

# Following reaction paths in organic photochemistry: The special role of surface crossings

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## Abstract:

In this paper we discuss the mechanistic importance of surface crossings in various types of organic photochemical reactions which include the photocycloaddition of alkenes and the photochemistry of butadiene and acrolein. We discuss both the role of conical intersections which occur between states of the same multiplicity (most commonly singlet-singlet) and of intersystem crossings that occur between states of different multiplicity (typically singlet-triplet).

## 1. Introduction.

Many photochemical reactions are non-adiabatic (1). In these cases the reaction starts on an excited state potential energy surface and proceeds to a bonding ground state configuration, i.e. a product or intermediate, via one or more surface crossings. Surface crossings may be divided into two types corresponding to crossings between states of the same multiplicity (most commonly singlet-singlet) or between states of different multiplicities (typically singlet-triplet). The former type induces an efficient internal conversion (IC) and can be seen as a "funnel" placed on the upper potential energy surface which shuttles the system to a lower potential energy surface of the *same* spin multiplicity (see Fig. 1a). When the full configuration space of a molecule is considered, these funnels assume the form of a conical intersection which is defined by the following statement (2): two states even with the same symmetry will intersect along a  $(n-2)$  dimensional hyperline as the energy is plotted against the  $n$  internal nuclear coordinates. The location and characterization of low-lying conical intersection points appears to yield information of central mechanistic importance for photochemistry. For instance, a conical intersection point may provide access to a limited number of competing ground state relaxation pathways each one leading to a different photoproduct. The crossing between states of *different* spin multiplicity (i.e. the second type of crossing (See Fig. 1b)) corresponds to a  $n-1$  dimensional set of points where intersystem crossing (ISC) may occur and cause the relaxation of the system to a state of different spin multiplicity. However not all the singlet-triplet crossing points lead to effective ISC. In fact, the ISC rate could be very low if spin-orbit coupling (SOC) is negligible or small. Therefore, both the geometrical structure and SOC of a such crossing point need to be taken into account when evaluating the photochemical efficiency of an ISC pathway.

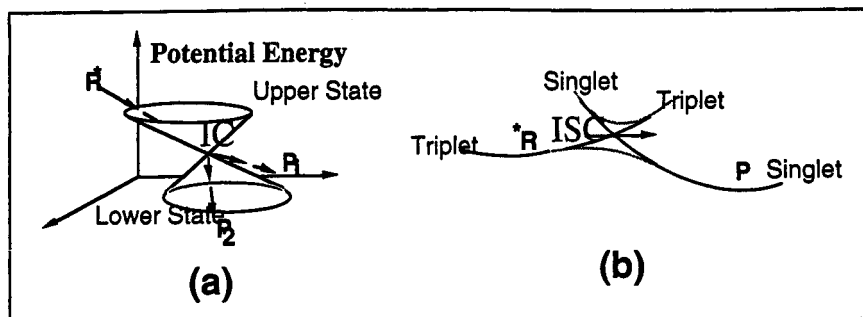


Fig.1 . Schematic representation of a conical intersection (a) and of an intersystem crossing (b).

Recently we have implemented the computational methodology to study surface crossings with the same level of accuracy that can be used to study conventional ground (or excited) state transition structure (3). In the case of a transition structure one searches, simultaneously, for an energy minimum with respect to  $n-1$  geometrical coordinates of the system and for an energy maximum with respect to the remaining coordinate. This coordinate corresponds to the *local* reaction path. In the case of a reaction involving fast radiationless decay through a conical intersection from a singlet excited state to the singlet, ground state (e.g.  $S_1/S_0$ ), one can search for an energy minimum with respect to the  $n-2$  geometrical coordinates spanning the intersection space (4). The two remaining coordinates define the so called branching space along which the  $S_1$  and  $S_0$  energies split and the degeneracy is lifted. This branching space contains all possible *local* reaction paths passing through the conical intersection. Alternatively, in triplet-sensitized reactions which usually involve triplet to ground state crossings one searches for the lowest energy point along the  $n-1$  triplet/singlet ( $T_1/S_0$ ) intersection space (5). In this case the branching space is one dimensional.

The mechanistic importance of crossing points has recently been demonstrated through an extensive computational mapping of the excited state potential energy surfaces of different organic systems. In this paper we summarize some of these computational results, which include the photocycloaddition of alkenes (6) and the photochemistry of butadiene (7) and acrolein (8). In all cases the discussion is limited to the structure of the crossing points, in particular of the conical intersections involved in these processes and to the mechanistic role of these crossing points. The three problems discussed in this paper are all characterized by a 4 electron /4 orbital  $\pi$  system, which differs either in the orientation of the  $\pi$  orbitals (comparison between ethylenes and butadiene) or in the additional presence of a lone pair (comparison between butadiene and acrolein). It will be shown that these differences determine significant changes in the geometrical/electronic structure of the conical intersections involved and in turn in the mechanism of the associated photochemical processes.

## 2. Computational details

All the calculations reported in this paper were carried out with the MC-SCF method (9) implemented in the GAUSSIAN 92 series of programs (10). The geometries of the excited state minima and transition structures are optimized using an MC-SCF gradient procedure and checked by analytical hessian. However the rigorous location of the intersection points has been performed using a nonstandard method (3) that has been implemented in a development version of the GAUSSIAN series of programs.

The MC-SCF active space chosen for the computational study of the photocycloaddition of two ethylenes and of the photochemistry of butadiene includes all  $\pi$ -orbitals and  $\pi$ -electrons of the molecular structure under investigation (i.e. a 4-electrons/4-orbitals valence space). In the study of the photochemistry of acrolein the valence space includes six electrons distributed in five orbitals originating from the  $\pi$ ,  $\pi^*$  orbitals of the C=C fragment and the  $\pi$ ,  $\pi^*$  and  $n$  orbitals of the C=O fragment.

## 3. The photochemical cycloaddition of olefins

Experimentally it is well known that olefins dimerize efficiently via both direct irradiation and sensitized photoexcitation (1). In the case of direct irradiation it has also been established that the stereochemistry of the reactant olefins is fully conserved during cyclobutane formation. In other words no *cis-trans* isomerization of the starting material takes place during the photoreaction. For example the 214 nm irradiation of *cis* but-2-ene in the liquid phase produces only *cis-anti-cis* tetramethylcyclobutane while irradiation of *trans* but-2-ene leads only to all-*trans* and *cis-anti-cis* tetramethylcyclobutane (11). This type of behaviour can only be explained by a reaction mechanism which involves a rapid radiationless decay at a well-defined point where the stereochemistry of the system cannot be lost. As we will now discuss, while the photosensitized ( $T_1$ ) photoreaction can well be understood in terms of triplet biradical intermediates, the direct irradiation ( $S_1$ ) photochemistry is explained by the presence of a  $S_1/S_0$  conical intersection.

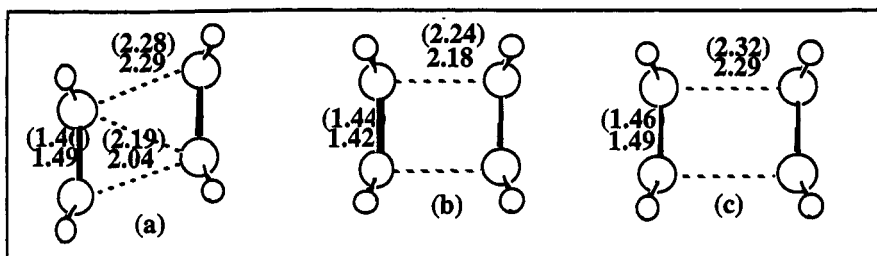


Fig. 2 CAS-SCF optimized structures for (a) the  $C_{2h}$   $S_1/S_0$  conical intersection, (b) the  $D_{2h}$  maximum and (c) the  $D_{2h}$  transition state found in the photochemical cycloaddition of two ethylenes. Values in bracket are obtained at the 4-31G level and the others at the STO-3G level.

The presently accepted mechanistic scheme for the singlet photochemical cycloaddition of two ethylenes is based on the model suggested by Van der Lugt and Oosteroff (12), which assumes a supra-supra path as the reaction co-ordinate. According to this scheme the  $S_1 \rightarrow S_0$  decay occurs at an avoided crossing between the  $D_{2h}$  minimum (**D**) of the doubly excited state ( $S_1$ ) and the  $D_{2h}$  maximum (**C**) of the ground state ( $S_0$ ) (for details see Fig.11 in ref.6b). This decay mechanism is not consistent with our MC-SCF/4-31G computations. While the full geometry optimizations carried out in the region of the avoided crossing confirms that **D** and **C** are both stationary points on the excited state surface, vibrational frequency computations show that **D** is a transition structure and **C** is a local maximum. Since the energy difference between **D** and **C** is larger than  $50 \text{ Kcal mol}^{-1}$  and **D** is a transition structure, an excited state relaxation pathway cannot really pass through **D**. The search for a true  $S_1$  minimum carried out at the same level of theory leads to two lowest energy regions of the excited state surface located far away from the supra-supra reaction co-ordinate. These regions are centred on two singularities (i.e. cusps) corresponding to upper halves of two identical conical intersections where the excited and ground state surfaces are degenerate. These intersections and surrounding regions are located at the bottom of the two valleys separated by the transition state **D** and correspond to the absolute minima of the  $S_1$  excited state surface.

Our computations suggest a mechanistic scheme which overcomes the difficulties of the previously proposed mechanism. In this scheme the photoreacting system falls down the funnels created by the conical intersections and passes almost directly to the ground state via fast IC. During this decay the stereochemistry of the olefin moiety is retained because: (i) the excited state lifetime is very short due to the presence of a conical intersection at the bottom of  $S_1$ , (ii) the conical intersection has a well defined and rigid molecular structure. This structure (which has  $C_{2h}$  symmetry) is shown in Fig. 2 where it is also compared to the structures of the "supra-supra"  $D_{2h}$  (ground state) maximum and (excited state) transition state.

The  $C_{2h}$  conical intersection arises from the crossing of the doubly excited  $(\pi)^2-(\pi^*)^2$  state with the ground state. In this structure the two interacting olefinic fragments are rigidly bound in a slightly pyramidalized but non-twisted conformation. As a consequence (in a substituted  $\pi$ -system) the system would decay to the ground state and form the four-member ring photoproduct without loss of stereochemistry. Thus, remarkably, the  $S_1$  reaction path for the photocycloaddition process appears to be very different in both geometrical structure and energetics from the proposed  $D_{2h}$  supra-supra reaction path. In fact, according to our computation, this last path seems to define a "ridge" rather than an energetically stable valley on the excited state surface. The computed reaction path is also very different from the cycloaddition reaction pathway found on the ground state. In fact, according to this pathway the thermal cycloaddition reaction involves the generation of diradical species which are structurally very different from the  $C_{2h}$  conical intersection structure seen above.

Finally, we comment briefly on triplet biradical cycloadditions. We have found two  $T_1$  biradical intermediates computed at MCSCF/DZ level of theory (see ref. 6b). These diradical structures, an *anti* and a *gauche* conformation respectively, correspond to the only equilibrium stationary points located on the  $T_1$  potential energy surface. Two corresponding *anti* and *gauche* biradical intermediates also exist on the  $S_0$  surface. The structures of the  $T_1$  and  $S_0$  biradicals are very close, however, the  $T_1$  triplet intermediates lie 20 Kcal mol<sup>-1</sup> above the corresponding singlet minima. In addition, the activation barrier for the formation of triplet biradicals on  $T_1$  (about 16 Kcal mol<sup>-1</sup>) is much smaller than that for the formation of the singlet biradicals (about 50 Kcal mol<sup>-1</sup>) on  $S_0$ . In contrast, the fragmentation barriers are 16.5 Kcal mol<sup>-1</sup> and 1.5 Kcal mol<sup>-1</sup> for the triplet and singlet biradicals respectively. In conclusion the triplet biradicals are easier to form and much more stable than the singlet biradicals. Given the facile *cis-trans* isomerization which can take place at both the CH<sub>2</sub> ends and the long excited state lifetime of the  $T_1$  biradicals, the stereochemistry of *cis* and *trans* olefins is not in general retained in the final ground state product (1).

#### 4. The photochemistry of butadiene.

Direct irradiation of butadienes yields a mixture of photoproducts which includes *s-cis/s-trans* isomers, double-bond *cis/trans* isomers, cyclobutenes, bicyclobutanes and 1-methyl cyclopropene (1,7). The proposed reaction paths associated with each observed photoproduct are, in general, very different since their formation involves geometrical changes which are dominated by different geometrical parameters. For instance, the accepted mechanism for cyclobutene formation is that proposed by Van der Lugt and Oosterhoff (12) where the  $S_1 \rightarrow S_0$  decay occurs from an avoided crossing minimum. Similar mechanistic schemes may be proposed for the other photochemical transformations of butadiene.

The singlet states involved in these transformations are the  $S_1$  state ( $1^1B_u$ , single excitation from HOMO to LUMO of the  $\pi$ -system) and the  $S_2$  state ( $2^1A_g$ , double excitation from HOMO to LUMO). Recent experimental work (13) has shown that the photochemical reaction of 1,3-dienes occurs in the  $2^1A_g$  state. Thus we have focused our attention on the  $2^1A_g$  state, that we have investigated in detail at the ab-initio MC-SCF level.

The results of this study indicate that, as in the case of the cycloaddition reactions, the decay funnel corresponds to a conical intersection point where the ground ( $1A_g$ ) and first excited ( $2A_g$ ) potential energy surfaces are degenerate and not to an avoided crossing minimum. Thus the accepted model discussed above has to be replaced with a more general mechanistic scheme which is described in detail in ref. 7. The central feature of this new mechanism is that the excited state motion of butadiene is dominated by a *s-cis/s-trans* excited state isomerization pathway (involving simultaneous rotation about the central C-C bond of the butadiene carbon framework and asynchronous disrotatory rotation of the two terminal methylenes) and not by a ring-closure co-ordinate as assumed in the old model. Furthermore the new co-ordinate does not lead to any excited state intermediate but to a conical intersection region where rapid IC takes place. Consequently, while the excited-state branch of the reaction coordinate (from either *s-cis* or *s-trans* excited-state butadiene) corresponds to *s-cis/s-trans* isomerization of the excited state reactant, this isomerization process is not completed because the reacting system is funnelled to the ground state (see Scheme III in ref. 7)

In the decay region we have fully optimized three different conical intersections denoted as *s-transoid*, *s-cisoid* and '*central*'. The geometry of these three crossing points is shown in Fig. 3. The *s-cisoid* conical intersection occurs at a C-C-C-C dihedral angle of 52° while the *central* conical intersection is located at 84° and the *s-transoid* conical intersection occurs at a dihedral angle of 119°. The *s-transoid* conical intersection is the lowest energy point on the excited state surface, with the *s-cisoid* and the *central* conical intersections lying 7 kcal mol<sup>-1</sup> and 11 kcal mol<sup>-1</sup> respectively above the *s-transoid* point. In practice

all three structures are likely to be part of the same  $n-2$  dimensional (i.e. 22-dimensional) intersection space of butadiene but have different energies. The geometries and the MC-SCF wave function of the three conical intersections suggest that the electronic structure at the conical intersection is, in general, that of a quasi-tetradical where four unpaired electrons are almost isolated on the four carbon atoms of the butadiene framework. This tetradical character is a common feature of the entire conical intersection region.

We have also carried out Intrinsic Reaction Coordinate (IRC) computations at the MC-SCF/4-31G level in order to obtain information on the actual accessibility of the conical intersection region. These results have shown that in all cases the conical intersection region is readily accessible starting from the four excited stationary points. In particular the process results to be extremely facile along the two pathways which start from the  $C_s$  *s-cis* and the  $S_2$  *s-trans* minima and which involve disrotatory motion of the two terminal  $CH_2$  groups. These findings provide a rigorous foundations for understanding the disrotatory stereochemical preference which has been observed for butadiene photochemical ring closure. In the *s-cis* region there are two stereochemically different pathways ( $C_s$  and  $C_2$ ) to the conical intersection region. Along the  $C_s$  pathway the system moves according to a disrotatory stereochemistry and enters the *s-cisoid* conical intersection region with a value of the dihedral angle below  $50^\circ$ , while along the  $C_2$  conrotatory pathway the system enters the *central* conical intersection with a value of the dihedral angle over  $80^\circ$ . Thus from a chemical point of view, this means that we should expect high degree of stereospecificity during the ring-closure of substituted butadienes: an excited-state butadiene enters the conical intersection region in a conformation already consistent with the production of only one ground state cyclobutene isomer. This finding establishes that the reaction co-ordinate found for butadiene ring-closure is very different from the co-ordinate expected on the basis of the Van der Lugt-Oosteroff model, which is based on the assumption that the excited state path must reflect the ground state paths for the same reaction. Our results demonstrate also that the origin and simultaneous formation of all the experimentally observed photoproducts of butadiene can be readily rationalized on the basis of the tetradical character of the conical intersections and of the possible recoupling paths. After passage through the conical intersection the system emerges at a very high energy region of the ground state potential energy surface, due to the fact that in a tetradical the four

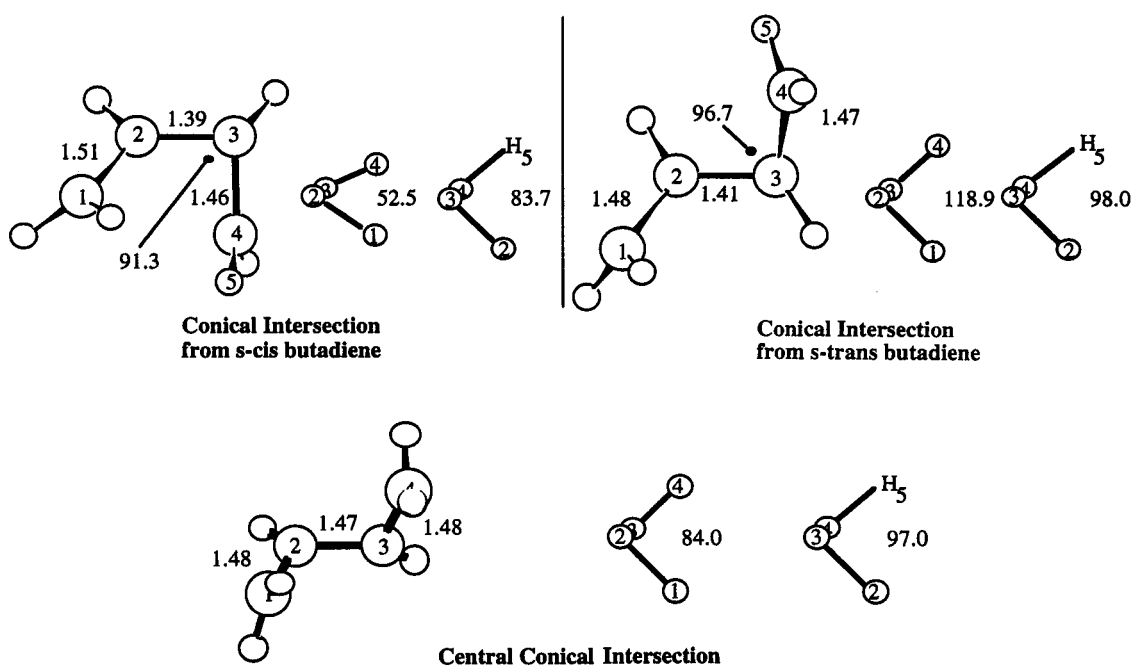


Fig. 3 Geometries of the three conical intersections computed at the 4-31G level.

valence  $\pi$  electrons are more or less uncoupled. The initial ground state trajectories in the vicinity of the apex of the cone will correlate with one of the possible spin recoupling pathways. In fact as one moves away from the apex of the cone the lowest energy ground state reaction valleys that may develop will be associated with energy-stabilizing processes where the four unpaired electrons will gradually recouple leading to the final formation of two new covalent bonds. A schematic view of these spin recoupling processes is given in Fig. 9 of ref. 7.

### 5. The photochemistry of acrolein.

In this section we describe the results of a MCSCF/6-31G\* computational study of the surface crossings in acrolein. From a strictly electronic point of view acrolein represent an analogue of butadiene as it comprises a four electrons/four orbitals  $\pi$ -system. However the photochemistry of butadiene and acrolein is very different due to the effect of the oxygen lone-pair ( $n$ ) orbital. In fact, while the photochemistry of butadiene yields a mixture of photoproducts which includes *s-cis/s-trans* isomers, double bond *cis-trans* isomers, cyclobutenes, bicyclobutanes and 1-methyl cyclopropene, the photochemistry of acrolein involves only *cis-trans* isomerization (14) and ring closure (15).

In acrolein the lowest energy excited states involved in the photochemical processes are  $^1(n-\pi^*)$ ,  $^3(n-\pi^*)$  and  $^3(\pi-\pi^*)$ . Thus the interplay between the relevant states in acrolein is much more complicated than in butadiene where the triplet states are not involved and only  $\pi-\pi^*$  excitations are relevant. The detailed study of the various possible decay routes is summarized in ref. 8. Also in this case the various photochemical mechanisms involve different types of conical intersections that are illustrated in Fig. 4.

The main feature of these conical intersections is their diradical character, with the two unpaired electrons localized one on the oxygen atom and the other on the terminal  $\text{CH}_2$  carbon. The interplay between the relevant states in acrolein occurs mainly in the triplet decay route that leads to double bond *cis-trans* isomerization.

This route, which is illustrated in Fig. 1 of ref. 8, starts from the photoexcitation to the  $S_1$   $^1(n-\pi^*)$  minimum, followed by a first intersystem crossing which occurs at the lowest energy  $S_1/T_2$  intersection between the  $^1(n-\pi^*)$  state and the  $^3(\pi-\pi^*)$  state at a planar geometry and is located only 4 Kcal mol<sup>-1</sup> above the  $S_1$  minimum. From the  $T_2$   $^3(\pi-\pi^*)$  sheet the system can access a low lying  $T_2/T_1$  conical intersection point, which is planar and which provides a fast radiationless decay channel from  $T_2$  to  $T_1$ .

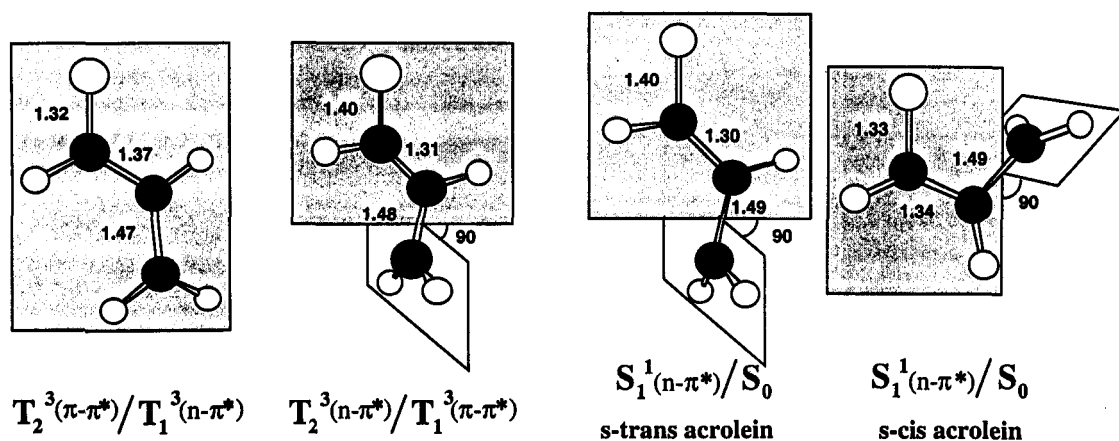


Fig.4 Geometries of acrolein conical intersections.

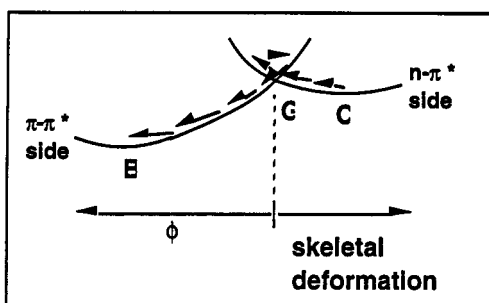


Fig.5 Schematic representation of the crossing mechanism.

The schematic representation of the crossing mechanism is shown in Fig.5. At the conical intersection point G (see Fig.5), the two triplet states  $^3(n-\pi^*)$  and  $^3(\pi-\pi^*)$  are degenerate. When the system decays to the  $T_1$  state, it reaches a valley on the  $^3(n-\pi^*)$  sheet centered on the planar minimum C which in turn relaxes to a lower energy  $T_1$  valley that belongs to the  $^3(\pi-\pi^*)$  sheet and is centered on point B via a C=C bond twisting coordinate.

The nature of the C $\rightarrow$ B relaxation process requires a careful discussion. In fact, while both points C and B are part of the same  $T_1$  surface, the nature of the electronic wavefunction at C and B is very different. Thus along the C $\rightarrow$ B path one must have a change in the character of the wavefunction. Despite extensive investigations we have found that this change does not occur adiabatically along  $T_1$  but involves a sudden change in the electronic nature of the surface. This change is associated with a crossing between the  $T_1$   $^3(\pi-\pi^*)$  and  $T_2$   $^3(n-\pi^*)$  and therefore it must involve a passage through the same intersection space intercepted by point G. The argument used to explain this behaviour hinges on the fact that, while the initial decay from G mainly leads to C, there is no true transition state between C and B because the conical intersection surface persists for  $\Phi > 0^\circ$  where  $\Phi$  is the rotational angle around the C=C double bond. Since the lowest energy point on the conical intersection lies only 5 Kcal mol $^{-1}$  above point C, the lowest energy passage from C to B can only occur via recrossing the conical intersection near point G structure. In conclusion this route leads mainly to the production of a short lived  $T_1$   $^3(\pi-\pi^*)$  twisted intermediate B which then decays via an intersystem crossing to the ground state leading to the isomerization of the acrolein double bond.

In addition to the  $T_2/T_1$  conical intersections, also  $S_1/S_0$  conical intersections are relevant. In this case we can compare these conical intersections with those already discussed for butadiene. The electronic structure of the butadiene conical intersections corresponds to a quasi tetraradical where the four electrons of the  $\pi$  system are only slightly coupled. These different electronic structures are the result of the fact that the excited states involved in the two types of conical intersections are different. In the case of butadiene, in fact, the  $S_1$  excited state is a doubly excited  $(\pi)^2-(\pi^*)^2$  state, while in acrolein  $S_1$  is a singly excited  $(n-\pi^*)$  state. In addition to the electronic structure, also the geometrical structure of the butadiene conical intersections is significantly different from that of the acrolein conical intersections. As previously pointed out the butadiene conical intersections have a highly non planar carbon skeleton, while the acrolein conical intersections have an heavy atom planar skeleton, where the central C-C bond is a fully formed double bond and the terminal  $CH_2$  group is rotated by  $90^\circ$ : On the basis of the differences observed in the geometric and electronic structure of *s-cis* and *s-trans* acrolein and butadiene conical intersections, it is possible to rationalize the photoproduct distribution originating from the corresponding decay channels. We first consider the *s-cis* conformer. The diradical nature of *s-cis* acrolein  $S_1/S_0$  conical intersections leads to the prediction that photochemical *s-cis* to *s-trans* isomerization could not possibly occur in acrolein. In contrast to butadiene, the acrolein framework is rigidly planar due to a fully formed double bond. Thus the system starts its

relaxation on  $S_1$  at a geometry which not includes a motion about the central C-C bond. In this case the  $90^\circ$  twisted terminal  $CH_2$  in the conical intersection structure will rotate back or forward to a planar form, causing double-bond isomerization product. This mechanism also operates in butadiene where one has conical intersections with  $90^\circ$  twisted terminal  $CH_2$  groups. While double bond *cis-trans* isomerization is the fastest process in butadiene photochemistry, *s-trans* to *s-cis* isomerization also occurs rapidly. This behaviour is mainly related to the highly twisted ( $50^\circ$ ) carbon framework of the butadiene conical intersection. The features of the *s-trans* acrolein decay are similar to those described above for the *s-cis* channel. Thus we expect double bond *cis-trans* isomerization as the major photochemical process.

Butadiene irradiation also produces two ring-closure photoproducts: cyclobutene and bicyclobutane. Cyclobutene has been proved to originate exclusively from *s-cis* butadiene whereas bicyclobutane is thought to originate from the *s-trans* conformer. While acrolein photoexcitation leads to oxetene, the four membered ring analogue of cyclobutene, no evidence has been found for the formation of oxabicyclobutane, the analogue of bicyclobutane. This behaviour can be explained by comparing the conical intersections of *s-cis* and *s-trans* butadiene and acrolein. In fact the structure of the *s-cis* acrolein conical intersection favors the ring closure process to oxetene. The C-O bond formation can occur after the system has decayed to  $S_0$  by spin-recoupling of the two unpaired electrons. Such a process will occur in competition with double bond *cis-trans* isomerization. On the other hand, the nature of the acrolein conical intersection structures suggests that the formation of the bicyclic product from *s-trans* or even *s-cis* geometries will be impossible. The formation of bicyclic product involves the formation of a three-membered ring diradical that must then close to the bicyclic product. This process is possible in butadiene where the conical intersection structures have a C-C-C bending angle with a near  $90^\circ$  value and consequently a certain amount of orbital overlap between positions 1 and 3. In contrast, in the acrolein conical intersection, as a result of the rigidly planar C-O skeleton, no 1,3 C-O or 1,3 C-C interaction is possible. Thus we predict that oxabicyclobutane formation is unlikely in  $\alpha,\beta$ -enones.

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