18110-71-9; **5a**, 103594-13-4; **5b**, 103594-14-5; **5c**, 103624-16-4; **5g**, 110391-83-8; **5h**, 103594-16-7; **6a**, 28093-86-9; **6b**, 103594-24-7; **6c**, 103594-23-6; **7**, 103594-26-9; **8**, 103594-27-0; **9**, 110392-00-2; **10**, 110392-03-5; **11**, 103594-17-8; **12a**, 19070-95-2; **12b**, 110391-84-9; **12c**, 103594-19-0; **12d**, 110391-85-0; **12e**, 103594-18-9; **12f**, 110391-86-1; **13a**, 103594-20-3; **13b**, 110391-87-2; **13c**, 103594-22-5; **13e**, 103594-21-4; **14**, 110391-88-3; **15b**, 14202-49-4; **16b**, 110391-99-6; **17a**, 15149-10-7; **17b**, 54411-10-8; **17c**, 54576-35-1; **17d**, 713-46-2; **17e**, 34221-43-7; **17f**, 85983-26-2; **18a**, 110391-89-4; **18b**, 110391-90-7; **18c**, 110391-91-8; **18d**, 110391-92-9; **18e**, 110391-93-0; **19a**, 23438-17-7; **19b**, 110391-94-1; **19c**, 110391-95-2; **19d**, 5394-57-0; **19e**, 55153-55-4; **20**, 110392-01-3; **21**, 110392-02-4; **22**, 72054-91-2; **28**, 110391-96-3; **29**, 110391-97-4; 2-$H_3CC_6H_4Li$, 6699-93-0; 4-$H_3COC_6H_4Li$, 14774-77-7; 3,4-$(H_3CO)_2C_6H_3Li$, 80245-51-8; 2-$BrC_6H_4CH_3$, 95-46-5; 4-$BrC_6H_4OCH_3$, 104-92-7; 3,4-$(CH_3O)_2C_6H_3I$, 5460-32-2; HO-*p*-$C_6H_4C_6H_4$-*o*-CH_3, 38262-85-0; H_3CO-*p*-$C_6H_4C_6H_4$-*o*-CO_2H, 18110-71-9; H_3CO-*p*-$C_6H_4C_6H_4$-*o*-CH_2OH, 110391-98-5; H_3CO-*p*-$C_6H_4C_6H_4$-*o*-CHO, 16064-04-3; 4-$H_3CC_6H_4OH$, 106-44-5; 4-EtC_6H_4OH, 123-07-9; 4-*i*-PrC_6H_4OH, 99-89-8; 4-*t*-BuC_6H_4OH, 98-54-4; 4-$PhCH_2C_6H_4OH$, 101-53-1; 4-$H_3CC_6H_4OCH_2CO_2H$, 940-64-7; 4-$H_3CC_6H_4OCH_2CO_2CH_3$, 38768-63-7; CD_3I, 865-50-9; 3,4-$(CH_3)2C_6H_4OH$, 95-65-8; 2-lithiothiophene, 2786-07-4; 4-methylnaphthol, 10240-08-1; ethylene carbonate, 96-49-1.

Supplementary Material Available: Experimental details for preparation of starting materials, ^1H NMR decoupling experiments and ^1H NMR spectra for **8** and **11**, and COSY 45 ^1H NMR spectrum for **11** (14 pages). Ordering information is given on any current masthead page.

An ab Initio Theoretical Study of the Base-Induced Ring Opening of Ethene Episulfoxide

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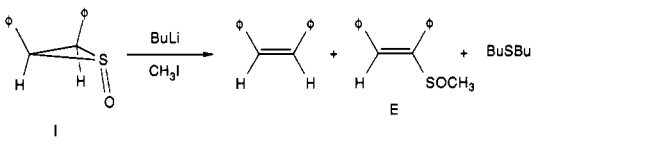
The ring opening of the syn and anti carbanions of ethene episulfoxide has been studied at the Hartree–Fock level with complete geometry optimization by using a minimal STO-3G* basis and a 3-21G basis augmented by diffuse sp functions on all heavy atoms plus d orbitals on sulfur. Relative energies were calculated with second order Møller–Plesset perturbations theory with the larger basis set. The two carbanions have about the same stability, but ring opening is much easier from the syn form. The inversion barrier for the anti–syn interconversion is slightly lower than the barrier for the ring opening of the anti carbanion and significantly higher than the barrier for the ring opening of the syn carbanion. The low barrier for ring opening of the syn carbanion is consistent with the higher yield and retention of stereochemistry observed in the organolithium mediated ring opening of cis-substituted episulfoxides. Inversion competing with ring opening accounts for the partial loss of stereospecificity observed in the trans-substituted episulfoxides.

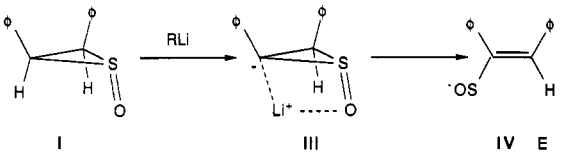
Organolithium derivatives can react with episulfoxides to give products due to attack both on sulfur and on hydrogen.[2,3] *cis*- (I) and *trans*- (II) stilbene episulfoxides, treated with butyllithium in ether at temperatures ranging from 0 to −78 °C, result in desulfurization and ring opening (Scheme I). Desulfurization proceeds via alkyl attack on the sulfur to form an oxysulfurane, which decomposes stereospecifically to the olefin.[2,3] Ring opening occurs by deprotonation to form a carbanion. In the case of *cis*- (I) and *trans*- (II) stilbene episulfoxides, the yields of ring-opening products were 31% and 1.5%, respectively. The *cis*-stilbene episulfoxide (I) ring opening is stereospecific, but the *trans*-stilbene episulfoxide (II) shows a partial loss of stereospecificity (formation of the *E* isomer).

In the ring opening, the base must attack one of the hydrogens. For *cis*-stilbene episulfoxide (I), hydrogen abstraction can produce only the syn carbanion III (Scheme II). This carbanion, possibly stabilized by chelation of Li^+, opens to give the ethenesulfenate anion IV, which is then alkylated by methyl halide. On the other hand, *trans*-stilbene episulfoxide (II), which has more hindered hydrogens and gives a poorer yield from ring opening, has two possible sites for deprotonation (Scheme III). Abstraction of the hydrogen syn to the oxygen leads to the syn carbanion V, which opens stereospecifically to the *Z* isomer VII. Abstraction of the other hydrogen produces a carbanion anti to the oxygen (VI), which can also open stereospecifically to the *Z* isomer VII. Differences in the kinetic acidity of the two hydrogens will determine the ratio of the syn and anti carbanions. However, the presence of the *E* isomer cannot be explained by dif-

Scheme I



Scheme II



† Camille and Henry Dreyfus Teacher–Scholar.

(1) (a) Istituto di Chimica Organica, Bologna, Italy. (b) Wayne State University. (c) Istituto di Chimica Organica, Torino, Italy, and Wayne State University.

(2) Maccagnani, G. *Organic Sulphur Chemistry*; Freidlina, R. Kh., and Skorova, A. E., Eds.; Pergamon: New York, 1981; p 123.

(3) (a) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Piccinelli, P. *Tetrahedron Lett.* **1979**, 1987. (b) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zani, P., to be published.

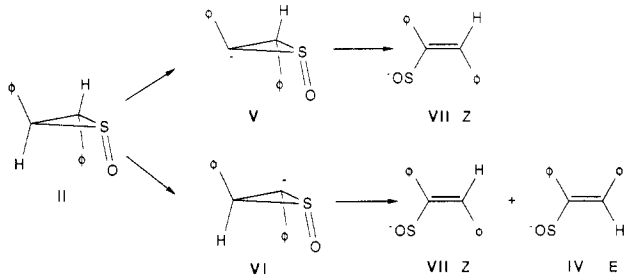
0022-3263/87/1952-4961$01.50/0

Table I. Total and Relative Energies for Ethene Episulfoxide Ring Opening

	E (RHF/STO-3G*)[a]	ΔE[b]	E (RHF/3-21+G + d(S))[a]	ΔE[b]	E (MP2/3-21+G + d(S))[a]	ΔE[b]
episulfoxide	−544.154087		−547.607123			
syn						
syn carbanion	−543.366360	0.0	−546.983448	0.0	−547.441601[c]	0.0
TS for ring opening	−543.322090	27.8	−546.969824	8.5	−547.440761[d]	0.5
trans-ethenesulfenate	−543.394299	−17.5	−547.073715	−56.6	−547.519594	−48.9
TS for inversion to anti	−543.338225	17.7	−546.968436	9.4	−547.429977	7.3
anti						
anti carbanion	−543.363832	0.0	−546.986583	0.0	−547.442097	0.0
TS for ring opening	−543.294840	43.3	−546.964385	13.9	−547.429131	8.1
cis-ethenesulfenate	−543.395439	−19.8	−547.076649	−56.5	−547.524993	−52.0
TS for inversion to syn	−543.338225	16.1	−546.968436	11.4	−547.429977	7.6

[a] Energies in hartrees. [b] Energy differences in kilocalories/mole. [c] At 20% of the distance from the syn minimum geometry to the syn transition rate geometry (linear interpolation). [d] At 60% of the distance from the syn minimum geometry to the syn transition rate geometry (linear interpolation).

Scheme III



ferences in the kinetic acidity. It has been postulated[3] that the anti carbanion VI inverts to give the syn carbanion III, which opens to the *E* isomer.

Since organolithium derivatives are used for the deprotonation, the possibility of lithium chelation must also be considered. For the syn carbanions, III and V, the lithium can be coordinated with both the oxygen and the carbanionic center, as shown in Scheme II. This would disfavor inversion and hence favor stereospecific ring opening. For the anti carbanion, the lithium cannot be coordinated with both the carbanion and the oxygen at the same time. Hence, interaction with lithium would be less stabilizing for the anti carbanion and would favor inversion and consequently loss of stereospecificity in ring opening.

The nature of the ring opening and the explanation of the stereochemistry can be examined theoretically with ethene episulfoxide as a model system. Although experimentally ethene episulfoxide yields only the product of desulfurization, a theoretical study of this model system can provide some insight into the following points: (1) the relative stability of the syn and anti α-sulfinyl carbanions formed by hydrogen abstraction; (2) the energy required for ring opening in the two cases; (3) the barrier for interconversion of the syn and anti carbanions (inversion of the carbanion); (4) the importance of other ring-opening paths leading to loss of stereospecificity; (5) the possibility of α-elimination competing with β-elimination for ring opening.

In the present paper the effect of solvation, the role of Li cation, and the effect of phenyl substituents in the ring-opening reaction are not explicitly studied. The nature of the desulfurization reaction and the kinetics of the deprotonation are also beyond the scope of this study.

Method

Ab initio computations were performed on the model system by using the Gaussian 80 and 82[4] series of programs

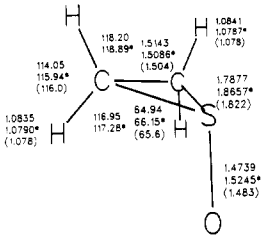


Figure 1. Optimized geometry of ethene episulfoxide. STO-3G* values (no superscript) and 3-21+G + d(S) values (asterisk). Experimental data in parentheses. Bond distances in angstroms, angles in degrees. Additional valence and dihedral angles are ∠XSO = 116.56, 111.62*, (112); $\angle SCCH_{syn}$ = −108.34, −104.04*; $\angle SCCH_{anti}$ = 109.34, 108.11* (X is the midpoint of the CC bond).

with two different basis sets. In a preliminary survey of the potential energy hypersurface, the STO-3G*[5] minimal basis was employed (d orbitals are present on sulfur only). The study was repeated with a split-valence shell 3-21G[6] basis set, augmented with diffuse sp functions (with the exponents suggested by Dunning[7]) on C, O, and S, and with a set of d orbitals (exponent 0.50) on S (all scale factors set to unity). This basis set is designated as 3-21+G + d(S) in this paper. All geometries of minima and transition states were fully optimized at the RHF level with both basis sets by using gradient methods. Several additional points along an approximate reaction path were obtained by linearly interpolating the geometrical parameters between the carbanion minima and the corresponding ring-opening transition states (20%, 40%, 60%, and 80% of the ring opening of the syn carbanion; 80% and 120% for the anti). Electron correlation energy was estimated by second order Møller–Plesset perturbation theory[8,9] (MP2) calculations with the 3-21+G + d(S) basis set at the RHF optimized geometries and for the additional points along the approximate reaction path.

(4) Gaussian 80: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A., *QCPE* **1981**, *13*, 406 and subsequent releases from Carnegie-Mellon University.

(5) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(6) Binkley, J. S.; Pople, J. A.; Hehre, W. J.; *J. Am. Chem. Soc.* **1980**, *102*, 939.

(7) Dunning, T. H.; Hay, P. G. *Modern Theoretical Chemistry*; Schaefer, H. F. III, Ed.; Plenum: New York, 1977; Vol. 4.

(8) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(9) Since no electron pairs are disrupted during the ring opening, the Hartree–Fock level should yield realistic structures, and a perturbative treatment of electron correlation should be adequate. An analogous situation arises in the S_N2 reaction. The situation is quite different for problems involving bond breaking without simultaneous bond making (e.g. bond dissociation potentials[10]) or for processes involving extensive spin recoupling (e.g., radical addition reactions and diradicaloid reaction mechanism).

(10) Handy, N. C.; Knowles, P. J.; Somasundram, K. *Theor. Chim. Acta* **1985**, *68*, 87.

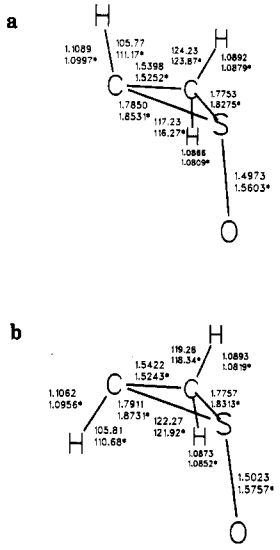


Figure 2. Optimized geometries of (a) the syn carbanion, (b) the anti carbanion. STO-3G* values (no superscript) and 3-21+G + d(S) values (asterisk). Bond distances in angstroms, angles in degrees. Additional valence and dihedral angles are (a) ∠XSO = 118.82, 115.65*; ∠C⁻XSO = 90.20, 90.42*; ∠SCC⁻H = 96.48, 97.45*; ∠SC⁻CH$_{syn}$ = 107.45, 103.46*; ∠SC⁻CH$_{anti}$ = −106.40, −105.70* and (b) ∠XSO = 119.10, 112.38*; ∠C⁻XSO = 98.70, 99.10*; ∠SCC⁻H = −99.33, −97.36*; ∠SC⁻CH$_{syn}$ = 103.38, 99.03*; ∠SC⁻CH$_{anti}$ = −110.41, −109.39* (X is the midpoint of the CC bond).

The computations were performed on the OH-5560 computer of the CSI-Piemonte (Torino, Italy), the VAX-11/780 of the Università di Bologna (Bologna, Italy), and a VAX-11/780 at Wayne State University (Detroit, Michigan).

Results

The optimized geometries are presented in Figures 1–5; the corresponding energies are reported in Table I. Ethene episulfoxide has been optimized to test whether the basis sets can adequately reproduce the experimental structure[11] of this class of compounds. As can be seen from Figure 1, the agreement seems acceptable for the geometrical parameters involved in the reaction (CC, CS bond lengths), particularly with the larger basis.

Two possible carbanions were considered, originating via hydrogen abstraction from the parent ethene episulfoxide: a syn carbanion, Figure 2a, where the carbanionic lone pair is roughly syn to the oxygen atom, and an anti carbanion, Figure 2b, where the lone pair is roughly anti to oxygen. Both the S–O bond and the C–S bond to the carbanionic center are longer in the anti conformer. However, the other C–S bond, the C–C bond, and the pyramidality of the carbanionic center are essentially the same for the syn and the anti conformers. With the extended basis set, the syn is less stable than the anti by 2.0 kcal/mol at the RHF level and 0.3 kcal/mol at the MP2 level. Since the syn and anti carbanions are nearly equal in energy, the thermodynamic acidities of the syn and anti hydrogens in ethene episulfoxide are nearly the same. This suggests (but does not demonstrate) that the kinetic acidities should also be similar.

The transition state for the inversion process that interconverts the syn and anti carbanions is shown in Figure 3. The planarization of the carbanionic center is accompanied by an opening of the C–C⁻–S angle (from 64° to 71°) and a shortening of the three bonds attached to the carbanionic center (CC, CS, and CH). With the extended basis set,[12] the barrier for inversion of the syn carbanion to the anti is 9.4 kcal/mol at the HF level and 7.3 kcal/mol at the MP2 level. With the same basis set, the CH_3^- inversion barrier at the RHF level is within 1 kcal/mol of the Hartree–Fock limit obtained by Duke.[14]

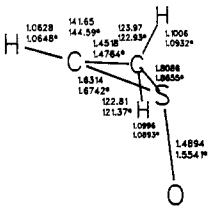


Figure 3. Optimized transition structure for the syn to anti carbanion inversion. STO-3G* values (no superscript) and 3-21+G + d(S) values (asterisk). Bond distances in angstroms, angles in degrees. Additional valence and dihedral angles are ∠XSO = 122.06, 118.51*; ∠C⁻XSO = 95.78, 95.92*; ∠SCC⁻H = 174.06, 177.80*; ∠SC⁻CH$_{syn}$ = 100.95, 96.49*; ∠SC⁻CH$_{anti}$ = −108.21, −105.65* (X is the midpoint of the CC bond).

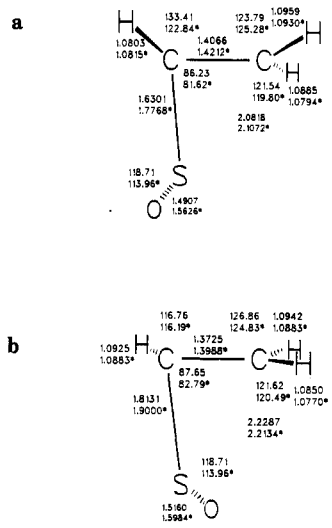


Figure 4. Optimized transiton-state structures for the ring opening: (a) transition state between syn carbanion and *trans*-ethenesulfenate; (b) transition state between anti carbanion and *cis*-ethenesulfenate. STO-3G* values (no superscript) and 3-21+G + d(S) values (asterisk). Additional dihedral angles are (a) ∠CC⁻SO = −130.57, −113.84*; ∠SCC⁻H = 157.34, 118.92*; ∠SC⁻CH$_{syn}$ = 82.03, 83.43*; ∠SC⁻CH$_{anti}$ = −124.99, −110.53* and (b) ∠CC⁻SO = −65.23, −75.43*; ∠SCC⁻H = 123.38, 109.48*; ∠SC⁻CH$_{syn}$ = 117.73, 106.19*; ∠SC⁻CH$_{anti}$ = −70.89, −81.05*.

The ring opening process leading to ethenesulfenate anion proceeds via the transition structures shown in Figure 4. Both correspond to a rotation at the terminal carbon atom in the same direction as the motion of the remaining H at the carbanionic center (Scheme IV, path A). This direction of rotation enhances the conjugation between p orbitals on the carbon atoms and stabilizes the transition state, yielding a double bond in the product with retention of the original stereochemistry. In principle, the terminal carbon could rotate in a direction opposite to the hydrogen at the carbanionic center (path B), leading to loss

(11) Saito, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 663.

(12) The minimal basis grossly overestimates the inversion barrier of CH_3^-, giving a $\Delta E^{\ddagger}$ = 24.0 kcal/mol. For a discussion of the role of different functions in the basis in obtaining pyramidalization angles and inversion barriers, see ref 13.

(13) Bernardi, F.; Mangini, A.; Tonachini, G.; Vivarelli, P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 11 (paper presented with some additional results available on request by G. Tonachini at the XVII M.W. Theoretical Chemistry Conference, Carbondale, IL, May 1984).

(14) Duke, A. J. *Chem. Phys. Lett.* **1973**, *21*, 275.

Table II. Comparison of the Transition State Geometries[a,b]

	∠CCS	% change	r (CC)	% change
syn carbanion	64.6 (64.1)	0	1.525 (1.540)	0
TS for ring opening	81.6 (86.2)	26.7 (33.8)	1.421 (1.407)	55.0 (65.8)
trans-ethenesulfenate	128.3 (129.4)	100.	1.336 (1.338)	100.
anti carbanion	64.3 (63.9)	0	1.524 (1.542)	0
TS for ring opening	82.8 (87.7)	29.7 (35.2)	1.399 (1.373)	65.4 (81.6)
cis-ethenesulfenate	126.5 (131.5)	100.	1.333 (1.335)	100.

[a] Bond lengths in angstroms and angles in degrees. [b] Data from the 3-21+G + d(S) computations (in parentheses data from the STO-3G* computations).

of stereospecificity. However, for this pathway, conjugation between the p orbitals is initially decreased, destabilizing the transition state. Several attempts to optimize the transition states for path B led to higher energy structures that returned to path A via inversion of the carbanion.

With both basis sets, the syn and anti transition states show a number of important structural differences. The degree of opening, described by the SCC angle or by the S–CH_2 distance, is larger for the anti transition state (see Table II). Secondly the HC^-–S bond undergoes a significant elongation in the anti transition state (from 1.87 Å in the carbanion to 1.90 Å), while in the syn transition state the HC^-–S bond is actually shorter than in the carbanion (from 1.85 Å to 1.78 Å). The corresponding C–S bond in the product is 1.75 Å. In addition, the C–C bond is appreciably longer in the syn transition state. However, both transition states show substantial CC double bond character. Overall the syn transition state appears to be earlier along the reaction coordinate, in agreement with the lower barrier. Finally, in the syn transition state, the SO bond is rotated away from the CH_2 group (∠CCSO = 114° compared to ∠CCSO = 91° in the syn carbanion) whereas in the anti transition state, it is rotated toward the CH_2 group (∠CCSO = 75° compared to ∠CCSO = 99° in the anti carbanion). Both ring openings correspond to a conrotatory motion of the S–O and CH_2 groups, as dictated by orbital phase continuity arguments (see the Discussion). The search for a transition structure corresponding to disrotatory motion proceeded toward a second order saddle point.

At the Hartree–Fock level with the 3-21+G + d(S) basis set, the barriers for ring opening are 8.5 kcal/mol for the syn carbanion and 13.9 kcal/mol for the anti carbanion.[15] When correlation energy is included, the barrier for the anti carbanion is reduced to 8.1 kcal/mol (a lowering of ca. 6 kcal/mol). The positions of the minimum and transition structure along the approximate reaction paths are not altered significantly. For the opening of the syn carbanion, correlation corrections reduce the barrier to 0.5 kcal/mol (an 8 kcal/mol lowering). Furthermore the syn minimum is shifted along the approximate reaction path toward the transition structure by ca. 20% of the distance between the minimum and the transition structure, and the transition structure is shifted by ca. 40% toward the minimum.

Two conformations were examined for the product ethenesulfenate anion: the oxygen atom trans to the terminal carbon atom, Figure 5a, arising from the syn opening (compare with the transition state structure, Figure 4a); and the oxygen cis with respect to the terminal carbon atom Figure 5b, arising from the anti opening (compare Figure 4b). The two structures are very similar in energy, the cis being 1.8 kcal/mol more stable at the RHF/3-21+G + d(S) level and 3.4 kcal/mol more stable

(15) The barriers are overestimated at the HF/STO-3G* level but show the same trend: $\Delta E^{\ddagger}_{syn}$ = 27.8, $\Delta E^{\ddagger}_{anti}$ = 43.3 kcal/mol.

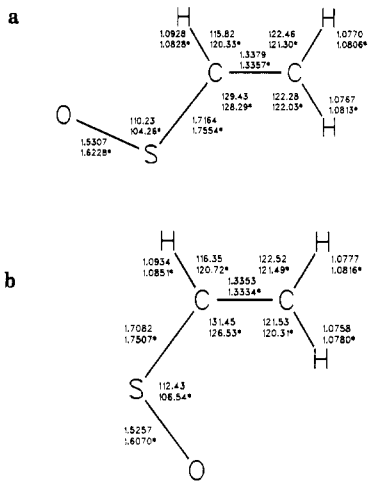


Figure 5. Optimized geometries of (a) trans and (b) *cis*-ethenesulfenate. STO-3G* values (no superscript) and 3-21+G + d(S) values (asterisk). Bond distances in angstroms, angles in degrees.

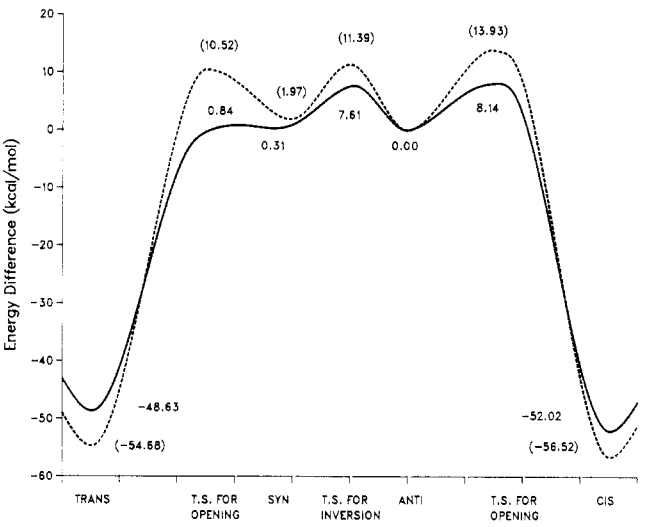


Figure 6. The energy profile for the ring opening and the inversion processes: left, the opening from the syn carbanion; right, the opening from the anti carbanion; center, the inversion process connecting the syn and the anti carbanion. Dashed line, RHF/3-21+G + d(S); solid line, MP2/3-21+G + d(S). Energy differences in kcal/mol. Numbers in parentheses refer to ΔE(RHF), others are ΔE(MP2).

at the MP2 level. The exothermicity for the opening of the syn carbanion is −56.6 kcal/mol at the RHF/3-21+G+d(S) level and −48.9 kcal/mol at the MP2 level; for the opening of the anti carbanion, the exothermicities are −56.5 and −52.0 kcal/mol, respectively.[16]

(16) The STO-3G* ΔE values are −17.5 kcal/mol from syn and −19.8 kcal/mol from anti. This is not unexpected because the minimal basis is known to overestimate small ring stabilities with respect to the isomeric open forms.[17]

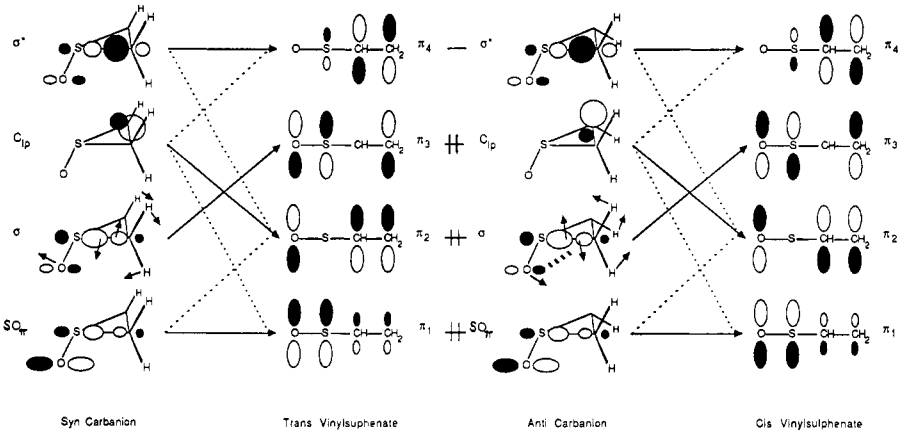
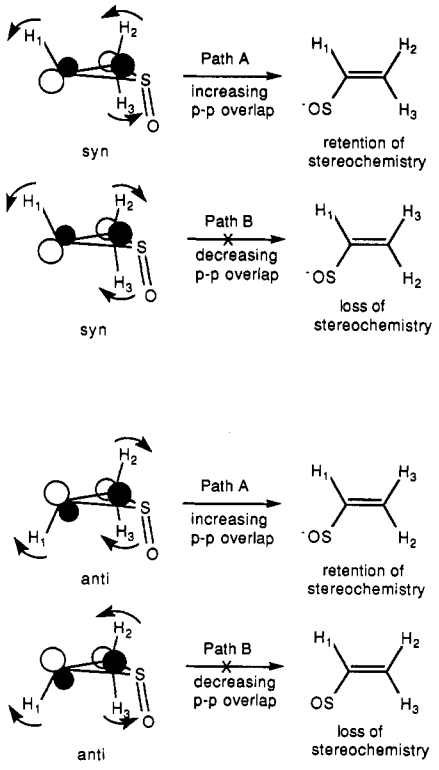


Figure 7. A qualitative orbital correlation diagram for the ring opening of the syn and anti carbanions. C_{lp} refers to the carbon sp lone pair, σ and σ^* to the S–C sigma bond, and SO_π to a π orbital of the S–O group.

Scheme IV



Discussion

The partial loss of stereospecificity observed when the *trans*-diphenyl-substituted system undergoes ring opening, has been attributed to inversion at the carbanionic center.[3] The driving force for this process was suggested to be the chelation of a Li cation between oxygen and the anionic center. The present calculations indicate that stereospecific ring opening of the syn carbanion and loss of stereospecificity in the ring opening of the trans carbanion occurs even in the absence of lithium chelation. The calculated energetics are summarized in Figure 6. For the syn carbanion, the barrier for ring opening is lower than for inversion. Therefore, ring opening with retention can occur more rapidly than inversion and loss of stereospecificity. For the anti carbanion, however, the ring opening and inversion barriers are comparable; inversion and loss of stereospecificity can compete with stereospecific ring opening. Thus the calculations are in agreement with experiment, and it is not necessary to invoke lithium chelation as the driving force.

The experimental studies were carried out with organolithium derivatives and phenyl-substituted episulfoxides. As discussed in the introduction, lithium coordination would enhance the retention of stereochemistry in the opening of the syn carbanion and the loss of stereochemistry in the anti carbanion by preferentially stabilizing the syn carbanion and transition state. Calculated electrostatic potentials support the proposed stronger interaction with the syn carbanion than with the anti. Phenyl substitution should stabilize all of the carbanionic species and reduce the exothermicity of the ring opening. The carbanion inversion barrier should also be lowered, promoting the loss of stereospecificity in the anti carbanion.

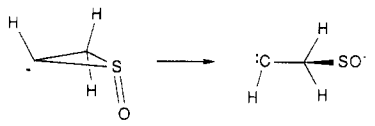
The essence of the ring-opening process in ethene episulfoxide is the conversion of a carbon lone pair and a C–S σ bond in the cyclic carbanion, into a π^*-type lone pair on the SO group and a C–C π bond in the product. The principal orbitals for the opening of the syn and the anti carbanions are illustrated in Figure 7. The relevant orbitals for the cyclic carbanions are shown in a simplified, localized representation: SO_π, a π orbital on the SO group with a small in-phase contribution form the sp^3 hybrid of the CH group; σ and σ^*, the bonding and antibonding orbitals for the C–S bond formed from the in-phase and out-of-phase combinations of an SO_{π^*} orbital and the sp^3 hybrid of the CH_2 group; and C_{lp}, the lone pair on the carbanionic center. The canonical orbitals are actually more complicated because of strong mixing with other ring orbitals. The four orbitals illustrated in Figure 7 interact during the ring opening and evolve into the butadiene dianion-like π system of ethenesulfenate (orbitals π_1–π_4).

As discussed above and shown in path A of Scheme IV, the CH_2 group always rotates in the same sense as the CH group, to maximize the π bond formation during the ring opening; this corresponds to maximizing the C_{lp}–σ^* stabilizing interaction. In turn, the SO group is required to rotate in the same direction as the CH_2 group (i.e., conrotatory) on the basis of orbital phase continuity arguments. Conrotatory motion transforms the C–S σ orbital into π_3; disrotation would transform it into π_4, the lowest empty orbital in the products. The carbon lone pair evolves into π_2 and is stabilized mainly by an interaction with σ^*; in turn σ^* correlates with π_4 and is destabilized by an interaction with the carbon lone pair.

Alternatively, the oxygen atom can be considered as a nonparticipating substituent of the three-membered ring. Then the ring opening of ethene episulfoxide is isoelec-

(17) (a) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5339. (b) Flanigan, M. C.; Komornicki, A.; McIver, J. W., Jr. In *Modern Theoretical Chemistry*; Segal, G. A., Ed.; Plenum: New York, 1977; Vol. 8, pp 29–30.

Scheme V



VIII

tronic with ring opening in cyclopropyl anion, which proceeds in a conrotatory manner as a result of the conservation of orbital symmetry.[18]

Both these interpretations explain why *trans*-ethenesulfenate is produced from the syn carbanion (via the transition structure shown in Figure 4a) and *cis*-ethenesulfenate is produced from the anti carbanion (via the transition structure shown in Figure 4b). The higher barrier for the anti carbanion ring opening can be rationalized by considering the secondary overlap in the $\sigma \rightarrow \pi_3$ transformation. For the syn carbanion, the oxygen rotates away from the CH_2 group. However, for the anti carbanion the oxygen rotates toward the CH_2 group, and there is an antibonding interaction between the oxygen and the CH_2 group (indicated by a heavy dashed line in Figure 7b).

The calculations discussed above refer to ring opening by β-elimination. Ring opening could also occur via α-elimination yielding the isomeric carbenic structure (Scheme V). In a MINDO/3 study of three-member rings and their isomers, Dewar and Ramsden[19] found that the acyclic carbenes either rearrange to the corresponding antiaromatic heterocycles without activation or are unstable and collapse without activation to the heterocumulenes (1,2 shift). Imposing a geometry constraint to prevent rearrangement, they found the carbenes to be 17 to 21 kcal/mol less stable than the corresponding heterocycle. Our ab initio calculations are in agreement with these results, since several attempts to optimize structures like VIII at the STO-3G* level resulted in the reclosure to the original cyclic carbanion. Recent experimental results with appropriately deuteriated episulfoxides also discount ring opening via α-elimination.[3b]

(18) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie-Academic: 1970.
(19) Dewar, M. J. S.; Ramsden, C. A.; *J. Chem. Soc., Chem. Commun.* 1973, 688.

Conclusions

The ab initio calculations on the syn and the anti carbanions obtained for the model system, ethene episulfoxide, indicate the following: 1. The two carbanions show about the same relative stability. 2. The activation energy for the ring-opening process is significantly lower for the syn carbanion. The possible interaction with Li cation would also favor the formation and opening of the syn form. Substituent effects in the experimentally studied compounds should act in the same direction. 3. The inversion barrier for the conversion of the anti carbanion to the syn is comparable to the barrier to ring opening, and thus accounts for the partial loss of stereospecificity. Considering the effect of substituents on inversion barriers, this process should be easier for the phenyl substituted episulfoxides studied experimentally and would enhance the partial loss of stereospecificity in the trans-disubstituted compound. Chelation of Li^+ would also increase the loss of stereospecificity by favoring the formation of the syn carbanion. 4. An alternative ring-opening pathway leading to loss of stereospecificity has been shown to be very unlikely. 5. The possibility of ring opening via α-elimination can be ruled out, in accord with experimental findings. The products would be carbenic structures which are unstable with respect to reclosure of the ring.

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Registry No. Ethene episulfoxide carbanion, 110224-75-4; ethylene episulfoxide, 7117-41-1; ethenesulfenate anion, 110224-76-5.

Diisophorone and Related Compounds. 20.[1] Diisophoranes Incorporating the 1,3-Thiazine Ring System: 8,11a-Methanocycloocta[*d*,*e*][3,1]benzothiazines

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S-(Diisophor-2(7)-en-1-yl)isothioureas **3–6** are obtained by the interaction of 1-chloro(or hydroxy)diisophor-2(7)-ene (**1**, **2**) with thiourea or its mono- or 1,1- or 1,3-disubstituted homologues and yield diisophor-2-(7)-ene-1-thiol (**7**) on treatment with alkali. In the case of 1-chloro(or hydroxy)diisophor-2(7)-en-3-ones (**12**, **13**), the same group of reactions is attended by simultaneous intramolecular cyclodehydration, resulting in 8,11a-methanocycloocta[*d*,*e*][3,1]benzothiazines **16–23**.

Introduction

One of the more striking properties of the three-dimensional structure of diisophorone (e.g., **12**) is the readiness with which an additional six- or seven-membered ring D may be attached to the molecule so as to incorporate carbon atoms C-1, C-2, and C-3 of the original carbon skeleton. The formation of such structures by replacement–elimination processes at C-1 and C-3 is exemplified by the condensation of the parent β-ketol **13** with ethane-1,2-diol to dioxepanes **A**[2] or with another molecule of

(1) Part 19: Kurzer, F.; Mitchell, J. B. O.; Patel, J. N. *Monatsh. Chem.*, in press.
(2) Furth, B.; Kossanyi, J.; Morizur, J. P.; Vandewalle, M. *Bull. Soc. Chim. Fr.* 1967, 1428.

0022-3263/87/1952-4966$01.50/0