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(14) (a) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Am. Chem. Soc.*, **90**, 5618 (1970); (b) W. S. Johnson, T. J. Brocksom, P. Loew, D. H. Rich, L. Werthemann, R. A. Arnold, T. Li, and D. J. Faulkner, *ibid.*, **92**, 4463 (1970); (c) D. J. Faulkner and M. R. Peterson, *ibid.*, **95**, 553 (1973); (d) S. B. Bowlus and J. A. Katzenellenbogen, *Tetrahedron Lett.*, 1277 (1973).

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(16) Several other routes to **1** are also generated by the program.

(17) Solid and dotted boxes indicate interfering functionality. For further details, see E. J. Corey, H. W. Orf, and D. A. Pensak, *J. Am. Chem. Soc.*, **98**, 203 (1976).

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Sulfene and the $^1CH_2/SO_2$ Potential Energy Surface[1a]

Lars Carlsen[1b] and James P. Snyder*

Department of General and Organic Chemistry, H. C. Ørsted Institute,
University of Copenhagen, DK-2100, Copenhagen, Denmark

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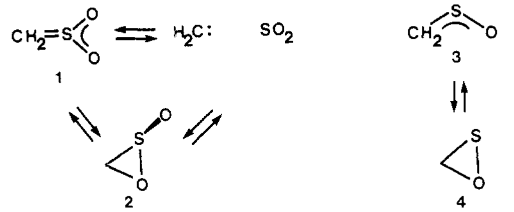
Sulfene, $CH_2{=}SO_2$ (1), is a highly reactive intermediate directly observable only at temperatures below −150 °C. Nonetheless it has been implicated in a variety of reactions in the gas phase and in solution. In particular its rearrangement to α-sultine 2, the cheletropic fragmentation of 2 to $^1CH_2$ and SO_2, and its formation from the latter moieties have drawn attention. Exploration of the potential energy surfaces of these transformations has been undertaken by means of CNDO/B semiempirical calculations and compared with results for the corresponding hydrocarbon systems. Within the CNDO/B framework, the replacement of π-deficient $^1CH_2$ by π-rich SO_2 produces no fundamental mechanistic variations in the $CH_2{=}SO_2$ or α-sultine forming reactions relative to the $CH_2{=}CH_2$ or cyclopropane producing processes. Small but significant differences in the potential energy surfaces are, however, observed. These can be associated with the π-electron distributions of the reacting fragments. The electrocyclic ring closure of sulfene to α-sultine is predicted to follow an "allowed" pathway. It differs from the cyclization of the isoelectronic allyl anion (σ–π correlation) and sulfine (π–π_S correlation) in that a third type of orbital correlation is evident: π–n. High-lying nonbonding oxygen levels introduced by S oxidation are responsible. We suggest the existence of a four-membered ring cyclic sulfoxylate ester 8 on the sulfene potential surface and argue for its intervention in the chemistry of the previously postulated α-sultine. Other sulfene isomers are ruled out as unlikely transients. Finally the cheletropic addition of $^1CH_2$ to SO_2 to give sulfoxylate 8 is identified as an "electron pair excess" pericyclic reaction. The essential "forbiddeness" of this and related reactions is discussed.

Although sulfur trioxide is a stable and familiar laboratory reagent, the carbon analogue, sulfene (**1**), is a fleeting intermediate directly observable only at temperatures below ca. −150 °C.[2] The behavior of sulfene in solution is characterized by capture of electrophiles at carbon and nucleophiles at sulfur.[2,3] Oligomerization occurs in the absence of external addends.[4] When sulfene is generated in the gas phase at high temperatures, formaldehyde and SO are formed.[4b,5] It has been suggested that intramolecular cyclization to the α-sultine **2** precedes ultimate fragmentation.[5,6] More recently the preparation of transitory **2** at 25 °C has been claimed to result from the addition of methylene, $^1CH_2$, to SO_2[7] and from the peracid oxidation of thiocarbonyl *S*-oxides.[8]



In connection with our continuing fascination with sulfene,[9] sulfine **3**,[10] and oxathiirane **4**,[11] we have investigated the interconversion of the isoelectronic species **1**, **2**, and $^1CH_2/SO_2$ by the CNDO/B procedure.[12] [Throughout this paper, CH_2 is singlet ($^1CH_2$) unless indicated otherwise.] Besides possibly illuminating the above experimental findings, the triad is of interest for two additional reasons. Singlet methylene dimerizes to ethylene[13] and adds to C–C couble bonds to give cyclopropanes.[14] With regard to the first process, a study of the formation of sulfene **1** from CH_2 and SO_2 permits an inquiry into the consequences of the existence of π electrons in one of the combining fragments. A comparison of cyclopropane and α-sultine formation raises the additional question of symmetry and its absence in a pair of model cheletropic reactions. The electrocyclic ring opening of **2** to sulfene addresses the symmetry issue as well. Previous calculations on heteroelectrocylic reactions for oxathiirane **3**[11a] and related systems[15] suggest unexpected electronic features may be associated with the potential energy surface connecting end-point minima.

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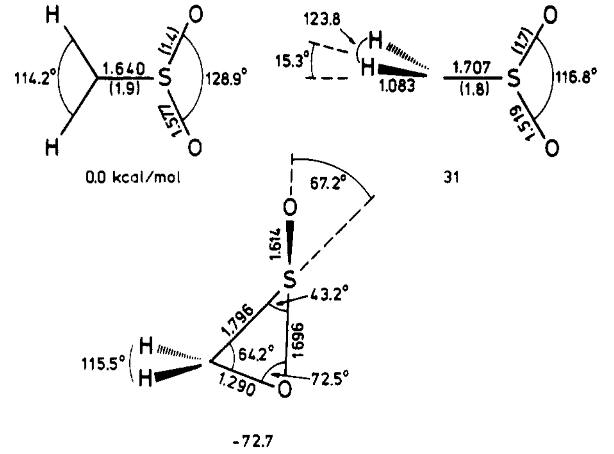
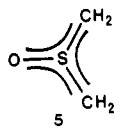


Figure 1. CNDO/B optimized geometries for planar sulfene 1, twisted sulfene, and α-sultine 2. Bond lengths are in Å; bond angles are in deg. Bond orders are given in parentheses. The relative calculated total energy is indicted beneath the structures (kcal/mol).

Ground-State Structures

The ground state geometries of sulfene 1 and α-sultine 2 were optimized completely as a function of the total energy with CNDO/B. Sulfur d orbitals are not incorporated in the method. The resulting structures are given in Figure 1. Sulfene is predicted to be planar in agreement with the shape of its isoelectronolog, sulfur trioxide.[16] Distortion of either the CH_2 or the SO_2 moiety out of plane causes a rise in the calculated total energy. The carbon-rich isoelectronic species 5 is likewise predicted to be planar by the extended Hückel method.[17]



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Two additional features deserve comment. The S–O bond length (1.577 Å calcd) is clearly overestimated when compared with either SO_2 (1.431 Å)[18] or SO_3 (1.43 Å).[16] A similar long S–O distance was predicted for sulfine, $CH_2{=}SO$.[10,19] CNDO/B is consistently deficient in this regard. For molecules involving π-delocalized S–O bonds, the bond lengthening can be remedied by the explicit inclusion of sulfur 3d orbitals or by employment of a sufficiently large basis set.[20] Secondly the OSO bond angle is predicted to be considerably expanded relative to the calculated value for SO_2 (115°[12]). Qualitatively this may be attributed to negative charge localization on oxygen. The accompanying oxygen–oxygen electron repulsion is relieved by angle opening. Although CNDO/B gives reasonable dipole moments, comparison with CNDO/2 and STO-3G calculations suggests that charge buildup is somewhat exaggerated.[21] Consequently although the trend from SO_2 to sulfene seems reasonable, we suspect that $\angle OSO_{calcd}$ is overestimated.

Rotation about the C–S double bond in 1 is accompanied by inversion at carbon (cf. Figure 1). As $CH_2{=}SO_2$ travels to the energy maximum, the C–S bond order[22] drops from 1.9 to 1.8 and the S–O quantity simultaneously rises from 1.4 to 1.7. Coincident with bond loosening and tightening the moderate negative charge at carbon (−0.21) and the large positive charge at sulfur (+1.2) in 1 rise to −0.64 and +1.7 respectively, while the values at H and O are essentially unchanged (+0.12 → +0.13 and −0.62 → −0.63, respectively). The polar nature of planar sulfene is thus enhanced in the rotational transition state, a species probably best described as the σ-bonded union of carbanion and $R{-}SO_2^+$ fragments. The OSO angle and the S–O bond length reductions are in accord with electron transfer from oxygen to sulfur.

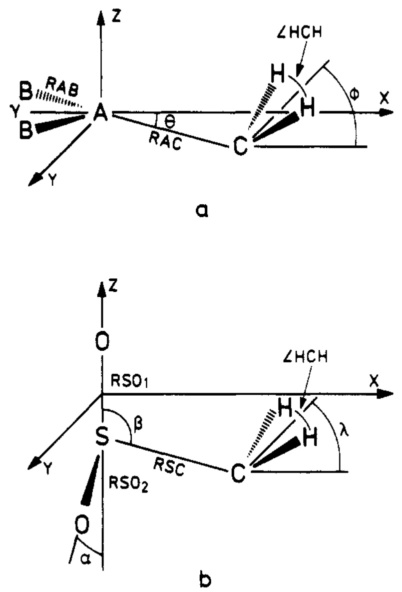


Figure 2. Reaction coordinate spaces for (a) the formation of sulfene from $^1CH_2$ and SO_2 and the dimerization of $^1CH_2$ to give ethylene; reaction coordinate is the A–C distance; optimized variables, γ, θ, φ, ∠HCH, and RAB (for RSO), and (b) α-sultine generation from $^1CH_2$ and SO_2; reaction coordinate is the S–C distance; optimized variables, α, β, λ, ∠HCH, and RSO_2.

The overall structure of α-sultine 2 is reasonable[23] with the exception of the extended S–O bond length. The remarks directed at sulfene likewise apply here. For consistency in the calculations described below, the CNDO/B optimized geometries[12] of SO_2 and singlet CH_2 were employed at the reaction end points.

Potential-Energy Surfaces

For the transformations considered in the present study, the reaction coordinate method has been adopted. That is, a specific bond distance or bond angle was fixed at various values on the potential surface between the ground state structures under investigation. For fragmentations the calculations were performed out to a separation of 3–4 Å. At each of the intermediate points the remainder of the geometric parameters were varied until the CNDO/B total energy reached a minimum.

The S–C distance was chosen as the reaction coordinate for the combination of SO_2 and singlet CH_2 to give sulfene. A plane of symmetry bisecting the two fragments and a constant C–H bond length (1.098 Å) were assumed throughout. The five remaining variables are defined by Figure 2a (A = S, B = O). For the sake of comparison to the hydrocarbon analogue, the calculations were repeated for the dimerization of CH_2 (A = C, B = H). Four angles were optimized (θ, φ, γ, ∠HCH); the C–H bond distance was fixed at 1.098 Å.

α-Sultine formation from SO_2 and CH_2 utilized the S–C distance as the reaction coordinate and involved optimization of six variables. The separate S–O bond length and the four angles (α, β, λ, ∠HCH) are depicted in Figure 2b. The lowest energy approach of CH_2 on the S–O bond resulted from maintainance of carbon in the *xz* plane orthogonal to the *yz* plane containing the SO_2 unit. The *xz* plane furthermore contains the S–O bond under attack and bisects the HCH angle. Displacement of CH_2 from this plane proved to be an energy raising motion.

The least well-behaved potential surface was found to be the ring closure of sulfene 1 to α-sultine 2. Initially the CSO angle was employed as reaction coordinate, with all other

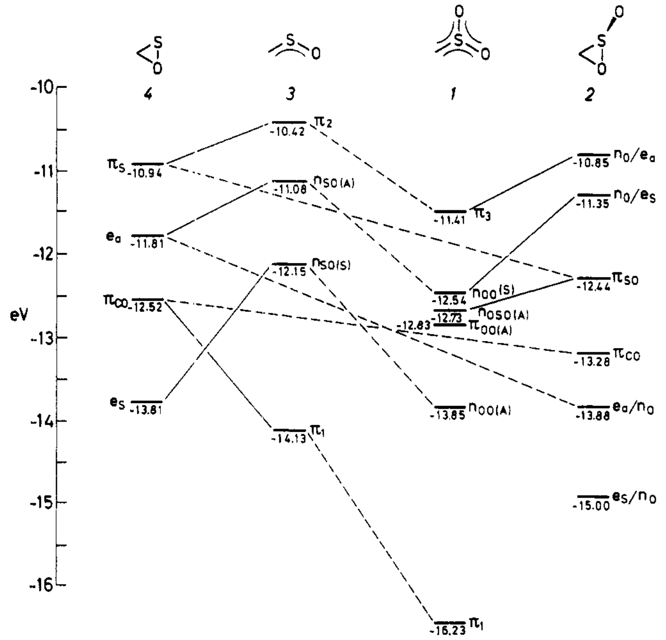


Figure 3. Oxidation of sulfine **3** and oxathiirane **4** and its consequences for the high-lying molecular orbitals (CNDO/B). Dashed lines connect **3** and **4** and the corresponding oxidized species **1** and **2**, respectively. The unbroken lines correlate acyclic and cyclic isomers (**3** → **4** and **1** → **2**).

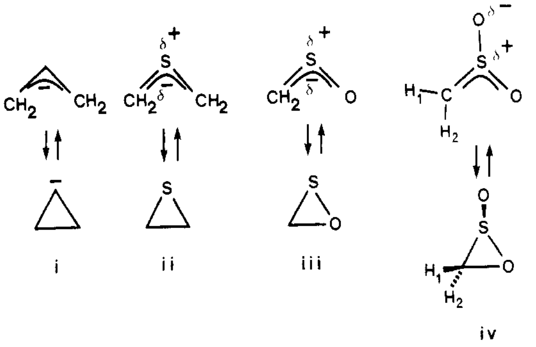
parameters being varied independently. Unfortunately discontinuities were encountered which are probably associated at least in part with the existence of the sulfene rotamer of Figure 1. Both this species and the ring closure maximum lie about 30 kcal/mol above sulfene **1**. Consequently in order to obtain a qualitative map of the cyclization, we finally incremented all bond angles between **1** and **2** and varied only the bond lengths C–S, C–O, and S–O.

The reaction coordinate approach has served in the theoretical study of reaction mechanisms at all levels of sophistication from extended Hückel to large basis set calculations which include CI. Nonetheless the recent work of Halgren and Lipscomb suggests that there are fundamental deficiencies in the selection of an arbitrary bond length or bond angle as guidepost along the potential surface.[24] Not only is there little assurance that the minimum energy pathway has been accurately plotted, but no guarantee can be provided for having traversed the lowest energy maximum, the transtion state. With these reservations in mind we compare our results to others derived by calculations using the same philosophy to construct the reaction pathway. Insofar as the "allowedness" or "forbiddeness" of a reaction is concerned,[25] the step-by-step details of molecular motion are less critical. An independent check on the qualitative course of the reaction can be made by reference to the orbital symmetry conservation principle,[26] its equivalent,[27] or a frontier orbital analysis. Likewise there is a reasonable precedent for expecting that the lack of sulfur d orbitals in CNDO/B will not influence the overall character of the predicted mechanisms.[28]

Sulfene–α-Sultine Interconversion.

The cyclization of sulfene to α-sultine **2** is profitably viewed as a member of the reaction series i to iv in which the allyl anion is progressively perturbed by sulfur and oxygen.

Transformations i–iii have been examined previously[11a,15,29] and have been found to proceed by an allowed route, that is all bonding MO's remain bonding throughout the computed reaction path. Closures i and ii require, of course, a conrotatory motion at the carbon termini. We find that reaction iv is likewise allowed as is evident by the absence of a frontier orbital crossing in the orbital correlation diagram. Although two diasteriomeric transition states are conceivable, we have examined only that indicated by iv in which H_1 and the exo oxygen move out of the sulfene plane in the same direction.



Since sulfene **1** can be regarded as the S-oxide of sulfine **3**, it is instructive to inquire whether the replacement of the sulfur lone pair in the latter by -O leads to any fundamental changes in the electronic nature of the reaction. The CNDO/B energy barrier for sulfine cyclization is 16 kcal/mol,[10] whereas that for the corresponding sulfene closure is computed to be considerably higher, 26 kcal/mol. While the absolute values cannot be taken seriously, the relative barrier heights are reflected by well-defined changes in MO energies for reactions iii and iv.

The dashed lines of Figure 3 depict the consequences of oxidizing either sulfine **3** or oxathiirane **4** for several high-lying occupied MO's.[30] For each of the correlatable levels there is a significant drop in energy. To a first approximation introduction of the electronegative oxygen serves to lower the energy of comparable orbitals by an amount proportional to the change in the coulomb integral at sulfur. The more positively charged sulfur, or alternately the S–O unit, binds the associated electrons to a greater degree than the unoxidized sulfine sulfur.

Oxide formation ($R_nX: \rightarrow R_nX^+{-}O^-$) alters the overall composition of the MO manifold near the frontier gap by introducing new π-type and lone-pair levels. Relative to sulfine, sulfene is thus enriched by the nearly degenerate and relatively low energy antisymmetric n_{OSO} and π_{OO} orbitals of Figure 3. By contrast the orbitals in α-sultine **2** with no directly comparable counterparts in oxathiirane **4** are the two highest lying levels corresponding to delocalized nonbonding oxygen lone electron pairs (n_{O/e_a} and n_{O/e_s}).[31] The appearance of the latter is a straightforward consequence of adding oxygen-bearing nonbonding electrons to cycle **4**. The origin of the new MO's in sulfene is apprehended by referring to the situation for the π set in Figure 4. On the left side of the diagram thioformaldehyde and a single oxygen atom are brought together to produce the two allyl-like MO's of sulfine. On the right we start with three localized electron distributions, two of which arise from the symmetry-adapted oxygen p–π pair. The symmetric $\pi_{OO}(S)$ level combines with π_{CS} of thioformaldehyde leading to π_1 and π_3 of sulfene. The new MO is thus $\pi_{OO}(A)$. It should be noted that in Figure 4 no explicit consideration is given to the inductive effect of the added oxygens. In a similar manner the in-plane oxygen lone pairs interact with the σ framework of $H_2C{=}S$ to yield the three sulfene MO's $n_{OO}(S)$, $n_{OO}(A)$, and $n_{OSO}(A)$ (cf. Figure 3). The latter is the extra orbital relative to sulfine.

The remaining point concerns the way in which the MO's transform as sulfene and α-sultine are converted into one another. For symmetric systems exemplified by reactions i and ii, the antisymmetric π-HOMO's of the open species are deformed in textbook fashion into the σ-MO associated with the newly created bond in the three-membered rings, a π–σ cor-

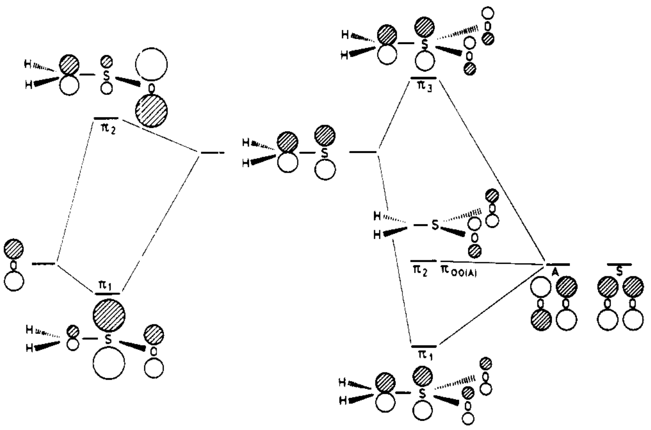


Figure 4. The PMO generation of π-MO's for sulfine 3 and sulfene 1 by the addition of one and two oxygen atoms respectively to thioformaldehyde.

relation. For the unsymmetrical sulfine **3** we have previously suggested that the π-HOMO becomes the p–π sulfur lone pair in **4**.[11a] Sulfene **1** within the CNDO/B framework exhibits yet another variation as indicated by the full lines on the right side of Figure 3. Thus the π-HOMO is reshaped as the high energy sulfoxide oxygen lone electron pair, a π–n correlation. Comparison of the sulfine/oxathiirane and sulfene/α-sultine HOMO and near-HOMO correlations (Figure 3) reveals that the former are energy releasing while the latter are energy consuming. It is tempting to speculate that the calculated barrier differential of 10 kcal/mol for cyclization of **1** and **3** owes its origin to this inverted behavior. In any case the relationship of reactions i–iv would appear to be superficial at the level of MO interchange, a conclusion supported by the theoretical behavior of other hetero systems isoelectronic with the allyl/cyclopropyl anion couple.[15]

Hoffmann and co-workers have studied the ring opening of ethylene episulfide (reaction ii) and that of the corresponding three-ring sulfoxide and sulfone by EH.[17] Whereas for ii there is a clear-cut preference for controtatory interconversion, monooxidation leads to the prediction that the disrotatory path becomes competitive. Dioxidation to the sulfone is accompanied by a crossover so that disrotation is indicated. No mention of the orbital correlation patterns as a function of oxygen content was made.

Sulfene from Singlet CH_2 and SO_2

The dimerization of singlet methylene involves the union of two high-energy fragments across a non-least-motion potential-energy surface.[13] The lone electron pair of one CH_2 is initially directed at the empty p orbital of the other; the planes subtended by each three-atom unit are nearly perpendicular (Figure 5a). The exothermic reaction ultimately produces planar ethylene.

The replacement of one CH_2 by SO_2 introduces a second fragment with both σ and π electrons. Furthermore the σ-sulfur electrons of SO_2 are delocalized considerably as a result of their mixing with the oxygen lone pairs. Although in principle SO_2 may attack the empty p-AO of CH_2 (Figure 5b) or CH_2 may impinge on the π system of SO_2 (Figure 5c), the latter can be discounted on the basis of the high degree of electron–electron repulsion to be encountered in such a transition state. The calculations described below reflect fully this expectation. The former σ-SO_2/p-CH_2 pathway is of interest relative to CH_2 dimerization since the presence of either the SO_2 π system or the diluted sulfur lone pair might make unanticipated stereoelectronic demands on the transition state.

Both the CH_2/CH_2 and CH_2/SO_2 combinations have been explored with CNDO/B as synopsized by the geometric variables of Figure 2a. At an RAC separation beyond 2.1 Å, the potential surfaces are rather flat. Full optimization is achieved only at great expense. Thus we restricted our comparison to the more important bond-forming portion of the reactions. Table I lists optimized parameters for both hyperplanes. Neither reaction exhibited an activation barrier.

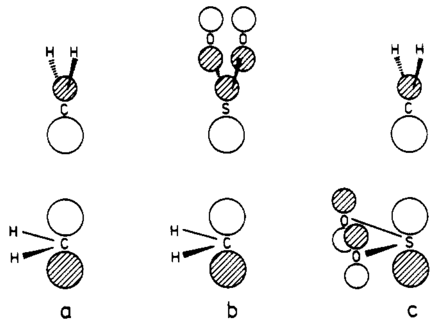


Figure 5. Possible initial reaction geometries for the combination of $^1CH_2$ and SO_2 to give ethylene (a) and sulfene 1 (b and c), respectively. The σ orbitals represent the HOMO for $^1CH_2$ and the highest energy, in-plane lone electron pair for SO_2. The p–π MO's correspond to the LUMO and HOMO for $^1CH_2$ and SO_2, respectively.

Table I. The Dimerization of Singlet CH_2 and the Combination of CH_2 and SO_2 as Prescribed by Figure 2a (Å, deg)

	RAC	RSO	γ	∠HCH	θ	ϕ
CH_2/CH_2	∞		104.4	104.4		
	2.30		104.6	104.6		
	2.00		108.6	105.1	0.6	83.7
	1.80		110.0	109.4	1.7	73.1
	1.60		121.2	121.2	0.0	0.0
	1.45		117.1	117.1	0.0	0.0
	1.376		114.9	114.9	0.0	0.0
CH_2/SO_2	∞	1.517	115.7	104.4		
	2.20	1.517	115.7	104.4		
	2.00	1.520	118.5	107.7	2.1	65.4
	1.90	1.530	121.1	113.3	2.6	54.3
	1.80	1.552	126.2	118.0	2.1	29.5
	1.72	1.567	128.6	116.9	0.0	0.0
	1.640	1.577	128.9	114.2	0.0	0.0

The overall non-least-motion paths for ethylene and sulfene production are quite similar as are the changes in the total charge distribution. In both cases the fragment serving as AB_2 sacrifices electrons to CH_2 until the point at which ϕ falls below 90°. Through the $\phi = 90 \rightarrow 0°$ phase the electron flow is reversed until the final balance is established. A similar two-stage charge adjustment was computed for the thermal cheletropic decomposition of diazirine.[32] The calculated electron transfer is in complete accord with a description of the reactions in PMO terms as shown in Figure 5a,b. As soon as the orthogonality of the virtual π-type orbitals on the attacking nucleophile and the σ lone pair of the electrophilic CH_2 is broken ($\phi < 90°$), the latter are capable of back donation and initiation of ultimate bond formation. It should be mentioned that the planar least-motion route to sulfene from CH_2 and SO_2 has also been examined. In agreement with quantitative and qualitative precedent, frontier orbital crossing appears as a signal of the energetic expense of this forbidden approach pathway.

The level correlation diagrams for our model processes are likewise similar (Figure 6). In particular the HOMO lone pair of methylene is smoothly transformed into the C–C and C–S π orbitals, respectively. This is depicted graphically for CH_2/SO_2 in Figure 7. At the start of the reaction the SO_2

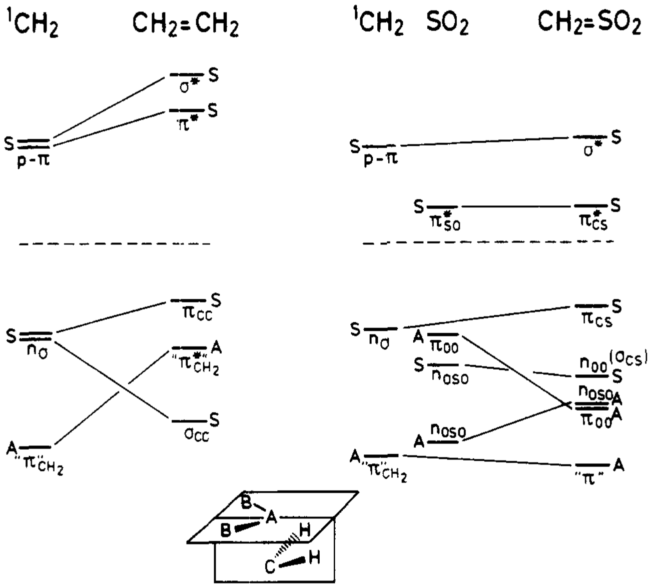


Figure 6. Level correlation diagrams (CNDO/B) for the non-least motion formation of ethylene and sulfene 1 from $^1CH_2/^1CH_2$, and $^1CH_2/SO_2$, respectively; cf. Figure 2a for the pathway definition and Figure 7 for deformation of the HOMO during sulfene formation.

moiety is devoid of electron density. Formation of the C–S bond is accompanied by rotation of the CH_2 group such that the original carbon sp^2 component is molded into a pure p contribution. Simultaneously the electron density at H vanishes while that at SO_2 grows in.[33]

In the CH_2/CH_2 reaction the second methylene electron pair (i.e., AB_2) is carried into the σ_{CC} orbital of $CH_2{=}CH_2$. The SO_2 lone pair (n_{OSO}) experiences an equivalent fate since it correlates with the sulfene level exhibiting mixed σ_{CS} and n_{OO} character. The other MO change of interest is connection of the nonbonding SO_2 π_{OO}-HOMO with its counterpart in sulfene (π_{OO}(A)). Thus both the hydrocarbon and heteroatom reactions are comparable in their essential details. No special electronic effects appear to arise from the substitution of SO_2 for CH_2 in the combination process supporting the suggestion that sulfene is experimentally accessible by this route.

Before leaving this section it is necessary to point out the existence of some fairly serious discrepancies between the CH_2 dimerization trajectory constructed here and that derived from an extended Hückel treatment.[13] First and foremost bond formation with CNDO/B occurs at very short C–C distances over a relatively compressed reaction coordinate (1.38–2.1 Å). The comparable EH values span the range 1.38–4.0 Å. Secondly the deviation of the unconstrained CH_2 from the x axis of Figure 2a is slight as reflected by ϕ_{max} = 1.7°. Again EH allows for a looser approach of the methylenes ($\phi_{max} > 35°$).[34] We attribute these differences to the inclusion of closed-shell repulsion effects via overlap in EH and its neglect in CNDO/B and other ZDO semiempirical schemes.[35,36] Thus the CH_2/CH_2 and CH_2/SO_2 transition states are calculated to be somewhat tighter than is undoubtedly the case in reality. This observation in conjunction with the above remarks concerning the reliability of the reaction coordinate technique forces us to place no quantitative significance on the geometric relationships of Table I. It is expected, nonetheless, that the computed hyperplanes mirror relative qualitative elements of the reactions under scrutiny.

A final point concerns the relative energy of the CH_2 on SO_2 vs. the SO_2 on CH_2 approaches indicated by Figure 5. For fixed geometry[38] fragments a calculation was performed for S–C distances ranging from 1.5 to 3.0 Å. At the lowest energy separation (ca. 1.75 Å) the SO_2 on CH_2 arrangement proved to be more stable by 13 kcal/mol in agreement with the energy-optimized pathway.

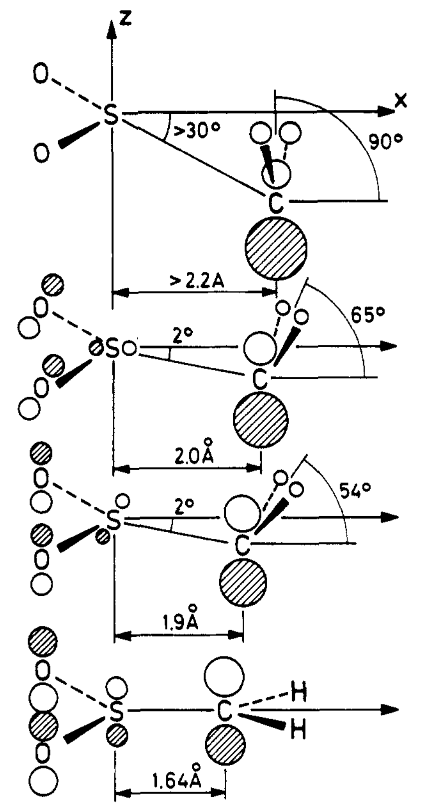


Figure 7. Transformation of the $^1CH_2$ HOMO lone pair to the sulfene π-HOMO as sulfene is formed from its fragments (CNDO/B); cf. Figure 6 for the full orbital correlation diagram.

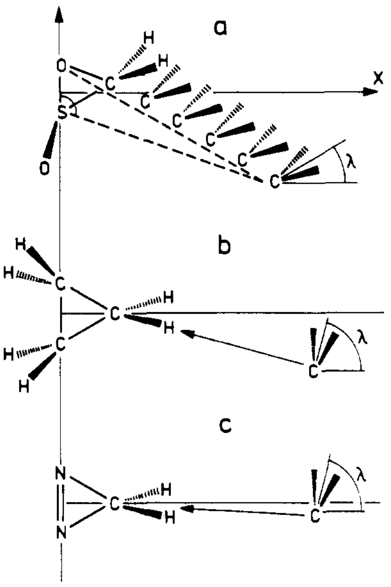


Figure 8. Pathway characteristics (CNDO/B) for the cheletropic addition of $^1CH_2$ to SO_2 (a), $CH_2{=}CH_2$ (b) and N_2 (c).

Addition of $^1CH_2$ to the OS=O Bond: α-Sultine

The coordinate space for α-sultine formation is depicted in Figure 2b. Optimization of the reaction pathway produced the instantaneous atomic positions indicated by Figure 8a. Variables β and λ are the essential quantities for determining the overall spatial disposition of the combining moieties.

Comparison of the results of the present study with the addition of $^1CH_2$ to $CH_2{=}CH_2$ (EH[14]) and N_2 (CNDO/B[32])

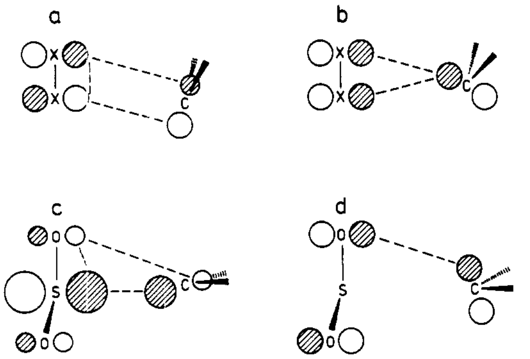


Figure 9. The frontier orbital description of the transition states for the allowed addition of $^1CH_2$ to a symmetric unsaturated functionality (X=X) and to the S=O bond of SO_2. Parts a and b depict $^1CH_2$(HOMO)/X=X(LUMO) and $^1CH_2$(LUMO)/X=X(HOMO), respectively. Parts c and d illustrate the $^1CH_2$(HOMO)/SO_2(LUMO) and $^1CH_2$(LUMO)/SO_2(HOMO) interactions, respectively. The orbital relationships are also useful for analyzing the transition states by the Hückel–Möbius method.

shows a significant although not fundamental difference. In the latter two cases λ varies from a maximum of 80–85° to a minimum of 0° (Figures 8b and 8c, respectively), whereas in the SO_2 addition it is found in the narrow range of 16–22°. In order to ensure that the computed differences are not the result of CNDO/B's tendency to produce early transition states, the $^1CH_2/CH_2{=}CH_2$–cyclopropane reaction was repeated with this parametrization and found to satisfactorily mimic the EH profile.[39] All three reactions can be analyzed quantitatively by considering the interaction of the frontier orbitals of the combining fragments. In Figure 9 (a and b) are shown the CH_2(HOMO)/X=X(LUMO) and CH_2(LUMO)/X=X(HOMO) interchanges, respectively. The non-least-motion paths are dictated by the requirement that the fragment orbitals of appropriate symmetry overlap as bonding sets in. Seen from the viewpoint of Dewar and Zimmerman,[27b,c] the X = N, CH_2 reactions involve four electrons in the transition state. The thermally "allowed" route demands an antiaromatic or a Möbius complex and necessitates a single orbital sign change (Figure 9a).

The parallel situation for union of SO_2 and CH_2 is depicted in Figure 9 (c and d). It should be noted that the replacement of the symmetrical X=X with SO_2 causes considerable change in the frontier density of the carbenophile. In particular in the LUMO of X=X the node is symmetrically disposed, while in SO_2 it lies much closer to oxygen. The result is that the sulfur contribution dominates the lowest virtual level of sulfur dioxide. Likewise the symmetry shown by the HOMO of X=X is lost completely by comparison with the S=O bond. The contribution of sulfur is exactly zero here. These differences mean that the lone electron pair of $^1CH_2$ will be directed strongly at sulfur along the approach trajectory in order to achieve maximum orbital overlap (Figure 9c). The diminutive λ reflecting the downward tilt of the CH_2 plane permits effective interaction with oxygen in both the HOMO and in the LUMO (Figure 9, c and d). A population analysis for the HOMO of the $^1CH_2/SO_2$ combination across the potential energy surface for α-sultine formation indicates that, although a considerable degree of asymmetry obtains, the basic pattern evidenced by the $^1CH_2/N_2$ addition[32] is maintained.

Finally, although the $^1CH_2/SO_2$ cheletropic union is allowed and electronically similar to cyclopropane formation, the α-sultine is not an obligatory intermediate. Alternatives are discussed below.

Other CH_2/SO_2 Transients and Transformations

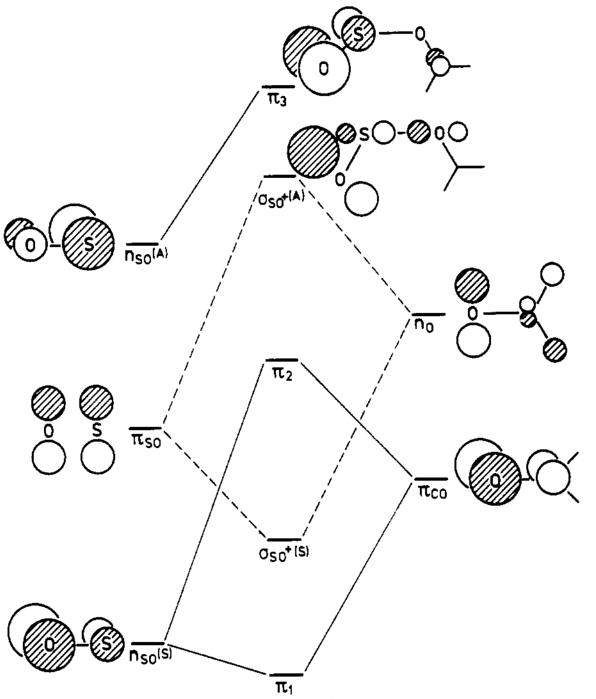
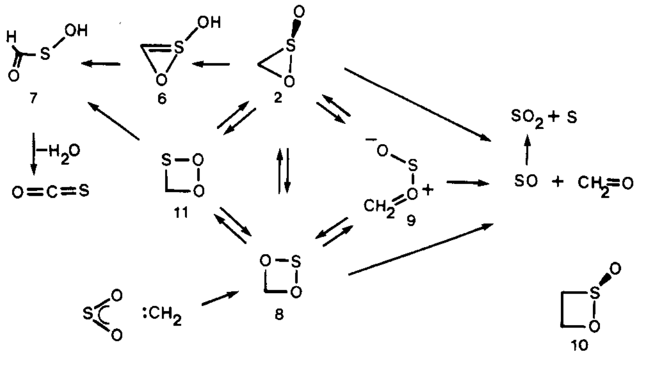


Figure 10. PMO interaction diagram for the formation of zwitterion 9 from ^1SO and $CH_2{=}O$.

Various reports on the intermediacy of α-sultine 2 offer two alternatives for its passage to products. The more popular speculation is ejection of SO to give the corresponding ketone or aldehyde.[4b,5] Singlet SO ultimately appears as SO_2, S_n, and polymer. A second decomposition route for 2 has been suggested to lead through species 6 and 7 and finally to carbonyl sulfide.[7]

Scheme I sketches three additional possibilities which have not been considered previously. The α-sultine might rearrange to the cyclic sulfoxylate ester 3 (1,3,2-dioxathietane) or undergo electrocyclic ring opening to the zwitterionic species 9. Both transformations of 2 are favorable from the point of view of strain release. Of particular interest cyclic sulfoxylates are known as stable compounds in larger rings.[40] Furthermore, although the sulfinate ester → sulfoxylate ester interconversion is not known, the reverse process has been observed.[41] CNDO/B suggests the energy gain from 2 to 8 to be 37 kcal/mol. The acyclic dipolar species 9 in principle is accessible from both 2 and 8; however, it is calculated to be thermochemically less stable than either of the cyclic isomers by 45 and 82 kcal/mol, respectively. Part of the energy difference undoubtedly resides in the well-known CNDO/INDO underestimate of strain in small rings, a quantity of 10–20 kcal/mol.[42] Significantly zwitterion 9 is likewise energy rich relative to ^1SO and $CH_2{=}O$ (ΔE = 40 kcal/mol). An attempt to optimize the geometry of 9 resulted in a smooth stretching of the central S–O bond to give the latter fragments. No energy barrier was encountered. The computed lability of 9 can be

Scheme I



appreciated by reference to Figure 10 which pictures selected MO's in the PMO formalism.

The three highest lying occupied levels are all strongly antibonding. To a first approximation species **9** can be regarded as π isoelectronic with the butadiene dianion. For the latter the HOMO is the symmetrical π_3 with bonding between C_2 and C_3 but antibonding at the termini. In the unsymmetrical system **9**, the central node of the HOMO has moved in the direction of O^+ causing the bonding element to vanish. The next π level, π_2, likewise possesses a node between S and O^+. Finally the second highest lying level, the antisymmetric combination of the in-plane π(SO) and the oxygen lone electron pair of formaldehyde, is σ antibonding between the same atoms. The sum of the destablization associated with π_3, π_2, and σ_{SO^+} in **9** may be taken as the factor responsible for the barrierless dissociation to ^1SO and $CH_2{=}O$. Seen from the viewpoint of the latter species, the situation is much like the combination of a pair of He atoms. The first-order closed-shell repulsion between the filled orbitals dominates the fragment complex and is overall antibonding.

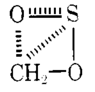
In view of this analysis we conclude that zwitterion **9** is most likely not involved in the further transformation of either **2** or **8**. Were **2** to begin to react by the electrocyclic pathway with initial cleavage of the CH_2–SO bond, the approach to the transition state would probably reflect the instability of **9** and thus lead to simultaneous O^+–SO rupture at the energy maximum. All in all an unsymmetrical cheletropic release of ^1SO seems to be the most suitable way of viewing the fragmentation of the α-sultine. There is ample precedent for this process.[43]

An equally attractive alternative and perhaps thermochemically preferred option is the rearrangement of **2** to **8** followed by a $({}_\sigma 2_s + {}_\sigma 2_a)$ cycloreversion to ^1SO and $CH_2{=}O$. Unsymmetrical heteropericyclic reactions often occur with reduced energy requirements relative to the symmetrical carbon analogue. And in certain cases where asymmetry creates a severe enough perturbation, the stereochemical distinction between various paths may be lost, all possible pathways being allowed and energetically competitive.[11a,15,44–46]

This appears to be the case for β-sultines **10** which fragment with a diminutive energy barrier[47] and with the capability for an in-plane $({}_\sigma 2_2 + {}_\sigma 2_s)$ dissociation.[28] Heteroelectrocyclic ring opening reactions likewise reflect both the energy reduction[48,49] and the stereochemical features[46,49] of perturbed processes. For this reason we have explored the unoptimized potential surfaces for both isomerization of α-sultine **2** to sulfoxylate **8** and fragmentation of the latter by an in-plane pathway. Conversion of **2** → **8** is calculated to cost 42 kcal/mol. The corresponding orbital correlation diagram shows that the filled MO's of starting material and product transform smoothly into one another indicative of an allowed, concerted process. The planar breakdown of sulfoxylate **8** to ^1SO and formaldehyde is accompanied by a frontier orbital crossing characteristic of a forbidden mechanism.[25] By implication the suprafacial–antarafacial route is preferred. Given the high content of heteroatoms in **8**, the concerted path may nonetheless occur easily relative to other possible pathways. In any case the high temperatures at which β-sultine **2** is postulated from certain precursors[4b,5] appear sufficient for promoting the **2** → **8** → $^1SO/CH_2{=}O$ sequence.

Both the latter and the cheletropic loss of ^1SO from α-sultine **2** appeal to us as energetically more feasible than enolization to the antiaromatic thiaoxirene **6** as suggested by Hiraoka.[7] The CNDO/B calculation places the thermochemical stability of this species at a value comparable with zwitterion **9**. The work which led to the postulation of intermediate **6** utilized photochemical and electron impact methods which might have generated a vibrationally or an electronically excited sultine. While it is difficult to comment on the fate of the latter, our calculations suggest that vibrational deexcitation to the energetic thiaoxirene system is not particularly competitive with other energy dispersal alternatives. The motivation for proposing **6** was the persistent appearance of carbonyl sulfide from the photolysis of sulfene precursors. Other mechanisms, however, can be written to accommodate this result.

For example, α-sultine **2** might rearrange to the 1,2,3-dioxathietane (**11**) followed by a hydrogen shift–ring opening step to give *S*-hydroxythioformic acid **7**. The ring expansion of **2** to **11**, unlike **2** → **8**, exhibits a frontier orbital crossing within the CNDO/B formalism. Significantly the latter passes through a three-center transition state with two lone pair bearing heteroatoms (**12**), whereas the energy maximum for the former contains three heteroatoms (**13**).



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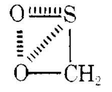
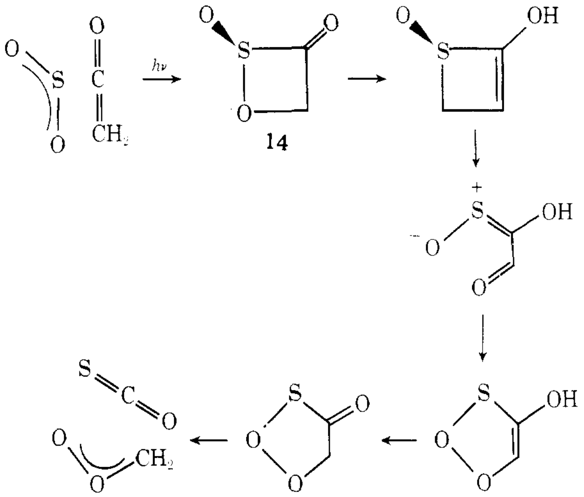


13

As we have pointed out previously,[15] pericycles with an excess of nonbonding electrons tend to express themselves via correlation diagrams reflecting nearly avoided crossings. A cheletropic example is considered in the next section. The presence of several heteroatoms may, however, facilitate a lowered energy barrier as mentioned above by effecting the necessary state mixing required for a "feasible" reaction.[50]

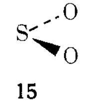
An additional alternative to the formation of small amounts of SCO obtained by irradiation of mixtures of ketene and SO_2[7] is the following. The initial reagents may cycloadd to give the 2,3-oxathietan-3-one-2 oxide **14** and transform as indicated



to ultimately produce carbonyl sulfide and the Criegee intermediate. Each of the steps finds a close analogy in related reactions.

The Cheletropic Addition of $^1CH_2$ to SO_2

The formation of sulfoxylate **8** by the cheletropic addition of $^1CH_2$ to SO_2 is shown in Scheme I. Since this appeared to be an attractive mechanistic route to COS via **8**, **11**, and **7**, and because to our knowledge simple carbenes are not known to participate in cheletropic ring formations to give four-mem-



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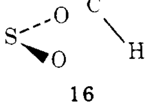

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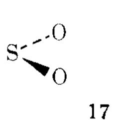
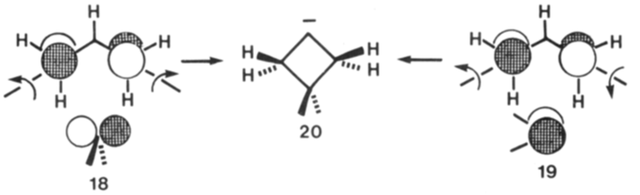


17

bered cycles,[51] several reaction trajectories for the $^1CH_2/SO_2 \rightarrow$ **8** combination were examined with CNDO/B. These are indicated by structures **15–17.** Each of the explicitly computed reactions proved to exhibit a frontier orbital crossing.

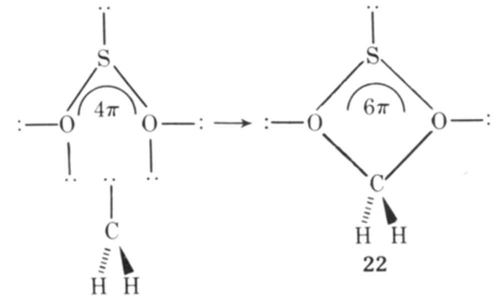
The situation is illuminated by first referring to the isoelectronic carbon system, the allyl anion, $^1CH_2$, and the cyclobutyl anion **20.**

Thermal combination of $^1CH_2$ and $(CH_2CHCH_2)^-$ by a least-motion path (**18**) obeys the orbital symmetry conservation principle provided the allyl anion undergoes a disrotatory deformation. Structure **18** indicates the appropriate combination of anion–HOMO and $^1CH_2$–LUMO. Similarly the non-least-motion trajectory (**19**) is acceptable, if the allyl anion reacts by a conrotation. Thus, as pointed out by Woodward and Hoffmann,[26] the two approaches of $^1CH_2$ are complementary and coupled to stereochemically distinct changes at the $C_3H_5^-$ termini. Equally important, the ability of the allyl anion to rotate during reaction breaks the σ–π separation and allows the π-HOMO to be transformed into σ_{CC} in the cyclobutyl anion, a σ–π correlation.



18 **20** **19**

A consideration of the $SO_2/^1CH_2$ case clearly shows that although the system is isoelectronic with the carbon structures, the possibility for achieving a thermally allowed reaction path does not exist. Lewis type structures for the hetero process are shown by **21** and **22.**



21 **22**

The fragment π orbitals (**21**) contain four electrons, the σ, six nonbonding pairs. In the planar product sulfoxylate **22,** the π system has six electrons, whereas the corresponding σ count is three nonbonding pairs and two C–O σ bonds. The comparison is unchanged by allowing the four-membered ring to assume a puckered conformation. Formally starting material and product differ by the double excitation of a nonbonding electron pair from **21** to **22.** That is, they correspond to different electronic configurations. Although a similar description applies to the carbon species **18–20,** a mechanism is available whereby the costly excitation is bypassed, namely rotation about the CH–CH_2 bonds during ring closure. The terminal hydrogen nuclei move through space and simultaneously carry the electrons in the C–H bonds from the σ to the π framework. The net result is a configurational type interchange.

The SO_2 moiety lacks such a mechanism. By virtue of the σ–π separation inherent in the MO formalism, the in-plane lone pairs are unable to "rotate" into the system of **22** during the cheletropic addition. Consequently, since neither the linear (**15, 16**) nor the nonlinear (**17**) trajectories are coupled to an orbital transposition on SO_2, all reaction paths are forbidden[25] and require state mixing for a successful traverse of the path from $^1CH_2/SO_2$ to **22.** This is an example of a general class of reactions with an "excess" of nonbonding electrons. The point at which allowed routes are prohibited arises when the number of lone pairs replacing hydrogens prevents the ground state configurational mixing described above for the allyl anion. Another case would be the cycloaddition of formaldehyde and singlet O_2.[52]

Acknowledgment. We are grateful to the Danish Natural Science Research Council for generous financial support.

Registry No.—1, 917-73-7; **2,** 65621-95-6; **3,** 40100-16-1; **4,** 53283-22-0; $^1CH_2$, 2465-56-7; SO_2, 7446-09-5.

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(34) In our coordinate system the CH_2 (or SO_2) nucleophile is positioned at the origin, whereas in the previous work[13] the electrophilic partner was so fixed.

(35) It has been shown that the neglect of overlap required by the ZDO theoretical framework can favor biradicaloid over synchronous transition states[36] and result in serious underestimation of nonbonded lone pair–lone pair repulsions.[37] For example, CNDO/2 and INDO produce weakly repulsive or attractive potential energy curves for the direct interaction of lone electron pairs. Application of the "water test"[37] (orthogonal approach) to CNDO/B results in a properly repulsive potential at all oxygen separations; nonetheless at 1.5 Å the destablization energy is 5 eV compared with 11 eV for EH. The corresponding 4-31G value is 8.8 eV.

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Diazenium Cations. 3. Formation and Oxidation of a *cis*-Trialkylhydrazine: *cis*-Azomethinimines[1]

James P. Snyder,* Michael Heyman, and Maryanne Gundestrup

Department of General and Organic Chemistry, University of Copenhagen, The H.C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

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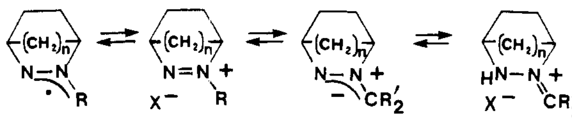
Isopropyl-substituted bicyclic diazenium cations i are readily isomerized via ylides iv to the corresponding *exo*-methylene iminium salts iii. Thus, in the presence of nucleophiles both are potential precursors to the little studied *cis*-trialkylhydrazine system. Treatment of either i or iii with CN^- under an inert atmosphere causes attack at carbon and leads to the corresponding oxygen-labile hydrazine. Facile air oxidation presumably generates a trialkylhydrazyl radical which ultimately results in production of azoalkane **6** and the tetrasubstituted cyanohydrazine **7**. Evidence is presented to show that **6** arises via an intermediate azomethinimine (**10c**) followed by protonation and subsequent dealkylation. The bicyclic hydrazine **7** is formed from a second intermediate, diazenium cation **11**, which experiences CN^- attack at nitrogen. The presence of an ylide intermediate is substantiated by demonstrating that azomethinimines iv are easily generated from a new series of both salts i and iii. Although in most instances the 1,3 dipoles were only trapped, isolation succeeded for a diphenyl derivative.

The recent isolation of bicyclic diazenium cations i has permitted exploratory studies of the chemistry of this many faceted function. Derivatives with R = H and alkyl show charge-transfer behavior[1-3] and facile electrochemical reduction to hydrazyl radicals ii.[4] When the substituent is 2,5-dinitrophenyl, chemical electron transfer leads to a complex equilibrium of open- and closed-shell species.[2] Simple protiodiazenium cations (i, R = H) are alkylated by alcohols of all kinds and serve as particularly efficient precursors to the *tert*-butyl cations.[1,2] Substituents bearing a proton α to $=N^+<$ (e.g., R = *i*-Pr) undergo rearrangement to the *exo*-iminium salt iii.[1] The reaction can be utilized for synthesis of the latter.



ii i iv iii

In the present discussion further examples of tautomeric pairs i and iii are reported. Their utility in the generation of azomethinimines iv is described. Furthermore, the preparation of a labile *cis*-trialkylhydrazine and its facile air oxidation have been investigated.

Trialkylhydrazine Formation and Oxidation. In principle, the iminium salts iii should be capable of accepting a nucleophile at carbon to produce the corresponding *cis*-tri-

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