Tetrahedron Letters No. 23, pp 2045 - 2048, 1977. Pergamon Press. Printed in Great Britain.

PERTURBED PERICYCLIC REACTIONS: THE RETROCYCLOADDITION OF β-SULTINES.[1]

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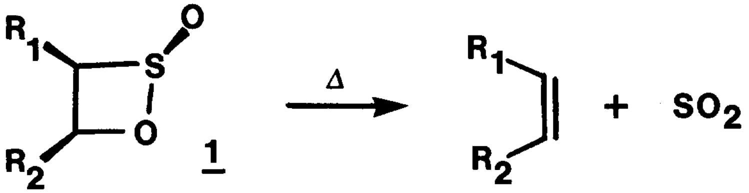
(Received in UK 13 April 1977; accepted for publication 25 April 1977)

The orbital symmetry conservation principle,[2] frontier orbital theory[3] and various derivative concepts[4,5] permit the straightforward rationalization of symmetric and near-symmetric pericyclic reactions. It appears, however, that strong asymmetrization of a concerted pathway, in particular by introduction of heteroatoms, can lead to considerably lowered energy barriers and loss of stereochemistry.[6,7] In these cases the hydrocarbon-based symmetry rules provide little assistance either as explicative or as predictive guides.

In the hope that a study of reaction abnormalities might ultimately lead to a better understanding of perturbed concerted reactions of all kinds, we have initiated a search for heteropericyclic processes with unusual features.[1,6a,8] The fragmentation of 1,2-oxathietan-2-oxides (β-sultines) falls in this category.



Thus derivatives of β-sultine 1 decompose to olefin and SO_2 below 30° stereospecifically and in high yield.[9] The rate of the reaction is, to a first approximation, insensitive to solvent polarity, while substituent effects suggest the absence of a biradical intermediate.[10] Furthermore the apparently concerted retrocycloaddition is much more facile than the stereospecific cis elimination of CO_2 and R-NCO from β-lactones[11] and β-lactams[12] respectively.

Accordingly we have investigated part of the potential energy surface for the (2 + 2) retrocycloaddition of β-sultine 1 ($R_1 = R_2 = H$) in order to learn if the strong hetero-asymmetry present is sufficient to lift the stereoelectronic requirement that fragment departure occur by a suprafacial-antarafacial pathway. The geometry of cycle 1 has been optimized by the CNDO/B parameterization.[13] The exo-oxygen is predicted to lie 62° out of the plane of the ring.[14] Experimental values were employed for the separated $CH_2{=}CH_2$ and SO_2 entities. The cycloreversion was then computed (CNDO/B) by maintaining the ring atoms in a common plane as the β-sultine was incrementally decomposed to products. Three separate motions of the exo-oxygen were considered: (i) rotation into the plane of the other heavy atoms (Figure 1a); (ii) rotation away from the CCSO plane (XY) so that the SO_2 plane (parallel to YZ) is ultimately orthogonal (Figure 1b); and (iii) maintenance of the exo-SO angle at 62°. Paths (i)-(iii) were repeated with CNDO/S,[15] a parameterization which incorporates d-orbitals on sulfur and furnishes reasonable ionization potentials.[1] Orbital correlation diagrams were constructed for the six computed reactions and each depicts a thermally "allowed" transformation: all bonding MO's are smoothly converted to bonding MO's. Thus, although we have not mapped out the minimum energy pathway for β-sultine cycloreversion, the calculations demonstrate that the highly strained $({}_{\sigma}2_s + {}_{\sigma}2_a)$ transition state is not obligatory in the present case.

The four highest occupied CNDO/S MO's of β-sultine 1 are listed in Figure 1 and their correlations via paths (i) and (ii) indicated. The HOMO and the fourth highest in energy can be recognized as mixtures of the exo-oxygen lone pair and the four-membered ring e_u MO's.[16] Were the HOMO of 1 derived from the symmetrical hydrocarbon, cyclobutane, an in-plane suprafacial-suprafacial rupture of the ring would leave two electrons in the antibonding ethylene π^*_{CC} orbital reflected by the left half of n_{O_5}/e_u (Figure 1). However asymmetry in a molecular system permits orbital components to shrink and grow as bonds are made and broken. In other words, nodal shifts can occur across the potential energy surface leading to new bonding and antiboning regions unavailable to a symmetrical array of atoms. Figure 2 depicts the situation for the deformation of the HOMO of 1 along path (i). At the outset of the reaction an antibonding relationship between C-1 and C-2 obtains. It should be noted that the corresponding node resides nearer C-2. As the fragments separate, the node moves in the direction of the latter and finally crosses it. Simultaneously the SO_2 contributions fade away. The result is the connection of n_{O_5}/e_u with π_{CC}; an unusual orbital correlation facilitating the preservation of bonding electrons in a bonding MO.

The changed orbital-component sign at C-2 is not a violation of the orbital symmetry conservation precept.[2] On the contrary it reflects a more general operation of it than ordinarily recognized. Similar orbital deformations operate for all unsymmetrical processes,[1,6a] although they become interpretively critical only for strongly perturbed reactions where unexpected stereochemical events may take place. Clearly the hydrocarbon rules,[2,3,4] the notion of orbital isomerism[5] or any other assumption concerning the integrity of orbital shape during reaction[17] are insufficient to analyze interconversions of this kind.

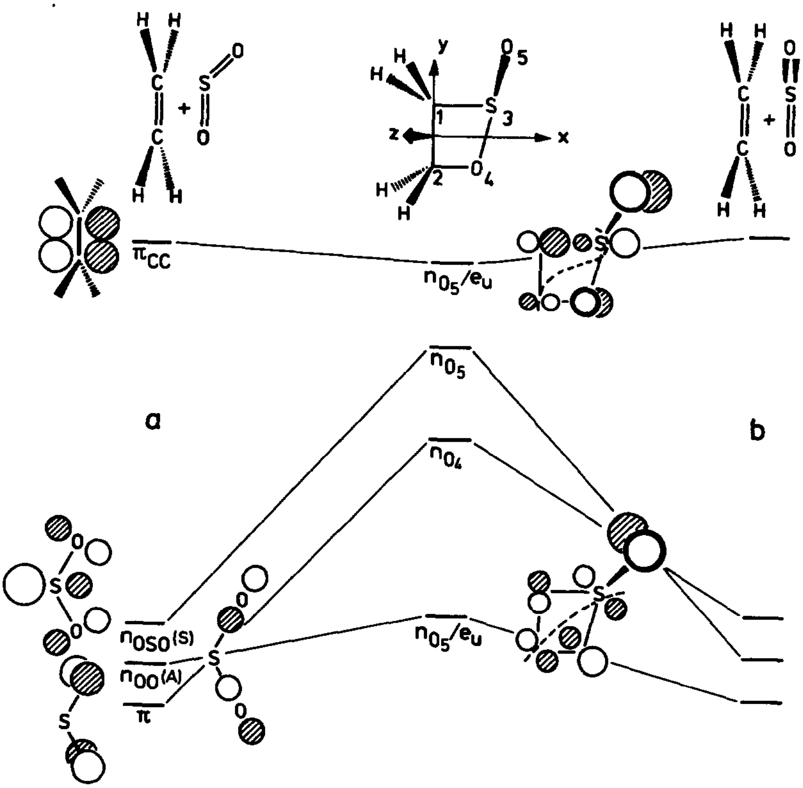


FIGURE 1. Occupied orbital correlation for the fragmentation of β-sultine 1 to $CH_2{=}CH_2$ and SO_2: a) in-plane pathway (i); b) in-plane pathway (ii).

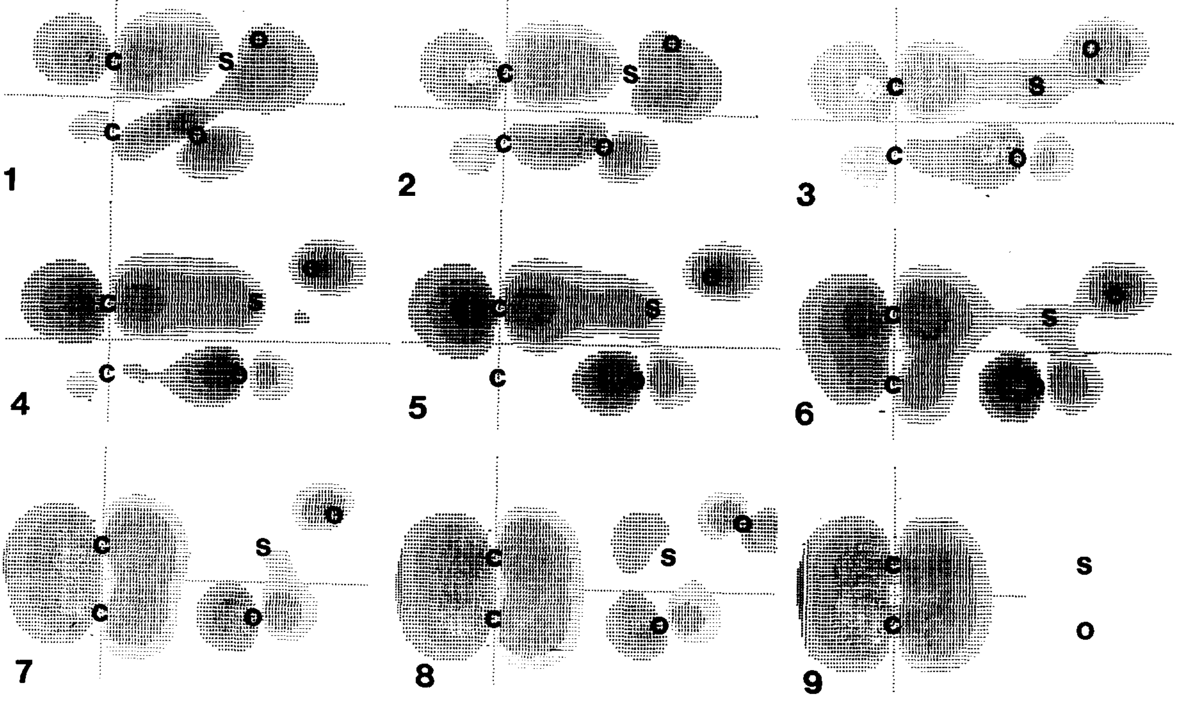


FIGURE 2. Orbital amplitude plot of the HOMO (CNDO/S) as β-sultine 1 is transformed to ethylene and SO_2 by fragmentation (i). The plane depicted is parallel to XY but displaced in the Z direction by 0.3 Å.

Acknowledgement. We are grateful to the Danish Natural Science Research Council for generous financial support. We are likewise appreciative to Professor Tony Durst (University of Ottawa) for stimulation, to Professor G. Pfister-Guillouzo (Université de Pau et des Pays de l'Adour) for a copy of CNDO/S and to Dr. Jens Spanget-Larsen (Technische Hochschule Darmstadt) for providing the orbital plotting routine (QCPE 313).

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