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 complex geometry optimization by using a minimal STO-3G* 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 stereochimistry observed in the organolithium mediated ring opening of cis-substituted episulfides. Inversion competing with ring opening accounts for the partial loss of stereospecificity observed in the trans-substituted episulfides.

Organolithium derivatives can react with episulfides to give products due to attack both on sulfur and on hydrogen. cis- (I) and trans- (II) stibene episulfides, treated with butylithium 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.3a Ring opening occurs by deprotonation to form a carbanion. In the case of cis- (I) and trans- (II) stibene episulfides, the yields of ring-opening products were 31% and 1.5%, respectively. The cis-stibene episulfide (I) ring opening is stereospecific, but the trans-stibene episulfide (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-stibene episulfide (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-stibene episulfide (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 diff-

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Scheme I

Scheme II

References

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Lithium can be coordinated with both the oxygen and the anti carbanion VI to give the syn carbanion VII, 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 ab initio computations on the model system by using the Gaussian 80 and 82 series of programs.

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

<table>
<thead>
<tr>
<th></th>
<th>$E$(RHF/STO-3G*)</th>
<th>$\Delta E^b$</th>
<th>$E$(RHF/3-21G+d(S))</th>
<th>$\Delta E^b$</th>
<th>$E$(MP2/3-21G+d(S))</th>
<th>$\Delta E^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn</td>
<td>-544.154087</td>
<td>-547.607123</td>
<td>-546.983448</td>
<td>0.0</td>
<td>-547.441601</td>
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<tr>
<td>TS for ring opening</td>
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<td>-547.073715</td>
<td>-56.6</td>
<td>-547.539594</td>
<td>-48.9</td>
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<tr>
<td>trans-ethenesulfenate</td>
<td>-543.392225</td>
<td>17.7</td>
<td>-547.958436</td>
<td>9.4</td>
<td>-547.429977</td>
<td>7.3</td>
</tr>
<tr>
<td>anti</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>anti carbanion</td>
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<td>0.0</td>
<td>-546.986583</td>
<td>0.0</td>
<td>-547.442097</td>
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</tr>
<tr>
<td>TS for ring opening</td>
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<td>-56.5</td>
<td>-547.324993</td>
<td>-52.0</td>
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<td>cis-ethenesulfenate</td>
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<td>-19.8</td>
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<tr>
<td>TS for inversion to syn</td>
<td>-543.358225</td>
<td>18.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Energies in hartrees. $^b$Energy differences in kilocalories/mole. $^\dagger$At 20% of the distance from the syn minimum geometry to the syn transition rate geometry (linear interpolation). $^\ddagger$At 60% of the distance from the syn minimum geometry to the syn transition rate geometry (linear interpolation).

- **Scheme III**

- **Figure 1.** Optimized geometry of ethene episulfoxide. STO-3G* values (no superscript) and 3-21G+ d(S) values (asterisk). Experimental data in parentheses. Bond distances in angstroms, angles in degrees. Additional valence and dihedral angles are $\angle{\text{XSO}} = 116.56, 111.62^\circ$, (112); $\angle{\text{SCCH}_{\text{mli}}}$ = -108.34, -104.04$^\circ$; $\angle{\text{SCCH}_{\text{mli}}}$ = 108.34, 108.11$^\circ$ (X is the midpoint of the CC bond) with two different basis sets. In a preliminary survey of different energies for ethene episulfoxide, the STO-3G* minimal basis set was employed (d orbitals are present on sulfur only). The study was repeated with a split-valence shell 3-21G basis set, augmented with diffuse sp functions (with the exponents suggested by Dunning) 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 3-21G+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 (MP2) calculations with the 3-21G+d(S) basis set at the RHF optimized geometries and for the additional points along the approximate reaction path.

### Method

Ab initio computations were performed on the model system by using the Gaussian 80 and 82 series of programs.
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) \( \alpha_{\text{XSO}} = 118.82, 115.65^\circ; \alpha_{\text{C-XSO}} = 90.20, 90.42^\circ; \alpha_{\text{SCC-H}} = 96.48, 97.45^\circ; \alpha_{\text{SCC-CH}} = 107.45, 109.46^\circ; \alpha_{\text{SCC-CH}_{\text{anti}}} = -106.40, -105.70^\circ \) and (b) \( \alpha_{\text{XSO}} = 119.10, 112.38^\circ; \alpha_{\text{C-XSO}} = 98.70, 99.10^\circ; \alpha_{\text{SCC-H}} = -99.33, -97.98^\circ; \alpha_{\text{SCC-CH}} = 103.98, 99.03^\circ; \alpha_{\text{SCC-CH}_{\text{anti}}} = -110.41, -109.39^\circ \) (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 pyramidalization 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 HF 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.\(^{14}\)

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 of the electron pair to oxygen and the formation of an additional bond.

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\(^{12}\) The minimal basis grossly overestimates the inversion barrier of CH\(_3\), giving a \( \Delta E^* = 24.6 \) kcal/mol. For a discussion of the role of different functions in the basis in obtaining pyramidalization angles and inversion barriers, see ref 13.


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–CH₂ 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 CH₂ group (offset SO = 114° compared to offset SO = 91° in the syn carbanion) whereas in the anti transition state, it is rotated toward the CH₂ group (offset SO = 75° compared to offset SO = 99° in the anti carbanion). Both ring openings correspond to a conrotatory motion of the S–O and CH₂ 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 at the MP2 level. The exothermicity for the opening of the syn carbanion is -56.5 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

¹⁵ The barriers are overestimated at the HF/STO-3G* level but show the same trend: ΔĉRHF = 27.8, ΔĉMP2 = 43.3 kcal/mol.

¹⁶ The STO-3G* Δĉ 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. $C_\text{up}$ refers to the carbon sp lone pair, $\sigma$ and $\sigma^*$ to the S–C sigma bond, and $SO_2$ to a $\pi$ orbital of the S–O group.

**Scheme IV**

**Path A**

**Syn**

Increasing p-p overlap

Retention of stereochemistry

**Path B**

Decreasing p-p overlap

Loss of stereochemistry

**Path A**

**Anti**

Increasing p-p overlap

Retention of stereochemistry

**Path B**

Decreasing p-p overlap

Loss of stereochemistry

**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. 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 exothermcity 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 $\sigma$ bond in the cyclic carbanion, into a $\pi^*$-type lone pair on the SO group and a C–C $\pi$ bond in the product. The principal orbitals for the cyclic carbanions are shown in a simplified, localized representation: $SO_2$, a $\pi$ orbital on the SO group with a small in-phase contribution form the sp3 hybrid of the CH group; $\sigma$ and $\sigma^*$, the bonding and antibonding orbitals for the C–S bond formed from the in-phase and out-of-phase combinations of an SO$_2$ orbital and the sp3 hybrid of the CH$_2$ group; and $C_{\text{up}}$, 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 $\pi$ system of ethenesulfenate (orbitals $\pi_1$–$\pi_4$).

As discussed above and shown in path A of Scheme IV, the CH$_3$ group always rotates in the same sense as the CH$_2$ group, to maximize the $\pi$ bond formation during the ring opening; this corresponds to maximizing the $C_{\text{up}}$–$\sigma^*$ 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 $\sigma$ orbital into $\pi_3$; disrotation would transform it into $\pi_4$, the lowest empty orbital in the products. The carbon lone pair evolves into $\pi_3$ and is stabilized mainly by an interaction with $\sigma^*$; in turn $\sigma^*$ correlates with $\pi_4$ 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 isoelc-

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D may be attached to the molecule so as to incorporate

\[ \text{Chem.} \]

1-dimensional structure of diisophorone (e.g., \[ \text{mensional structure of diisophorone (e.g.,} \]

ininess with which an additional six- or seven-membered ring

aromatic heterocycles without activation or are unst-

results, since several attempts to optimize structures like

Our ab initio calculations are in agreement with these

rearrangement, they found the carbenes to be 17 to 21

able and collapse without activation to the heterocumul-

the oxygen rotates toward the \( \text{CH}_2 \) group, and there is an

antibonding interaction between the oxygen and the CH,

away from the \( \text{CH}_2 \) group. However, for the anti carbanion

the oxygen rotates toward the \( \text{CH}_2 \) group, and there is an

antibonding interaction between the oxygen and the \( \text{CH}_2 \)

group (indicated by a heavy dashed line in Figure 7b). The higher

transformation. For the syn carbanion, the oxygen rotates

in press.

1973, 688.


The ab initio calculations on the syn and the anti car-

banions obtained for the model system, ethene epilsul-

oxide, 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 \( \text{Li}^+ \) 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. Con-

sidering 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-dissubsi-

tute compound. Chelation of \( \text{Li}^+ \) 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 \( \alpha-

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.

Diisophorane and Related Compounds. 20. \(^1\) Diisophoranes Incorporating

the 1,3-Thiazine Ring System:

8,11a-Methanocycloocta[\(d,e] [3,1] \text{benzothiazines}\)

Frederick Kurzer,* Paul R. Davies, and Stanley S. Langer

Royal Free Hospital School of Medicine, University of London, London NW3 2PF, England

Received February 9, 1987

S-(Diisophor-2(7)-en-1-yl)disothioures 3-6 are obtained by the interaction of 1-chloro(or hydroxy)diisop-

hor-2(7)-ene (1, 2) with thiourea or its mono- or 1,1- or 1,3-disubstituted homologues and yield diisophor-2-

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the same group of reactions is attended by simultaneous intramolecular cyclodehydration, resulting in 8,11a-

methanocycloocta[\(d,e] [3,1] \text{benzothiazines} 16-23.

Introduction

One of the more striking properties of the three-di-

mensional structure of diisophorone (e.g., 12) is the read-

iness 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 replace-

ment-elimination processes at C-1 and C-3 is exemplified

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