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ON THE MECHANISM OF STEREOSPECIFIC S(^{3}P) AND O(^{3}P) ADDITIONS TO OLEFINS

E. LEPPIN and K. GOLLNICK
Max-Planck-Institut für Kohlenforschung, Abt. Strahlenchemie,
Mülheim-Ruhr, Germany

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Stereochemical aspects of the addition of divalent species such as carbenes (1,2), nitrenes (3), oxygen atoms (4), and sulfur atoms (5) to C=C double bonds have been widely studied. While the majority of these species in their singlet states were found to add stereospecifically, triplet carbenes and triplet nitrenes almost always add in a non-stereospecific manner. Triplet sulfur atoms, S(^{3}P), however, were shown unequivocally to add stereospecifically in the gas phase (5) as well as in the liquid phase (6). In the latter experiments, S(^{3}P) in p-xylene gave rise to 100 % of trans-1,2-dimethylthiirane from trans-2-butene, and to 95 % of cis-1,2-dimethylthiirane from cis-2-butene.

According to Skell's hypothesis (7), the stereochemistry of such addition reactions is governed by the spin conservation principle. It predicts a two-step machanism for the addition of a triplet species to a C=C double bond forming a triplet diradical which after spin inversion closes to a three-membered cyclic product. In case of carbenes and nitrenes, rotation about the C-C bond of the intermediate diradical must then occur at a much faster rate than spin inversion thus leading to non-stereospecific products. In order to account for the stereospecificity in S(^{3}P) addition reactions, it was postulated that in the intermediate diradical C-C bond rotation is slowed down by the heavy S-atom which at the same time enhances the triplet to singlet spin inversion (5). Recently, this hypothesis was modified by ascribing the prevention of C-C bond rotation in this intermediate to the interaction between the p-orbital at the terminal methylene carbon and the two degenerate non-bonding p-orbitals of the sulfur thus forming a σ-π hybrid bond (8).

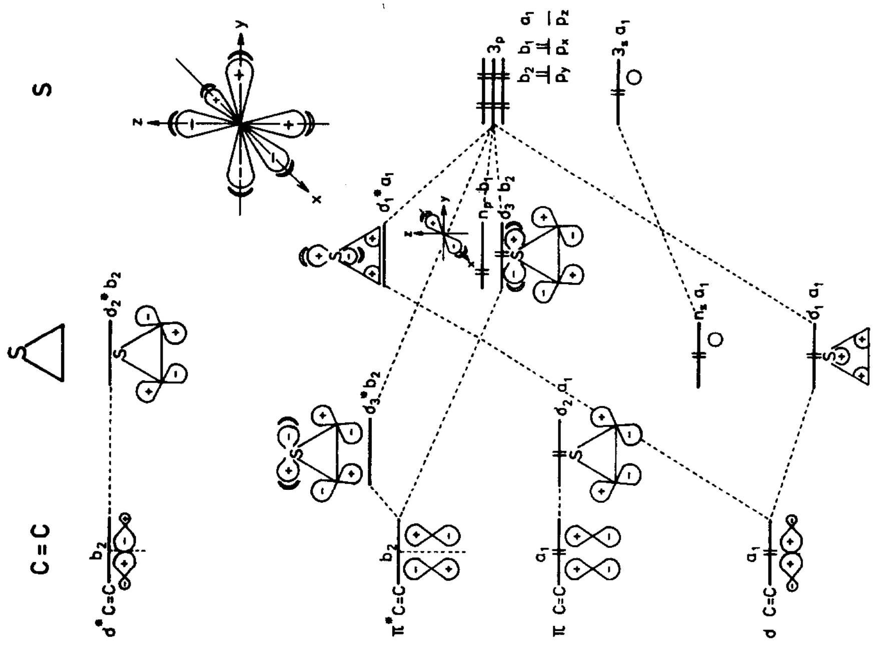

Fig.1: Molecular Orbital Energy Diagram for Thiirane (Symmetry: C_{2v})

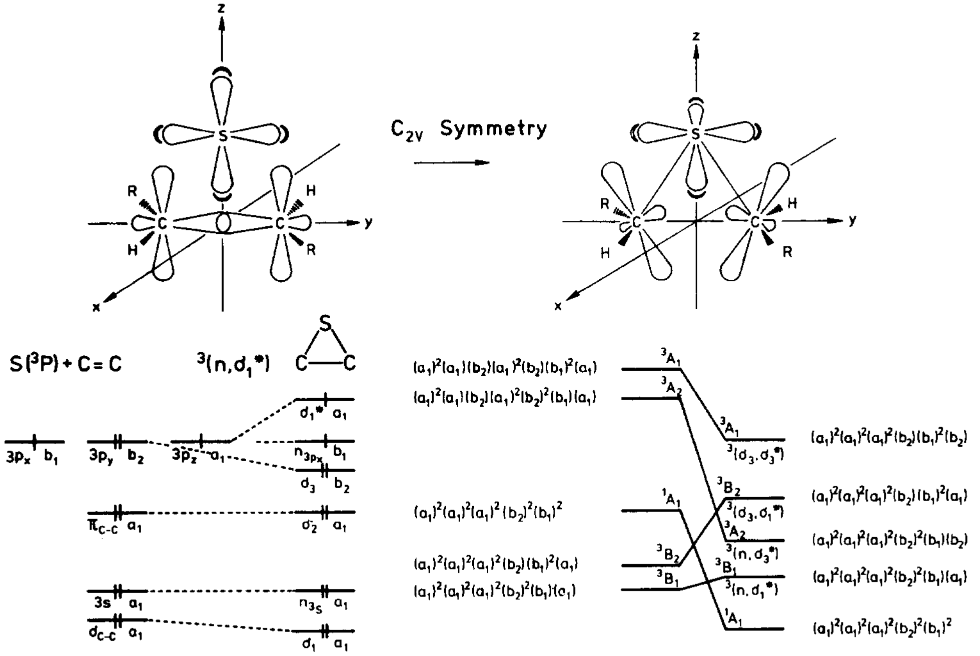

Fig.2: a) Molecular Orbital Correlation
b) State Correlation Diagram*) for Addition of S-Atoms to Ethylene

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*) The excited singlet states corresponding to the four triplet states are derived from interactions of $S(^1S_0)$ with ground state and excited ethylene.

Recently, delocalized σ-orbitals proposed by Walsh (9) many years ago were shown to be much better suited than localized orbitals for describing cyclopropropane in its ground and excited configurations resulting from singlet and/or triplet methylene addition to (singlet ground-state) ethylene (10,11). There are then six Walsh orbitals, σ_1, σ_2, σ_3 and σ_1^*, σ_2^*, σ_3^*, together with two nonbonding orbitals of the sulfur atom needed to describe the thiirane molecule. According to Fig. 1*), the lowest excited configuration of thiirane results from a promotion of a n_p electron of sulfur into the σ_1^* orbital. This $n_p \longrightarrow \sigma_1^*$ transition is symmetry-allowed but should have only a small transition moment in the x-axis. The next three transitions are $n_p \longrightarrow \sigma_3^*$ (symmetry-forbidden), $\sigma_3 \longrightarrow \sigma_1^*$ (symmetry-allowed with a small transition moment in the y-axis) and $\sigma_3 \longrightarrow \sigma_3^*$ (symmetry-allowed with a large transition moment in the z-axis).

In accord with the proposed MO scheme, the UV spectrum of thiirane (12) shows two resolved weak bands at the long-wavelength side of the spectrum followed by a strong band (the $n_p \longrightarrow \sigma_3^*$ transition is expected not to show up in the spectrum). In agreement with the designation of the longest wavelength transition as $n_p \longrightarrow \sigma_1^*$, a hypsochromic shift of about 500 cm^{-1} is observed for this band when the solvent is changed from n-hexane to ethyl alcohol (13).

If a sulfur atom approaches ethylene as depicted in Fig. 2a, all orbitals of the reactants continuously transform into the orbitals of the product. This approach is symmetry-allowed for $S(^3P)$ as well as for $S(^1D)$ (Fig. 2b). With $S(^1D)$, ground state thiirane is produced directly, while with $S(^3P)$, two intermediate triplet states of thiirane, $^3(n,\sigma_1^*)$ and $^3(\sigma_3,\sigma_1^*)$, may be formed. But only $^3(n,\sigma_1^*)$ should lead to a thiirane in which the geometry of the starting ethylene is retained, because in σ,σ^*-configurations the molecule should be rather flexible due to the removal of one bonding electron from the highest occupied Walsh orbital.

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*) The shapes and energetic positions of the thiirane orbitals agree with those obtained from a preliminary Extended Hückel calculation. The authors are very grateful to Dr. von Bünau of this institute for supplying them with these results. - Since the sulfur d-orbitals are not included in this approach, the same diagram should be applicable to oxirane; furthermore, the following discussions should also apply to oxygen atom reactions.

In contrast to S(^{3}P) which adds stereospecifically to cis- and trans-2-butene in the gas as well as in the liquid phase, O(^{3}P) adds to cis-2-butene non-stereospecifically in the gas phase at 300°K as well as in the condensed phase at 77°K; with trans-2-butene, however, a temperature-dependent stereospecificity is observed: trans-/cis-1,2-dimethyloxirane = 17 (77°K, condensed phase), and = 2 (300°K, gas phase) (14).

In order to explain the experimental results, we propose an energy profile for thiiranes (and oxiranes) as a function of the angle of twist around the C-C bond as shown in Fig. 3. Assuming that the vertical excitation energies are the same for the cis- and the corresponding trans-thiiranes (oxiranes), the energy differences between the cis- and trans-$^3(n,\sigma_1^*)$- as well as between cis- and trans-$^3(\sigma_3,\sigma_1^*)$-state molecules should equal the difference in the enthalpies of formation of the two ground-state molecules*). While twisting of the ground-state and unperturbed $^3(n,\sigma_1^*)$-state molecules should be prohibited by high energy barriers, no such energy barriers should exist for twisting of unperturbed $^3(\sigma_3,\sigma_1^*)$-thiiranes (oxiranes) as has been discussed for excited (σ,σ^*)-cyclopropanes (10). By interaction of the $^3(n,\sigma^*)$- and $^3(\sigma,\sigma^*)$-potential energy curves near the crossing points, however, interconversion of the two $^3(n,\sigma_1^*)$-state molecules becomes possible (Fig. 3) with its probability being determined by the energy separations, $E_{A,cis}$ and $E_{A,trans}$, between the twisted triplet and the cis-$^3(n,\sigma_1^*)$- and trans-$^3(n,\sigma_1^*)$-state, respectively.

Thus, in the case of S(^{3}P) addition to 2-butenes at room temperature, population of the twisted triplet state of 1,2-dimethylthiirane by thermal activation appears to be impossible from the initially formed trans-$^3(n,\sigma_1^*)$ state and only slightly to occur from the initially formed cis-$^3(n,\sigma_1^*)$ state. In the case of O(^{3}P) addition, however, $E_{A,cis}$ is obviously small enough as to allow cis ⟶ trans isomerization even at 77°K, while $E_{A,trans}$ is high enough as to prevent trans ⟶ cis isomerization at this low temperature.

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*) Evidence for distinct triplet-cis- and triplet-trans-1,2-dimethyloxiranes has been found recently (14).

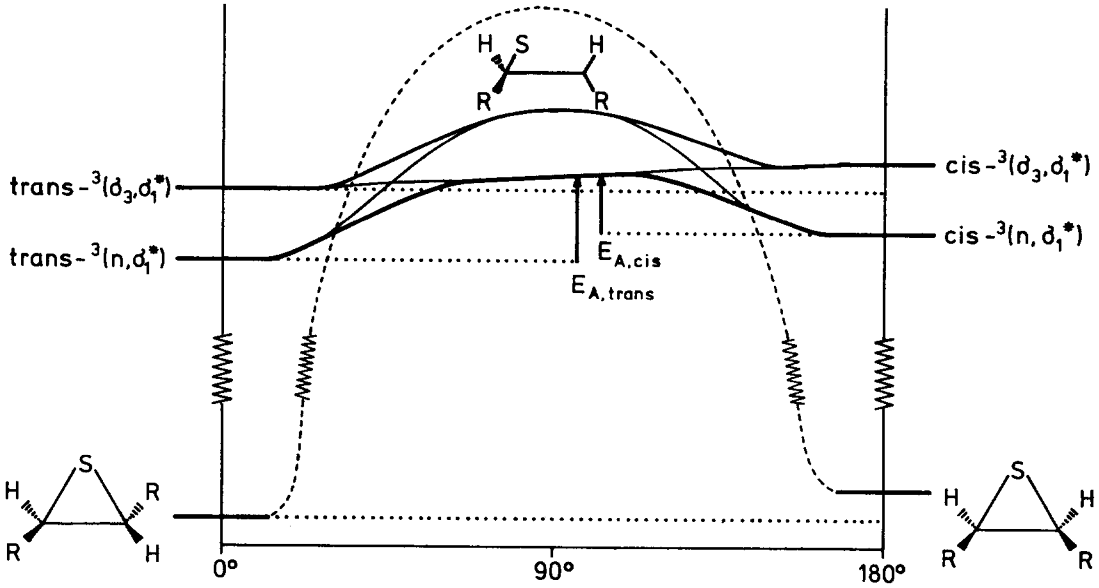

Fig.3: Energy Profile for Thiiranes as a Function of the Angle of Twist Around the C-C Bond

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