A Model Study of the Mechanism of the Type B (Di-π-methane) and Lumiketone Rearrangement in Rotationally Constrained α,β-Enones

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The ground and excited state potential energy surface topology along the $^{1,3}(n-\pi^*)$ reaction path for the type B (structurally equivalent to the di-π-methane rearrangement) and the $^3(\pi-\pi^*)$ lumiketone rearrangements of rotationally constrained α,β-enones (e.g. 2-cyclohexenones) have been modeled by CAS-SCF computations of a *geometrically constrained* 2(*Z*)-pentenal molecule and 2(*Z*),5-hexadienal. For the $^{1,3}(n-\pi^*)$ type B reaction, the computations indicate that funnels for intersystem crossing (ISC) and internal conversion (IC) occur on the product side of the excited state reaction path after the sigmatropic migration has taken place. This surface crossing must be a feature that does not depend on the nature (alkyl or benzyl) substitution. For the $^3(\pi-\pi^*)$ lumiketone reaction path, funnels for ISC exist on both the reactant and product side of the $^3(\pi-\pi^*)$ reaction path. The ground state reaction path will take place only if ISC on the reactant side is made efficient by increasing the spin−orbit coupling in polar solvents.

Introduction

Excited state chemical reactivity is controlled by (i) energy barriers on the excited state branch of the reaction path, (ii) the existence of funnels where efficient radiationless decay to the ground state can take place, and (iii) barriers to reaction on the ground state branch of the reaction path.[1] In this paper we present a model of the photochemical rearrangement of cyclic (thus rotationally constrained) α,β-enones.[2] From a theoretical point of view, the mechanisms of such reactions are interesting because of the presence and interaction of the C═O and the C═C functional groups and the fact that because cis−trans isomerization cannot take place in cyclic enones, these molecular photorearrangements become major reactions. We shall demonstrate that the type B rearrangement is an *excited state adiabatic* reaction (i.e. the funnel lies on the product side of the excited state reaction path, in agreement with the results obtained by Zimmerman[3]) and the lumiketone rearrangement is, essentially, a *ground state adiabatic* reaction (i.e. the funnel lies on the reactant side of the excited state reaction path and the photoexcitation process merely supplies the energy to overcome the ground state activation barrier).

The photochemistry of 2-cyclohexenones is particularly rich and the molecular rearrangements of the 4,4-disubstituted derivatives, the type B enone, and lumiketone rearrangements (see Scheme 1) provide well-documented examples.[1−20] After the initial photoexcitation the system ends up in the triplet manifold regardless of the type of excitation due to a highly efficient S_1/T_1 intersystem crossing.[5,6] The products of the reaction

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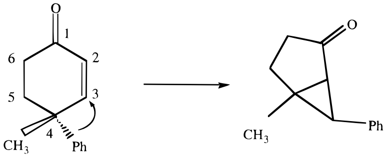
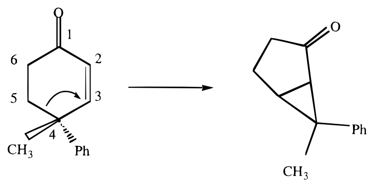
Scheme 1

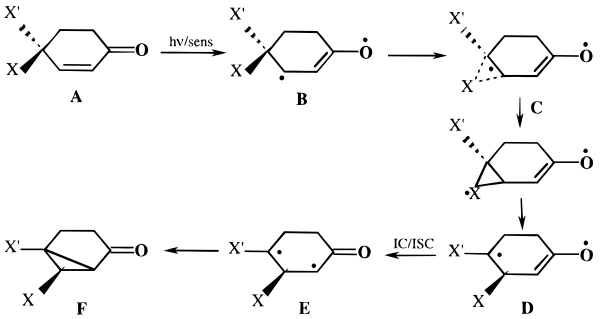
Type B rearrangement



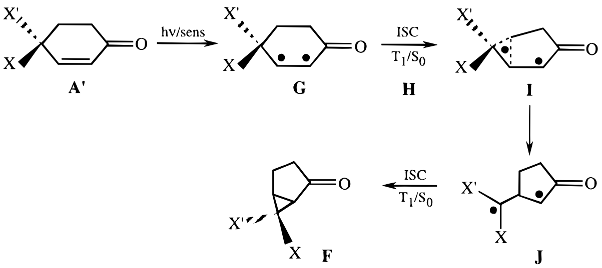
Lumiketone rearrangement



Scheme 2



Scheme 3



appear to be controlled by which excited state is populated:[2,6−9] $^{1,3}(n-\pi^*)$ in the case of the type B rearrangement or $^3(\pi-\pi^*)$ for the lumiketone reaction. In Schemes 2 and 3 we give a sequence of structures that represents a summary of various mechanisms proposed for these reactions[2,3,6,8−10] in the literature. While the sequence of geometric structures that occur along the reaction path is well-understood, whether such structures are real intermediates or not, where the points of internal conversion (IC) or intersystem crossing (ISC) can occur, and whether the transition state (TS) lies on the excited state or on the ground state remain open questions.

The type B rearrangement (discovered in 1964[14]), formally similar to the di-π-methane rearrangement but quite different mechanistically, is assumed to occur through the $^3(n-\pi^*)$ state.[3b,6,9,10,12,13] The sequence of structures **B**−**D** in Scheme 2 assumes that the reaction takes place on the excited state with ISC/IC to a ground state biradical **E** which closes to give the final product **F**. However, ISC/IC in the region of **B** is theoretically possible, in which case the transition state **C** would occur in the ground state. The type B rearrangement in 2-cyclohexenones occurs in nonpolar and polar solvents[2,6] when one of the substituents in C_γ is aryl or vinyl.[2] The major product is endo.

In the lumiketone sequence (Scheme 3), the excited state $^3(\pi-\pi^*)$ is usually assumed to be twisted (**H**) and the reaction takes place after ISC via a transition state **I** in the ground state. However, a transition state **I*** could exist on the excited state surface. In this case the ISC would have to occur somewhere along the reaction path between **J** and **F**. The lumiketone rearrangement is commonly observed for flexible (i.e. twisting around the C=C bond is not significantly inhibited) 2-cyclohexenones with two substituents on C_γ, one of them alkyl.[2b] The reaction only occurs in polar solvents and the yield increases with dielectric constant or H-bonding character.[2,6] Both rearrangements are stereospecific (retention at C_δ inversion at C_γ), although exceptions have been found in the case of the lumiketone reaction[15,16] and the type B reaction is also stereoselective. Both reactions give very low yields that in general do not depend on the conditions of direct or sensitized excitation.[2,5,6,9] Because of the observed stereospecificity, polar states and diradicals are ruled out as intermediates[2,9] and the existence of a ground state *trans*-cyclohexenone intermediate is controversial.[8,17]

The properties of α,β-enones in general are well-understood on the basis of experimental work and recent theoretical computations on acrolein. The two triplet $^3(n-\pi^*)$ and $^3(\pi-\pi^*)$ states lie very close in energy.[3a,7,8,11,18,19] The $^3(n-\pi^*)$ minimum is planar [2,8−11,18] and the $^3(\pi-\pi^*)$ minimum is twisted in nonrigid enones.[8,10−12] The long lifetime of the $^3(\pi-\pi^*)$ state in rigid systems indicates that ISC must occur from the twisted structure.[2,8,11,18] It is usually assumed that crossing of S_1 $^1(\pi-\pi^*)$ with the $^3(\pi-\pi^*)$ or $^3(n-\pi^*)$ surface probably occurs at a planar geometry near the Franck−Condon (FC) region. This intersystem crossing is specially rapid and efficient[5,7,20] for both rigid and nonrigid enones as the result of a large spin−orbit coupling (SOC). In a recent work we have studied the intertwining of the $^1(n-\pi^*)$ with the $^3(\pi-\pi^*)$ or $^3(n-\pi^*)$ states in acrolein.[21] We have located a point of ISC between the $^1(n-\pi^*)$ (S_1) and the $^3(\pi-\pi^*)$ (T_2) surfaces at a planar geometry. We have subsequently computed the SOC at that point (64.57 cm^{-1}), which confirms that ISC between $^1(n-\pi^*)$ and $^3(\pi-\pi^*)$ will be efficient and rationalizes the similar reactivity observed for direct or sensitized processes. We have also located a conical intersection between the two triplet excited states at a planar geometry, which serves as a funnel to the planar $^3(n-\pi^*)$ state minimum. To return to the $^3(\pi-\pi^*)$ surface, a small barrier must be overcome, so the population of the twisted $^3(\pi-\pi^*)$ minimum of nonrigid enones depends on the height of the barrier. In this region the $^3(\pi-\pi^*)$ triplet surface is almost degenerate with the ground state, but the SOC at this geometry is very small, so ISC will be inefficient. On the other hand, for rigid enones either the planar $^3(n-\pi^*)$ minimum or a planar $^3(\pi-\pi^*)$ structure must be the reactive species.

We now discuss the simplified model (Scheme 4) used in this work. For the lumiketone rearrangement, we can model the mechanism by considering the migration of an alkyl γ carbon substituent. Accordingly, we shall model the 4-aryl-4-alkylcyclohex-2-enone (Scheme 1) with a simpler acyclic system, the 2(*Z*)-pentenal (i.e. $X = CH_3$ is Schemes 2 and 3), which is constrained rotationally to avoid exploring the reaction paths of linear α,β-enones

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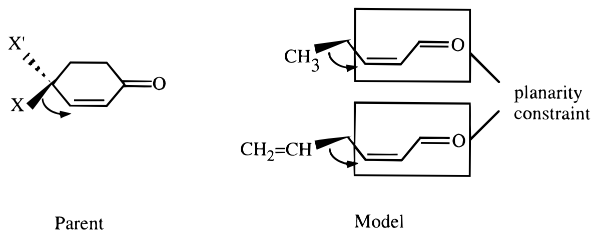
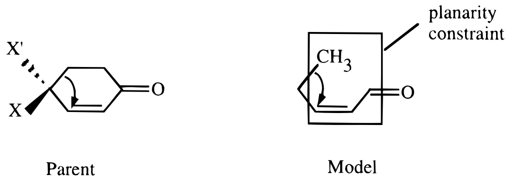
Scheme 4

Type B rearrangement model



Lumiketone rearrangement model



(Scheme 4). However, for the type B rearrangement, the transition state region (**C** in Scheme 2) cannot be properly treated unless X is a phenyl or a vinyl group[9] which is able to delocalize the odd electron in the migrating group. Thus for the type B reaction path we have also considered the migration of a vinyl group substituent on carbon atom 4 (using 2(*Z*),5-hexadienal as a model; Scheme 4) as well as the migration of an alkyl carbon substituent for comparison.

Computational Details

All of the CAS-SCF results presented in this paper have been produced using the MC-SCF program distributed in *Gaussian 94*[22] using a 6-31G* basis. The location of the surface crossings corresponding to conical intersection points and singlet−triplet crossings has been carried out using the method[23] which is also available in the *Gaussian* package. Spin−orbit coupling constants have been calculated in an approximation using scaled nuclear charges[24] and one-electron integrals of the H_{LS} operator.

The choice of active space in our computations requires some comment. For the $^3(\pi-\pi^*)$ and $^3(n-\pi^*)$ excited states, the electronic configuration of the O atom is $(2p^{\pi})^2(n)^1$ or $(2p^{\pi})^1(n)^2$. Thus in addition to a p orbital on the carbonyl carbon and C_α,C_β, C_γ, and C_δ, one needs two active orbitals on the O atom to give a seven-orbital 8-electron active space. However, near double occupancy of one of the orbitals (e.g. fully formed σ bond) causes convergence problems because of the invariance of the energy to active−inactive orbital rotations. Accordingly, it was necessary to reduce the active space to perform the geometry optimization of some critical points and recomputethe energy at the optimized geometry using the full active space. The SOC computations were carried out with the same active spaces.

Results and Discussion

The 4-aryl-4-alkylcyclohex-2-enone (Scheme 1) is modeled with 2(*Z*)-pentenal (i.e. X being CH_3 in Schemes 2 and 3) and with 2(*Z*),5-hexadienal for the calculations on the transition state region of the type B reaction path (i.e. X being $CH{=}CH_2$). In order to simulate the constraint of the cyclohexenone ring, for the $^{1,3}(n-\pi^*)$ reaction path—the type B reaction—the 2(*Z*)-pentenal geometries were *constrained to have a planar skeleton* (i.e. excluding the migrating group; see Scheme 4). For the $^3(\pi-\pi^*)$ reaction path, the 2(*Z*)-pentenal geometries were *constrained so that the* CH_3 *lies in the same plane as the carbonyl carbon,* C_α *and* C_β. Consequently, the CH_3 migration simulates the ring contraction typical of the lumiketone rearrangement.

In fact, the effect of such constraints is small and the value of the gradient in the full space remains very small and is quoted below with the structures (Tables 1 and 2). Our objective is to determine the points of ISC and IC and thus determine which structures from Schemes 2 and 3 lie on the excited state branch of the reaction path and which structures lie on the ground state part.

The ground and excited state potential energy surface topology is summarized in Figure 1 for the $^{1,3}(n-\pi^*)$ reaction path (i.e. type B model) and in Figure 2 for the $^3(\pi-\pi^*)$ reaction path (i.e. lumiketone model). For the type B model we use **X** to denote structures with an alkyl substituent and $\underline{\mathbf{X}}$ to denote structures with a vinyl substituent. The energetics are collected in tables 1 and 2 and the optimized structures are collected in Figure 3. For the $^{1,3}(n-\pi^*)$ type B model (Figure 1), there is no funnel for ISC/IC on the reactant side (near **B**). Further, the valence tautomerism (**D**-**E** Scheme 2) is a surface crossing. In contrast, for the $^3(\pi-\pi^*)$ lumiketone reaction path (Figure 2), one finds funnels for ISC on the reactant (**H**) and product (**J**) side in the excited state energy profile. However, the excited state barrier is very high, so it is clear that photoexcitation supplies the energy for the ground state reaction via **I**.

$^{1,3}(n-\pi^*)$ Type B Enone Rearrangement Pathways. The reaction paths starting from the FC region **A** are illustrated in Figure 1 (light curve) for the 2(*Z*)-pentenal model, simulating a sigmatropic shift and (bold curve) for selected points calculated with the 2(*Z*),5-hexadienal model. At the minimum energy point **B** for both $^1(n-\pi^*)$ and $^3(n-\pi^*)$ states there is a S_0-T_1 40 kcal mol^{-1} gap. Thus ISC will be very inefficient. In spite of extensive searches, we were not able to locate a low-energy surface S/T crossing in this region. It is thus clear that the [1,2] shift must take place adiabatically on the excited state.

The TS for the migration of the methyl group on the $^3(n-\pi^*)$ surface **C*** lies ca. 70 kcal mol^{-1} above **B** on both T_1 and S_1. For the model involving vinyl migration, the surface topology changes and the single transition state **C*** is replaced by a minimum $\underline{\mathbf{C}}$ and a transition state $\mathbf{TS}_{\underline{\mathbf{B}}\rightarrow\underline{\mathbf{C}}*}$ with a much lower barrier (42 kcal mol^{-1}). (This structure could not be fully optimized due to an almost freely rotating CH_2 group on the vinyl). Thus the transition state in the type B rearrangement is stabilized when the migrating group (X in Scheme 2) is a phenyl or vinyl group. We have also located a TS for the migration of the methyl group on the S_0 surface; however, there is no funnel to reach the S_0 after the initial excitation.

On the product side of the TS, there is an intermediate **D** ($\underline{\mathbf{D}}$) for $^{1,3}(n-\pi^*)$ states. The C−O distance is long.

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Table 1. Energies of the Critical Points of the Type B Rearrangement Reaction for the Model Systems 2(*Z*)-Pentenal and 2(*Z*),5-Hexadienal[e]

			forces		vertical energies to other states			
geometry	state	E^a (ΔE^b)	max	RMS	S_0	^{3}(n−π*)	^{1}(n−π*)	^{3}(π−π*)
reactant minimum (**A**)	S_0	0.8936^c (0.0)	0.0100	0.0030		0.7591^c (84.4)	0.7507^c (89.7)	0.7507^c (89.7)
planar minimum ($\mathbf{B}^*_{\mathbf{Triplet}}$)	^{3}(n−π*)	0.7833^c (69.2)	0.0008	0.0003	0.8661^c (17.3)		0.7782^c (72.4)	0.7512^c (89.3)
planar minimum ($\mathbf{B}^*_{\mathbf{Singlet}}$)	^{1}(n−π*)	0.7789^c (72.0)	0.0011	0.0003	0.8619^c (19.9)	0.7830^c (69.4)		0.7730^c (75.7)
planar TS ($\mathbf{C}^*_{\mathbf{Triplet}}$)	^{3}(n−π*)	0.6715^c (139.4)	0.0009	0.0002	0.7471^c (91.9)			
planar TS ($\mathbf{C}^*_{\mathbf{Singlet}}$)	^{1}(n−π*)	0.6702^c (140.2)	0.0002	0.00007	0.7051^c (117.5)	0.6838^c (131.6)		0.6719^c (139.1)
planar TS ($\mathbf{C}_{\mathbf{S_0}}$)	S_0	0.7563^c (86.2)	0.0052	0.0011				
intermediate min ($\mathbf{D}^*_{\mathbf{Triplet}}$)	^{3}(n−π*)	0.7565^c (86.0)	0.0087	0.0002	0.7746^c (74.7)			0.7751^c (74.4)
intermediate min ($\mathbf{D}^*_{\mathbf{Singlet}}$)	^{1}(n−π*)	0.7571^c (85.7)	0.0008	0.0002	0.7750^c (74.4)	0.7571^c (85.7)		0.7756^c (74.0)
S_0/^{1}(n−π*) CI (**E**)	S_0	0.7358^c (99.1)	0.0076	0.0021		0.7359^c (99.0)	0.7341^c (100.6)	0.7379^c (97.7)
product exo conform. (**F**)	S_0	0.8566^c (23.2)	0.0009	0.0004				
product endo conform. (**F**)	S_0	0.8540^c (24.8)	0.0003	0.0002				
planar minimum ($\underline{\mathbf{B}}$)	^{3}(n−π*)	0.6263^d (0.0)	0.0003	0.0002	0.7101^d (−52.6)		0.6209^d (3.3)	0.6136^d (7.9)
planar minimum ($\underline{\mathbf{C}}$)	^{3}(n−π*)	0.5947^d (19.8)	0.0030	0.0008	0.6136^d (8.0)		0.5947^d (19.8)	0.6136^d (8.0)
planar minimum ($\underline{\mathbf{D}}$)	^{3}(n−π*)	0.5989^d (17.2)	0.0003	0.0002	0.5986^d (17.4)		0.5988^d (17.2)	0.6170^d (5.8)
planar TS ($\underline{\mathbf{B}}\rightarrow\underline{\mathbf{C}}$)	^{3}(n−π*)	0.5587^d (42.4)	0.0042	0.0015	0.6262^d (−0.1)		0.5799^d (29.1)	0.6185^d (4.9)

[a] Energies in E_h. [b] Relative energies in kcal mol^{-1}. [c] +268. [d] +306. [e] Labels correspond to Figure 1 and 2. The entry "Vertical Energies to Other States" refers to the energies of other electronic states computed at the geometry of column 1 (e.g. S_1 energy computed at S_0-optimized geometry)

Table 2. Energies and Geometries of the Critical Points of the Reaction Path of Lumiketone Rearrangement for the Model System 2(*Z*)-Pentenal[c]

			forces		vertical energies to other states			
Geometry	state	$E^a + 268(\Delta E^b)$	max	RMS	S_0	^{3}(n−π*)	^{1}(n−π*)	**3(π−π*)**
reactant minimum (**A**)	S_0	0.8866 (4.4)	0.0003	0.0002		0.7524 (88.6)	0.7444 (93.6)	0.7443 (93.7)
planar TS (**G**)	^{3}(π−π*)	0.7795 (71.6)	0.0008	0.0002	0.8655 (17.6)	0.7659 (80.1)	0.7605 (83.5)	
rotated minimum (**H**)	^{3}(π−π*)	0.7999 (58.8)	0.012	0.003	0.7917 (63.9)	0.7381 (97.6)	0.7380 (97.6)	
rotated transition state ($\mathbf{I}_{\mathbf{S_0}}$)	S_0	0.7582 (85.0)	0.002	0.0005				
rotated transition state ($\mathbf{I}^*_{\mathbf{Triplet}}$)	^{3}(π−π*)	0.6965 (123.7)	0.0002	0.00006				
half rotated TS ($\mathbf{I'}^*_{\mathbf{Triplet}}$)	^{3}(π−π*)	0.6918 (126.6)	0.006	0.002				
intermediate minimum (**J**)	^{3}(π−π*)	0.7913 (64.2)	0.0005	0.0001	0.7902 (64.9)	0.7316 (101.6)		

[a] Energies in E_h. [b] Relative energies in kcal mol^{-1}. [c] Labels correspond to Figures 1 and 2. The entry "Vertical Energies to Other States" refers to the energies of other electronic states computed at the geometry of column 1 (e.g. S_1 energy computed at S_0-optimized geometry.

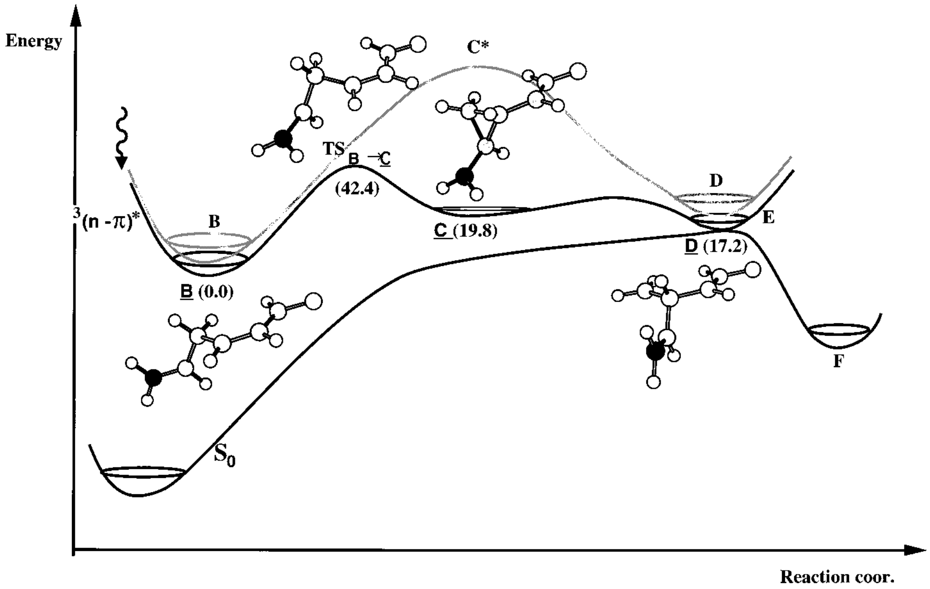

Figure 1. Schematic representation of the type B enone rearrangement reaction path: 2(*Z*)-pentenal (light curve), 2(*Z*),5-hexadienal (bold curve). Values in parentheses correspond to relative energies in kcal mol^{-1}.

(This geometry is independent of whether the migrating group is alkyl or vinyl.) This intermediate lies some 12 kcal mol^{-1} above the S_0 and the ^{3}(π−π*) states for 2(*Z*)-pentenal. At a geometry very close to the intermediate we have optimized (without geometrical constraint) an S_0/S_1 conical intersection **E**. At this geometry the S_0, ^{3}(n−π*) and ^{1}(n−π*) are degenerate. The SOC S_0 ^{3}(n−π*) is 64 cm^{-1}. The other SOC's are almost zero. Surface crossing at **E** arises simply because there is a carbonyl carbon−C_α double bond (1.30 Å) which leaves a degenerate isolated O $(2p^{\pi})^2(n)^1 \leftrightarrow$ O $(2p^{\pi})^1(n)^2$ configuration with an unpaired electron on C_γ. This crossing must exist with or without phenyl substitution. Product ring formation (**F**) from this point occurs without barrier.

^{3}(π−π*) Lumiketone Reaction Path. For the ^{3}(π−π*) lumiketone reaction path, the geometries have been

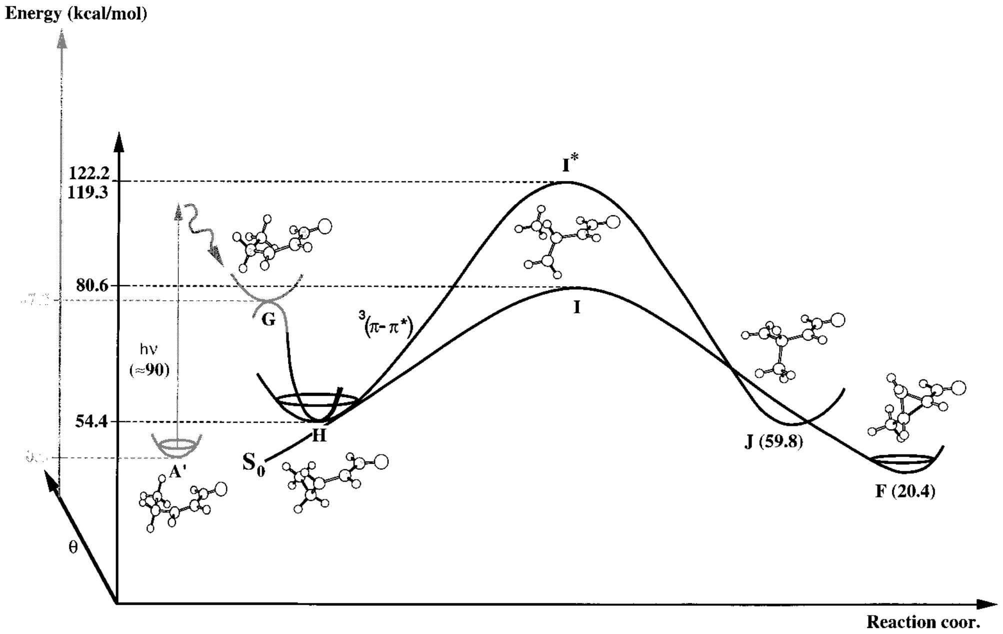

Figure 2. Schematic representation of the lumiketone rearrangement reaction path modeled with 2(*Z*)-pentenal.

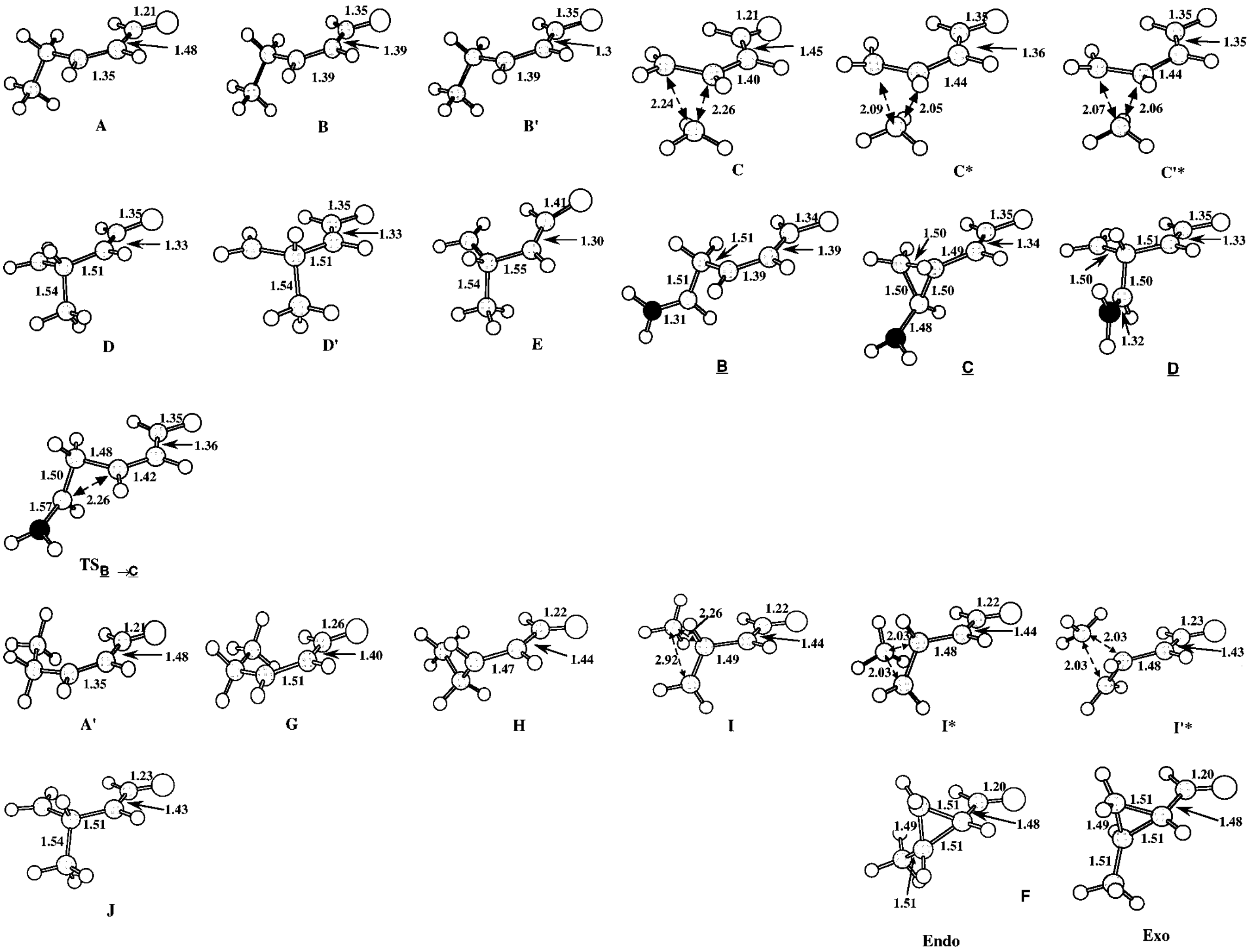

Figure 3. Main structural features of optimized structures on the type B rearrangement reaction path (**A**–**E** and **B**–**D**) the lumiketone rearrangement reaction path (**A′**, **G**–**J**), and the ground state products **F**.

constrained so that migrating CH_3 lies in the same plane as the carbonyl carbon, C_α, and C_β in order to simulate the effect of the ring in cyclohexenone.

The relaxed structure **G** provides the reference point for the excited state branch of the reaction coordinate. It is a transition state with respect to rotation about the

$C_\alpha - C_\beta$ bond leading to **H**, the $^3(\pi-\pi^*)$ twisted minimum where the $^3(\pi-\pi^*)$ surface touches S_0. The computed spin–orbit coupling is 0.014 cm^{-1}. If the enone is rigid, **G** will be a minimum, as the twisting will be inhibited and relaxation to **H** will be impossible, in agreement with the experimental fact that for rigid enones this reaction does not take place. In nonpolar solvents there is no efficient mechanism for decay because of the small value of the spin–orbit coupling. In polar solvents, the S_0 state can take on some zwiterionic character and the SOC will become larger, increasing the efficiency of intersystem crossing.

From **H** there is the possibility of excited state migration via a TS **I*** or ground state migration via **I**. We have optimized two structures with a transition vector for methyl migration on the $^3(\pi-\pi^*)$ surface with a different angle of rotation around the C_α-C_β bond (107° and 53°), but they differ only by 3 kcal mol^{-1}. This migration path terminates at a diradical minimum **J**. At this point the $^3(\pi-\pi^*)$ surface is almost degenerate with S_0 (less than 1 kcal mol^{-1} difference), but SOC is almost zero. This fact together with the very high excited state barrier makes the $^3(\pi-\pi^*)$ reaction path unlikely.

The TS **I** for the migration on the S_0 surface lies some 40 kcal mol^{-1} lower than **I*** on the $^3(\pi-\pi^*)$ state. The accessibility of this TS depends upon the efficiency of ISC at **H**. It would appear that the ground state path will be active only if this ISC can be made efficient in polar solvents. Because the GS path is the only accessible one, the experimental fact that the lumiketone reaction takes place only in polar solvents is rationalized.

Conclusions

The ground and excited state potential energy surface topology for the $^{1,3}(n-\pi^*)$ reaction path for the type B rearrangement and the $^3(\pi-\pi^*)$ lumiketone reaction path has been modeled with methyl migration in rotationally constrained 2(*Z*)-pentenal and ethyl migration in 2(*Z*),5-hexadienal and the results obtained give a satisfactory explanation of the experimental evidence. Our calculations support the hypothesis that two distinct triplet states are involved[6,9,10,12] in the two rearrangements. The fact that both reactions are mostly stereospecific[2,9,15,16] is consistent with the reaction paths proposed, since the only intermediates found, $\underline{\mathbf{C}}$ and **H**, must be very short lived. For the $\underline{\mathbf{C}}$ minimum, the short lifetime arises from the lack of activation energy to move to the **D/E** structure. In the case of the **H** minimum, the short lifetime arises from the very efficient decay to the S_0 surface, where there is no minimum. Nevertheless, the position of this funnel with respect to the excited state minima may change with substituents, so the diradical intermediate could have a nonnegligible lifetime.[15,16,25,26] This feature could explain the small yield of the minor stereoisomeric product, as some experimentalists suggest.[25] The similar reactivity under direct excitation or sensitized conditions is explained by the efficient ISC from S_1 to the triplet manifold in the FC region[5–7,9,12] shown in our previous study of acrolein.[21]

For the $^{1,3}(n-\pi^*)$ type B model there is no funnel for ISC/IC on the reactant side. Rather, the valence tautomerism **D**-**E** (Scheme 2) yields a surface crossing on the product side of the excited state reaction path where efficient ISC yields the final product. While the barrier height for the $^{1,3}(n-\pi^*)$ type B cannot be determined without phenyl or vinyl substitution, the surface crossing must be a feature that does not depend on substitution. Aryl substituents on C_4 certainly delocalize the odd electron in the TS structure of type B rearrangement and change the "local" topology of the surface, lowering the barrier (experimentally, the reaction can only take place[2,6] under these conditions). The phenyl-bridged structure that has been suggested as an intermediate of the reaction[9] is confirmed by our results. Zimmerman's calculations, carried out at several levels of accuracy (MNDO-CI and AM1 methods),[5,3b] also suggested the existence of a phenyl-bridged structure as intermediate in preference to a concerted reaction, where he found a sharp increase in the SOC (calculated at MCSCF level using a big active space) when a structure analogous to intermediate **D** began to close. He also suggested that decay back to S_0 must occur at the open diradical in preference to a concerted migration.

For the $^3(\pi-\pi^*)$ lumiketone reaction path, funnels for ISC exist on both the reactant and product side of the $^3(\pi-\pi^*)$ reaction path. The ground state reaction path will become effective if ISC on the reactant side is made efficient by increasing the SOC, as observed when the reaction is carried out in polar solvents.[2,6] Our results are also consistent with the fact that the lumiketone reaction is only observed for flexible enones[2] because the computed reaction path goes through the twisted $^3(\pi-\pi^*)$ minimum.

The aim of this work was to explain the mechanisms of two of the possible [1–3] shift reactions of cyclohexenones. Accordingly, our study has attempted to model the reaction paths proposed for these reactions. Other experimental results on the cyclohexenones suggest the existence of additional surface crossings. The low yields of the rearrangements[2] and the absence of fluorescence[7] and phosphorescence in nonrigid enones[8,18] must be due to a deactivation path back to reactants from S_1 and a facile path from the triplet states to that deactivation path. The various S_1/S_0 crossings documented for acrolein[21] may play a role here.

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