.*, **91**, 7775 (1969); (c) J. R. Wiseman, H. F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969); (d) J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970). For related papers see ref 4.

(4) (a) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970); (b) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969); (c) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (d) G. J. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123, 1129 (1972); (e) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (f) P. Warner, R. LaRose, C. M. Lee, and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972); (g) J. E. Gano and L. Eisenberg, *ibid.*, **95**, 972 (1973); D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972).

(5) (a) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 1342 (1973); see also (b) P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953); (c) E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *Angew. Chem., Int. Ed. Engl.*, **3**, 642 (1964); (d) F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, **86**, 3168 (1964).

(6) All new compounds reported gave satisfactory ir, nmr, and mass spectra and acceptable elemental analyses.

(7) A similar isomerization is observed during the addition of methyllithium to bicyclo[3.3.1]non-1-ene.[4a]

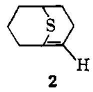
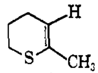
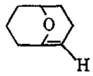
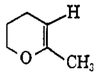
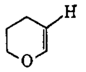
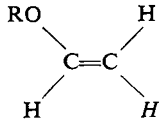
(8) J. M. Coulter and J. M. Leurs, *Tetrahedron Lett.*, 3715 (1966).

(9) (a) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966).

(10) L. Bateman and F. W. Shipley, *J. Chem. Soc.*, 2888 (1958).

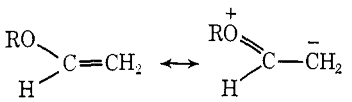
(11) See IUPAC Tentative Rules for Nomenclature in Organic Chemistry, Section E-2, *J. Org. Chem.*, **35**, 2849 (1970).

Table I. Nmr Chemical Shifts of Vinyl Hydrogens β to Oxygen and Sulfur

Compound	Chemical shift of vinyl hydrogens (δ)	Ref
 2	6.25	*a*
 11	5.34	*a*
Bicyclo[3.3.1]non-1-ene	5.62	*c*
Cyclohexene	5.63	
 1	5.74	*b*
 12	4.34	*b*
	4.55	*e*
	3.75-3.78	*d*

[a] This work. [b] Reference 5a. [c] Reference 3d. [d] J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962). [e] R. M. Silverstein and G. C. Bassler, "Spectrophotometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 200.

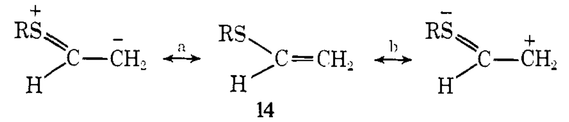
causes the β vinyl hydrogens to resonate at approximately 1.3 ppm higher field than alkene vinyl hydrogens. This interaction, which is equivalent to the resonance interaction depicted in **13**, is absent in bridged vinyl ether **1** owing to an unfavorable orientation of the orbitals.[5a]



$$\mathrm{RO(H)C{=}CH_2} \longleftrightarrow \mathrm{RO^{+}{=}C(H){-}CH_2^{-}}$$

13

In vinyl sulfides, the nmr resonance position of the β hydrogens is only 0.3 ppm higher than that of alkene vinyl hydrogens. Sulfur may donate electron density to the β position of a vinyl sulfide by mixing of a 3p orbital with the π and π* orbitals (**14**, resonance arrow a) and at the same time may accept electron density into a 3d orbital from the π bond (resonance arrow b).[12] This

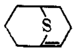
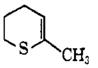
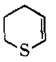


$$\mathrm{RS^{+}{=}C(H){-}CH_2^{-}} \xleftrightarrow{a} \mathrm{RS(H)C{=}CH_2} \xleftrightarrow{b} \mathrm{RS^{-}{=}C(H){-}CH_2^{+}}$$

14

combination of dative and acceptive resonance by sulfur explains the slightly upfield-shifted nmr resonance position of the β protons of normal vinyl sulfides. In bicyclic vinyl sulfide **2**, the dative resonance (a) is inhibited while the acceptive resonance (b) is allowed by the orientation of the pertinent orbitals. Thus, the vinyl hydrogen of **2** is strongly dishielded.

Table II. Ultraviolet Spectra of Saturated and Unsaturated Sulfides

Compound	λ_{max} (ε)	Solvent	Ref
 2	196 (4700) 210 (4560)	Pentane	*a*
Dimethyl sulfide	210 (1020) 229 (138)	Ethanol	*b*
Diethyl sulfide	210 (1780) 229 (138)	Ethanol	*b*
Dibutyl sulfide	210 (1230) 229 (138)	Ethanol	*b*
	207 (1630) 235 (70)	Methanol	*c*
 11	228 (6000) 248 (2700)	Pentane	*a*
Butyl vinyl sulfide	229 (7000) 240 (5500)	Cyclohexane	*c*
Butyl 1-butenyl sulfide	232 (6300) 248 (4500)	Cyclohexene	*c*
	226 (5300) 251 (2600)	Cyclohexane	*c*

[a] This work. [b] E. A. Fehnel and M. Carmack, *J. Amer. Chem Soc.*, **81**, 84 (1949). [c] M. Prochazka and M. Palecek, *Collect. Czech. Chem. Commun.*, **32**, 3149 (1967).

Table II contains the ultraviolet spectra of various saturated and unsaturated sulfides.[13] It is evident that bridged sulfide **2** is not a typical vinyl sulfide. The spectrum appears to be a combination of the absorption bands due to an isolated carbon double bond and a saturated dialkyl sulfide. The twisting has completely disrupted the conjugation seen in normal α,β-unsaturated sulfides.

We shall report on the chemical reactions of **2** in our full paper.

Acknowledgment. This research was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(12) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, Chapters 1 and 2.

(13) For compilations of ultraviolet spectra see (a) ref 12, appendix I; (b) R. C. Passerini in "Organic Sulfur Compounds," N. Kharasch, Ed., Vol. I, Pergammon Press, New York, N. Y., 1967, Chapter 7; (c) E. Block, *Quart. Rev. Sulfur Chem.*, **4**, 237 (1969).

(14) National Institutes of Health Graduate Fellow, 1970–1973; NDEA Graduate Fellow, 1969–1970.

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Geometrical Isomers of 9-Thiabicyclo[3.3.1]non-1-ene 9,9-Dioxides from β-Eliminations from Bridged Halo Sulfones[1,2]

Sir:

In 1969 Paquette and Houser[3] reported that treatment of *endo*-2-chloro sulfone (**1**) with potassium *tert*-butox-

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(1) Paper VIII in the Bredt's Rule series. For paper VII see C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 6120 (1973).

(2) Taken in part from the Ph.D. Dissertation of C. B. Quinn, University of Michigan, 1973.

(3) (a) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969); (b) R. W. Houser, Ph.D. Dissertation, Ohio State University, 1970. These authors do not explicitly assign the stereochemistry of **3** but their discussion of the stereochemistry of the reaction of *tert*-butyl alcohol with **3** is consistent only with the zusammen configuraiton.