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Theoretical Study of the Photochemical [2 + 2]-Cycloadditions of Cyclic and Acyclic α,*β*-Unsaturated Carbonyl Compounds to Ethylene

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The ground and first triplet excited-state potential energy surfaces of the [2 + 2]-cycloadditions of 2-cyclohexenone, methyl acrylate, and methyl crotonate to ethylene have been studied by means of CASSCF and DFT-B3LYP calculations. The attack of ethylene to the $^3(\pi-\pi^*)$ α,*β*-unsaturated carbonyl compound leads to the formation of a triplet 1,4-biradical intermediate that evolves to the ground-state potential energy surface. The outcome of the reaction is governed by the competition between the deactivation of the $^3(\pi-\pi^*)$ α,*β*-unsaturated carbonyl compound itself and its reaction with ethylene to form the triplet 1,4-biradical. For 2-cyclohexenone, the potential energy barrier corresponding to the formation of the biradical intermediate is lower than for the acyclic systems. On the other hand, the energy necessary to reach the crossing point between the $^3(\pi-\pi^*)$ and the ground-state potential energy surfaces is lower for the acyclic systems than for 2-cyclohexenone. For methyl acrylate and methyl crotonate, the decay of the $^3(\pi-\pi^*)$ state of the isolated molecule is therefore expected to be faster than the formation of the 1,4-biradical, so that the [2 + 2]-cycloaddition will not take place. However, for 2-cyclohexenone the formation of the triplet 1,4-biradical is favorable, and the process will lead to the formation of the corresponding cyclobutane derivative.

Introduction

The photochemical [2 + 2]-cycloaddition is one of the most useful methods in the synthesis of cyclobutane derivatives.[1] A large number of reactions involving α,*β*-unsaturated cyclic enones,[2−4] cycloalkenyl esters,[5] and lactones[6] have been reported in the literature. However, examples of such reactions with acyclic compounds are scarce.[7] For example, 2-cyclohexenone reacts with several olefins, such as 1,1-diethoxyethylene, yielding the corresponding cyclobutane derivative in good yield.[2] However, when we attempted the reaction with several open-chain pentenoates, the corresponding cyclobutanes were not

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formed, and *Z*-*E* isomerization of the C−C double bond was observed.[8]

Several studies based on triplet sensitization and quenching techniques have concluded that the photochemical [2 + 2]-cycloaddition involves the $^3(\pi-\pi^*)$ state of the α,β-unsaturated carbonyl compound.[9] The lifetimes of these transients range between 15 and 900 ns.[10] The deactivation of such species to the ground state through intersystem crossing competes with the cyclobutane formation reaction.

The photophysics of acrolein[11] and several cyclic enones[12] has been studied by means of CASSCF calculations. The most efficient deactivation path has been shown to involve the $^3(\pi-\pi^*)$ state of the enone. The energy necessary to reach the crossing point between this state and the ground state greatly depends on the rigidity of the system and is in good qualitative agreement with the observed lifetimes.[12]

Recently, a CASSCF study of the ground and triplet excited-state surfaces of the reaction between acrolein and ethylene has been reported.[13] In the first part of the reaction, ethylene attacks acrolein in the triplet state to form a triplet biradical intermediate. This intermediate easily undergoes intersystem crossing to the ground-state surface where two different processes may take place: ring closure or reversion to reactants. These results indicate that the product selectivity is determined by transition states on both the ground and triplet excited-state surfaces, in good agreement with the experimental results reported by Weedon et al.[4]

More recently, the reaction between $^3(\pi-\pi^*)$ acrolein and ethylene has also been studied by Bertrand et al.[14] using semiempirical, ab initio, and density functional methods.

The purpose of this paper is to rationalize the different behavior of cyclic and acyclic α,β-unsaturated carbonyl compounds in photochemical [2 + 2]-cycloadditions. For this reason, we present a theoretical study of the ground- and excited-state potential energy surfaces corresponding to the cycloadditions of ethylene to 2-cyclohexenone, methyl acrylate, and methyl crotonate. The reaction of acrolein has also been considered for comparison.[13]

Computational Details

Molecular geometries have been fully optimized at the CASSCF[15] and DFT-B3LYP[16,17] levels of calculation. The standard 6-31G(d) basis set has been used in all cases.[18] Harmonic vibrational frequencies of all stationary points have been computed to characterize them as energy minima (all frequencies are real) or transition states (one and only one imaginary frequency).

For the reaction between the α,β-unsaturated carbonyl compounds and ethylene, the active space for the CASSCF calculations includes all π orbitals of the fragments (i.e., six electrons in six orbitals) as in ref 13.

For methyl acrylate and methyl crotonate, the lowest energy points of surface crossing[19] between the T_1 $^3(\pi-\pi^*)$ and S_0 states of the isolated molecules have been located using the methodology described in previous works[11−12,20] with state-averaged orbitals and a weighting of 50%/50% to the triplet and singlet states. The active space comprised six electrons in five orbitals, which include the π and π* orbitals of the C=C and C=O moieties and the oxygen n orbital. This active space was used so that energetics can be compared directly with refs 11 and 12 (as the n orbital does not need to be in the active space to describe the $^3(\pi-\pi^*)$ state).

In the B3LYP calculations of open shell systems a spin-unrestricted formalism has been used. For open shell singlet states, spin-unrestricted calculations have been done by breaking the symmetry between α and β spin densities. For the minima on the singlet surface (**s2a, s2g**) the resulting $\langle S^2\rangle$ is between 0.9 and 1.0, so they are biradicals with an equal mix between the triplet and singlet spin states.[22] The $\langle S^2\rangle$ values for the transitions states **TS(s2/s1)** are approximately 0.6 (less spin contamination), and for **TS(s2g/s3)** the values are between 0.9 and 1.0. The triplet stationary points have an $\langle S^2\rangle$ close to 2.0 as expected. Spin-projected energies were estimated using the formula given in ref 22.

All calculations have been done using the Gaussian 98 program.[21]

Results and Discussion

As has already been shown,[11,12] the most efficient photophysical relaxation path for a photoexcited α,β-unsaturated carbonyl compound involves the formation of a twisted $^3(\pi-\pi^*)$ intermediate (**t1**). Scheme 1 sum-

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SCHEME 1

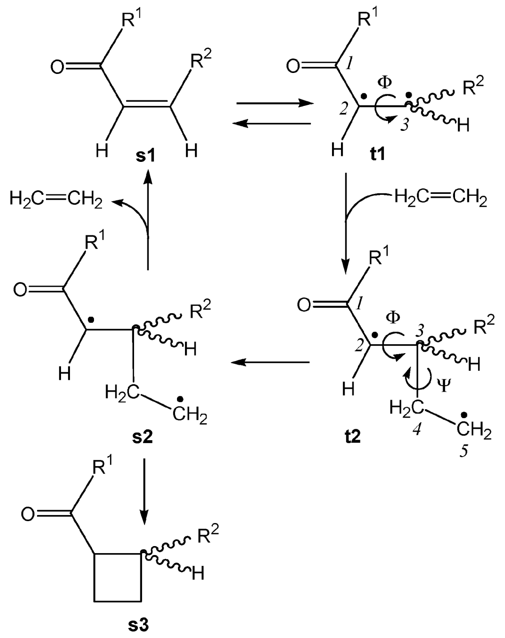

TABLE 1. Singlet-Triplet Excitation Energies[a] of α,β-Unsaturated Carbonyl Compounds Computed with B3LYP (CASSCF[b])

	ΔE	
cyclohexenone	63.9	(68.1)[c]
acrolein	57.4	(60.2)[d]
methyl acrylate	60.4	(61.5)
methyl crotonate	61.0	(62.1)

[a] In kcal mol^{-1}. [b] Six electrons in five orbitals. [c] Reference 12. [d] Reference 11.

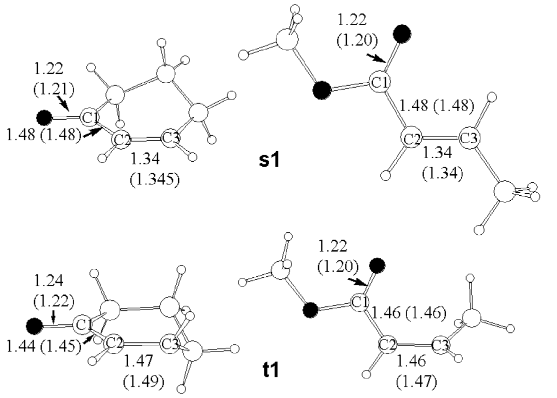

FIGURE 1. Structures of the ground state (**s1**) and $^3(\pi-\pi^*)$ excited state (**t1**) minima of 2-cyclohexenone and methyl crotonate. Selected bond distances obtained at the B3LYP (CASSCF) levels of calculation are in Å.

TABLE 2. Energies[a] Computed at the B3LYP (CASSCF[b]) Level of Calculation for Stationary Points[c] Corresponding to the Attack of Ethylene to $^3(\pi-\pi^*)$ α,β-Unsaturated Carbonyl Compounds (t1)

	cyclohexenone		acrolein[d]		methyl acrylate	methyl crotonate
TS(t1/t2a)	2.9	(11.9)	5.1	(14.6)	4.5	5.4
TS(t1/t2g-in)	1.8	(11.1)	5.0	(14.6)	4.3	5.4
TS(t1/t2g-out)	2.4	(11.7)	5.0	(14.6)	4.3	5.3
t2a	−27.6	(−18.8)	−26.2	(−15.2)	−27.2	−22.7
t2g-in	−27.4	(−18.5)	−26.0	(−15.3)	−27.4	−23.1
t2g-out	−27.7	(−19.1)	−26.1	(−14.9)	−27.3	−22.3
s2a	−28.1	(−19.3)	−27.6	(−16.8)	−29.2	−25.1
s2g-in	−27.5	(−18.6)	−26.3	(−15.3)	−28.1	−24.3
s2g-out	−28.4	(−19.6)	−26.7	(−15.2)	−28.1	−22.9

[a] Relative to **t1** + ethylene. In kcal mol^{-1}. [b] Six electrons in six orbitals. [c] See Scheme 1 and Figures 2 and 3. [d] CASSCF results taken from ref 13.

marizes the most relevant processes for the reaction between **t1** and ethylene. For an acyclic system the torsion angle around the C3−C2 bond, Φ, is close to −90°.[11] On the other hand, for cyclic compounds Φ greatly depends on the rigidity of the molecule, and values ranging between −64° and −23° have been reported for cycloheptenone and cyclopentenone, respectively.[12]

Intermediate **t1** can decay to the ground state (**s1**, Scheme 1) through an intersystem crossing. Alternatively, if its lifetime is long enough, **t1** can react with ethylene to form a triplet 1,4-biradical (**t2**). We have only considered the attack of ethylene to the β C atom of **t1**, since this has been shown to be the most favorable one for acrolein.[13] **t2** can evolve to the corresponding singlet biradical **s2** through an intersystem crossing. Once on the singlet potential energy surface there are two possible reaction paths. The first one is fragmentation into ethylene and the α,β-unsaturated carbonyl compound **s1** in its ground state (back to reactants) with a possible *Z*−*E* isomerization, whereas the alternative path leads to the formation of the corresponding cyclobutane **s3**.

Table 1 presents the adiabatic singlet−triplet excitation energies computed for 2-cyclohexenone, acrolein, methyl acrylate, and methyl crotonate. The geometries corresponding to 2-cyclohexenone and methyl crotonate in their ground and $^3(\pi-\pi^*)$ states are presented in Figure 1. We can observe a good agreement between B3LYP and CASSCF calculations both in the excitation energies and in the geometries.

The attack of ethylene to a triplet α,β-unsaturated carbonyl compound (**t1**) leads to the formation of **t2**. This intermediate can present several conformers arising from the rotation around the C4−C3 bond (see Scheme 1). In particular, we have considered the following conformers: *anti* (**t2a**, ψ around 180°), *gauche-in* (**t2g-in**, ψ around +60°), and *gauche-out* (**t2g-out**, ψ around −60°).

The potential energy barriers and reaction energies for the formation of these **t2** intermediates are presented in Table 2. The structures of the stationary points corresponding to the reactions of 2-cyclohexenone and methyl crotonate are shown in Figures 2 and 3, respectively.

Table 2 shows that, for a particular α,β-unsaturated carbonyl compound, the three conformers of **t2** all have very similar energies and that the corresponding energy barriers are also very similar. The comparison between values obtained at different levels of theory shows that the CASSCF method overestimates the potential energy barriers and underestimates the exothermicity of the formation of **t2** with respect to B3LYP. Similar results have already been reported for other cycloaddition reactions[22,23] and are due to the lack of dynamical electron correlation in the CASSCF calculations. Regardless of

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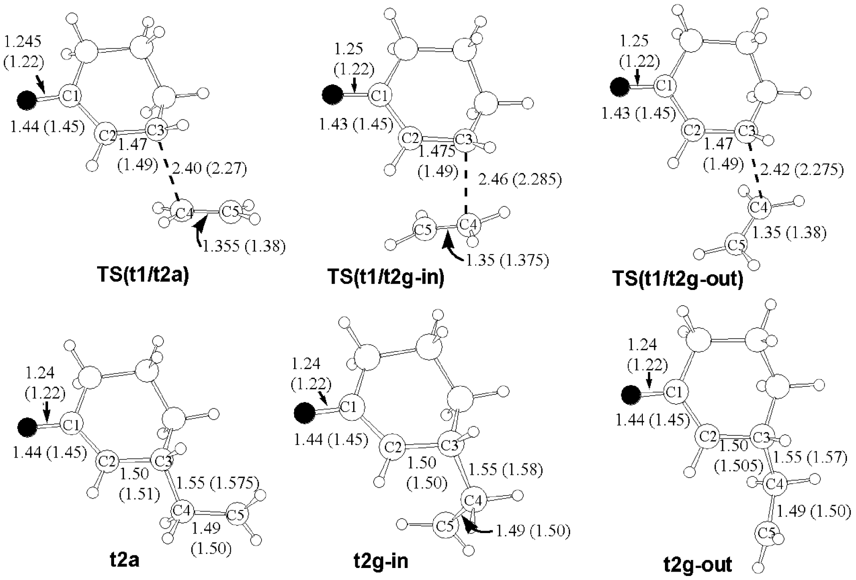

FIGURE 2. Structures of stationary points corresponding to the attack of ethylene to $^3(\pi-\pi^*)$ 2-cyclohexenone **t1**. Selected interatomic distances obtained at the B3LYP (CASSCF) levels of calculation are in Å.

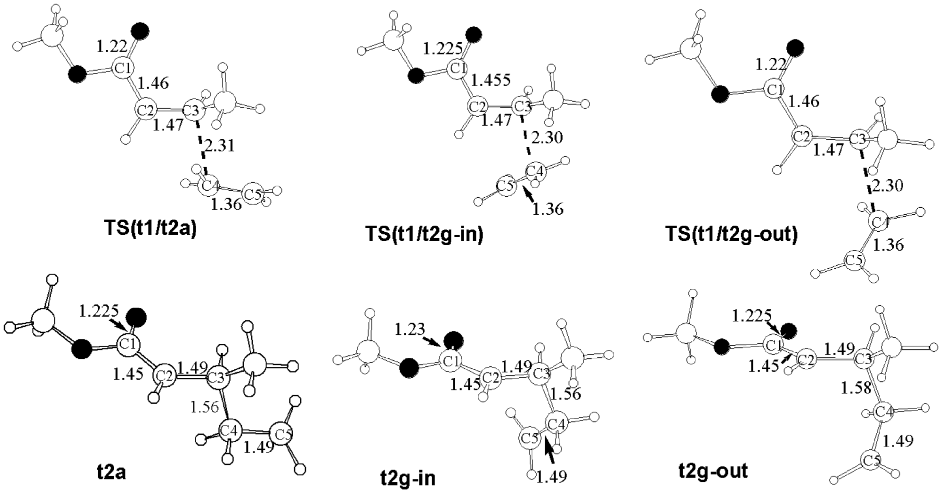

FIGURE 3. Structures of stationary points corresponding to the attack of ethylene to $^3(\pi-\pi^*)$ methyl crotonate **t1**. Selected interatomic distances obtained at the B3LYP level of calculation are in Å.

these differences, the results obtained with both methods show that, for the acyclic systems, the potential energy barriers corresponding to the formation of **t2** are notably larger than for 2-cyclohexenone.

Regarding the geometries of the transition states (see Figures 2 and 3), we can observe that the C4–C3 distance is larger for the B3LYP transition states than for the CASSCF ones. The values of C3–C2 and C5–C4 show that B3LYP predicts earlier transition states than CASSCF. For methyl crotonate the C4–C3 distances at the transition states are slightly shorter than for 2-cyclohexenone, so that for the acyclic system the transition state appears later on the reaction coordinate. A similar result is observed for acrolein and methyl acrylate.

The next step in the process is intersystem crossing to the ground-state potential energy surface. For the reaction between acrolein and ethylene, Wilsey et al.[13] have shown that in the region of the 1,4-biradical intermediate, the triplet and the singlet potential energy surfaces are very close in energy, so that there is a large range of geometries over which intersystem crossing can occur. We have optimized the geometries of several conformers of the singlet 1,4-biradicals (**s2**). Their energies, which have been included in Table 2, are very similar to those of the triplet biradicals (**t2**). The structures of the **s2** intermediates corresponding to the 2-cyclohexenone and methyl crotonate reactions are shown in Figures 4 and 5, respectively. By comparing these structures with the ones corresponding to the triplet potential energy surface (Figures 2 and 3) we can observe that they are very similar. Intersystem crossing will therefore be efficient in the region of **t2**.

For the B3LYP calculations on the singlet potential energy surface a spin-unrestricted formalism has been used so that they present spin-contamination and do not correspond to true singlets. However, the **s2**/**t2** energy differences computed at the B3LYP level of calculation are very similar to the CASSCF results. Spin-projec-

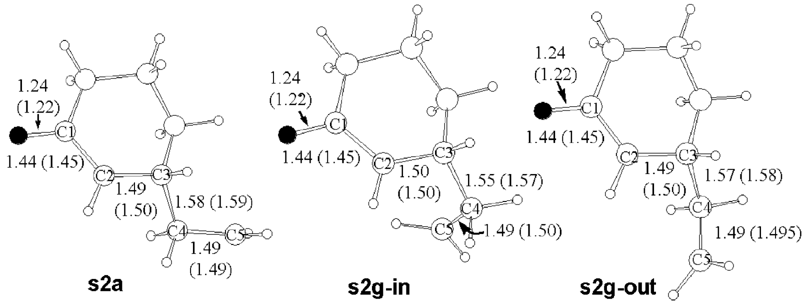

FIGURE 4. Structures of singlet 1,4-biradicals corresponding to the reaction between 2-cyclohexenone and ethylene. Selected bond distances obtained at the B3LYP (CASSCF) levels of calculation are in Å.

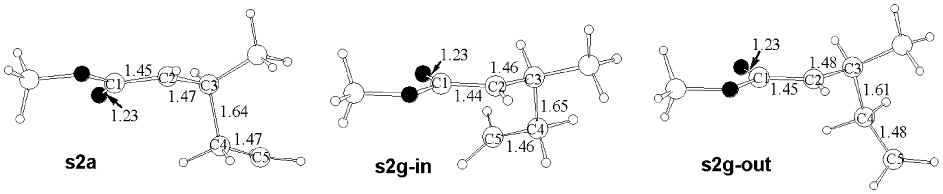

FIGURE 5. Structures of singlet 1,4-biradicals corresponding to the reaction between methyl crotonate and ethylene. Selected bond distances obtained at the B3LYP (CASSCF) levels of calculation are in Å.

tion[22,24] lowers the energy of the **s2** intermediates with respect to the values reported in Table 2. For 2-cyclohexenone the correction is always lower than 1 kcal mol^{-1}. For the acyclic systems the corrections are larger, the maximum value being 4.1 kcal mol^{-1} for the methyl crotonate **s2g-in** intermediate. Goldstein et al.[22] have shown that for the H_2 dissociation curve, the true singlet energy lies between the spin-contaminated result and the spin-projected result. As a consequence, the B3LYP results for the singlet potential energy surface can only be used with caution.

Regarding the geometries of the different conformers of **s2**, Figure 4 shows that the CASSCF and B3LYP methods lead to very similar results, the largest deviation being 0.02 Å for the C1−O bond length. Figure 5 shows that for methyl crotonate the C3−C4 bond length is slightly larger than for cyclohexenone (Figure 4). On the other hand, the C3−C2 and C4−C5 bonds are slightly shorter.

We have also located the transition states corresponding to the *anti*/*gauche* conformational rearrangements for **t2** and **s2**. The computed potential energy barriers are presented in Table 3. For 2-cyclohexenone and acrolein, there is a very close agreement between the B3LYP and CASSCF results. The energy barriers are similar for both electronic states, their values ranging between 2.7 and 5.5 kcal mol^{-1}. The largest values correspond to the *anti*/*gauche-in* rearrangement in 2-cyclohexenone and to the *anti*/*gauche-out* conversion in methyl crotonate. This result is due to the steric repulsion between the terminal methylene group of the ethylene moiety and the alkyl substituent at C3 (see Figures 2−5). For acrolein and methyl acrylate, both substituents at C3 are hydrogens and there is no such repulsion.

Once on the ground-state potential energy surface, **s2** may lead to cyclobutane or to fragmentation into **s1** and ethylene. Cyclobutane formation requires a *gauche* conformation for **s2** (**s2g-in** or **s2g-out**), while fragmentation can be produced from any of the **s2** conformers. Figure 6 presents schematic energy profiles corresponding to these processes, as well as to conformational rearrangements of **t2** and **s2**. The computed potential energy barriers are presented in Table 4, and the structures of the transition states corresponding to fragmentation for 2-cyclohexenone and methyl crotonate are shown in Figures 7 and 8, respectively.

TABLE 3. Potential Energy Barriers[a] Computed at the B3LYP (CASSCF[b]) Level of Calculation for the *anti/gauche* Conformational Rearrangements in 1,4-Biradicals

	cyclohexenone		acrolein[c]		methyl acrylate	methyl crotonate
t2a → t2g-in	5.2	(5.5)	3.1	(3.7)	3.0	3.0
t2a → t2g-out	3.1	(3.2)	3.0	(3.5)	3.0	5.0
s2a → s2g-in	4.3	(4.7)	2.7	(3.2)	3.0	3.4
s2a → s2g-out	4.2	(3.9)	3.3	(3.5)	3.2	5.3

[a] In kcal mol^{-1}. [b] Six electrons in six orbitals. [c] CASSCF results taken from ref 13.

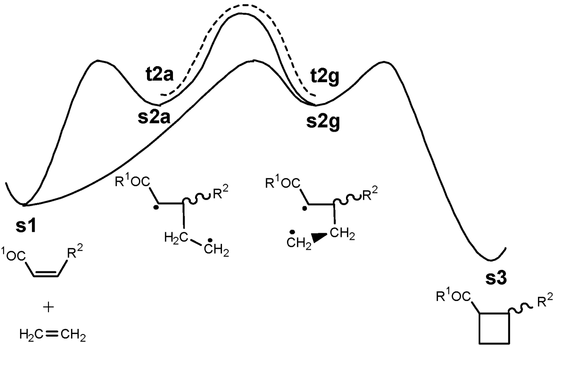

FIGURE 6. Schematic energy profile corresponding to the evolution of 1,4-biradicals on the ground (solid line) and excited (dashed line) states.

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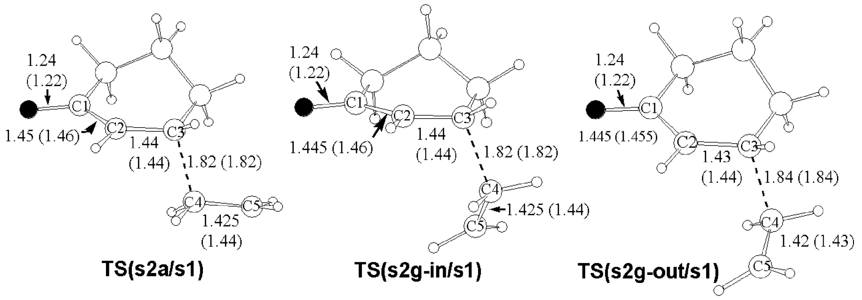
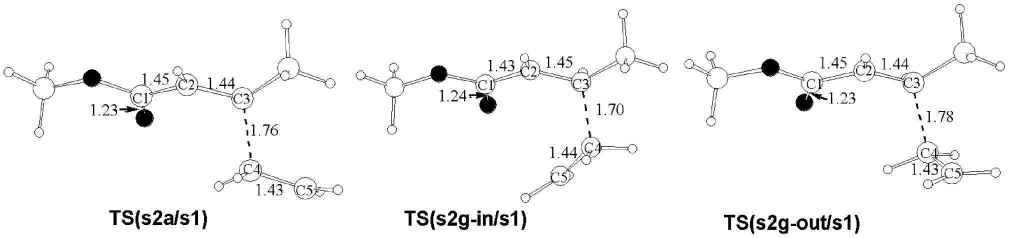


TS(s2a/s1) **TS(s2g-in/s1)** **TS(s2g-out/s1)**

FIGURE 7. Structures of transition states corresponding to the fragmentation of the singlet 1,4-biradicals corresponding to the reaction between 2-cyclohexenone and ethylene. Selected interatomic distances obtained at the B3LYP (CASSCF) levels of calculation are in Å.



TS(s2a/s1) **TS(s2g-in/s1)** **TS(s2g-out/s1)**

FIGURE 8. Structures of transition states corresponding to the fragmentation of the singlet 1,4-biradicals corresponding to the reaction between methyl crotonate and ethylene. Selected interatomic distances obtained at the B3LYP level of calculation are in Å.

TABLE 4. Potential Energy Barriers[a] Computed at the B3LYP (CASSCF[b]) Level of Calculation for Stationary Points Corresponding to the Reactions of Singlet 1,4-Biradicals

	cyclohexenone		acrolein[c]		methyl acrylate	methyl crotonate
		Cyclobutane Formation				
s2g-in → **s3**			0.1	(0.6)	0.0	
s2g-out → **s3**				(0.8)		
		Fragmentation				
s2a → **s1**	3.2	(4.0)	2.0	(2.4)	1.0	0.4
s2g-in → **s1**	5.1	(6.6)	2.8	(3.1)	-	0.1
s2g-out → **s1**	4.9	(6.7)	2.8	(3.4)	1.6	1.0

[a] In kcal mol^{-1}. [b] Six electrons in six orbitals. [c] CASSCF results taken from ref 13.

For acrolein the cyclization transition states obtained at the CASSCF level involve energy barriers in the range 0.6−0.8 kcal mol^{-1}. At the B3LYP level of calculation we have located the transition state corresponding to the *gauche-in* conformer of **s2**, with an energy barrier of only 0.1 kcal mol^{-1}. The same transition state has been located for methyl acrylate, with an energy barrier of only 0.04 kcal mol^{-1}. In all other cases, including the CASSCF calculations of the 2-cyclohexenone reaction, all attempts to locate cyclization transition states failed and lead instead to either cyclobutane or to a transition state corresponding to methylene rotation. Ring closure is very exothermic, and cyclobutanes **s3** are at least 50 kcal mol^{-1} lower in energy than **s2a** at the B3LYP level of calculation. From these results it is reasonable to assume that ring closure from a *gauche* conformer of a singlet 1,4-biradical involves very small energy barriers, so that it is expected to be very fast.

The alternative process for a singlet 1,4-biradical **s2** is fragmentation into **s1** and ethylene. The fragmentation of **s2** may take place from either a *gauche* or an *anti* conformer. Here, we have been able to locate the transition states corresponding to all the systems, and the computed potential energy barriers are given in Table 4. For the *gauche-in* conformer of the methyl acrylate system, the B3LYP transition state is 0.1 kcal mol^{-1} lower in energy than the corresponding **s2g-in** minimum. This is due to a different degree of spin-contamination (the values of $\langle S^2 \rangle$ are 0.968 for **s2g-in** and 0.495 for the transition state). In general, when the correction for spin-projection is included, all of the B3LYP transition states become lower in energy than the corresponding intermediates. All of these results show that the potential energy surface for the singlet 1,4-biradicals (**s2**) is rather flat, as has already been observed for singlet tetramethylene.[25−27]

For 2-cyclohexenone and acrolein there is a reasonably good agreement between the B3LYP and CASSCF fragmentation barriers, and the computed values are larger for 2-cyclohexenone than for acrolein. In general, the fragmentation barrier is lower for **s2a** than for the *gauche* conformers. The only exceptions are methyl acrylate and methyl crotonate where the fragmentation of **s2g-in** seems much more favorable. This may be due to a stabilizing interaction between the terminal methylene group of the ethylene moiety and the carbonyl group at the transition states (see Figure 8). This interaction is possible in the **s2g-in** intermediates of methyl acrylate and methyl crotonate, since in both cases the ester moiety presents an *s-cis* arrangement of the C=C and C=O double bonds. On the other hand, for acrolein the *s-trans* arrangement is the most favorable one, and for 2-cyclohexenone only the *s-trans* arrangement is possible.

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TABLE 5. Gibbs Energies[a] for Stationary Points Corresponding to the Formation of Triplet 1,4-Biradicals

	cyclohexenone	acrolein	methyl acrylate	methyl crotonate
TS(t1/t2a)	13.2	15.7	15.1	17.0
t2a	−14.6	−13.3	−14.7	−9.5
TS(t1/t2g-in)	12.3	15.6	14.9	16.7
t2g-in	−14.2	−13.2	−13.7	−9.0
TS(t1/t2g-out)	12.8	15.6	14.9	16.8
t2g-out	−14.7	−12.9	−14.1	−8.6

[a] Values relative to **t1** + ethylene computed at 1 atm and 298.15 K. In kcal mol^{-1}.

If we compare the fragmentation barriers (Table 4) with the conformational rearrangement barriers (Table 3), we can observe that for 2-cyclohexenone and acrolein both magnitudes are similar. For methyl acrylate and methyl crotonate, fragmentation barriers are notably lower than those corresponding to the *anti*/*gauche* rearrangement.

In general, for the *gauche* conformers the fragmentation barriers are larger than the ring-closure ones, so that the latter process is clearly the most favorable one. On the other hand, fragmentation of the *anti* conformer involves a lower energy barrier.

The results presented up to now show that in all cases the reaction of ethylene with **t1** leads to the formation of a triplet 1,4-biradical **t2**, which can easily evolve to the corresponding singlet biradical **s2**. The most favorable process for the *gauche-in* and *gauche-out* conformers is the ring closure to form the corresponding cyclobutanes, whereas for the *anti* conformer conversion to a *gauche* structure will compete with fragmentation into **s1** and ethylene. With this picture in mind, the key step seems to be the initial attack of ethylene to **t1** that will determine which conformer of the 1,4-biradical is formed preferentially.

Table 5 presents the Gibbs energy computed at the B3LYP level of calculation for the stationary points corresponding to the attack of ethylene to **t1**. For 2-cyclohexenone, the formation of **t2g-in** is more favorable than that of **t2a**, so that the formation of cyclobutane is favorable, in good agreement with experimental results. Regarding the acyclic systems, the Gibbs activation energies corresponding to the formation of the different conformers of **t2** are very similar, with a slight preference for the *gauche* intermediates. According to this result, cyclobutane formation should be observed for these systems, probably with a lower yield than for 2-cyclohexenone. However, this is not the case, so the analysis of the formation or decomposition of 1,4-biradicals is not enough to rationalize the different behavior observed for cyclic and acyclic α,β-unsaturated carbonyl compounds in the photochemical [2 + 2]-cycloadditions.

We must also take into account the fact that **t1** can also decay to **s1** through an intersystem crossing and that this process will compete with the reaction with ethylene (see Figure 9). Table 6 presents the energies necessary to reach the $^3(\pi-\pi^*)/S_0$ intersection points for the α,β-unsaturated carbonyl compounds studied here. These intersection points cannot be located using DFT methods. However, for cyclic enones we have shown that single-point B3LYP calculations at the CASSCF critical points yield energy differences in reasonable agreement with the CASSCF values.[12] The values presented in Table 6 show that the same behavior is observed for methyl acrylate and methyl crotonate.

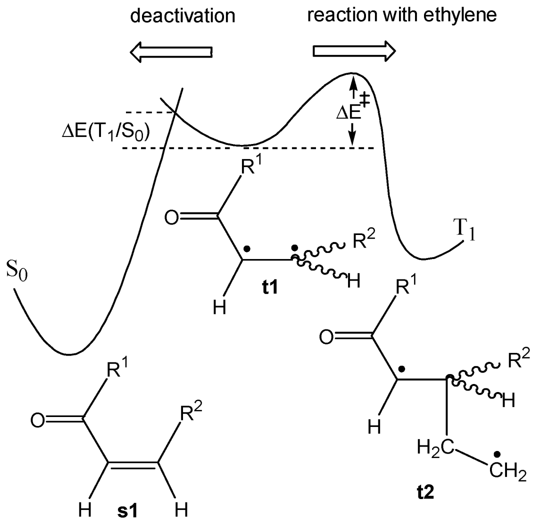

FIGURE 9. Schematic energy profiles corresponding to the competition between deactivation of a $^3(\pi-\pi^*)$ α,β-unsaturated carbonyl compound (**t1**) and its reaction with ethylene.

TABLE 6. Energy Difference[a] between the Minimum of the $^3(\pi-\pi^*)$ State (t1) and the $^3(\pi-\pi^*)/S_0$ Intersection

	CASSCF[b]	B3LYP[c]
cyclohexenone[d]	1.5	1.4
acrolein[d,e]	0.3	0.1
methyl acrylate	0.3	0.1
methyl crotonate	0.3	0.3

[a] In kcal mol^{-1}. [b] Six electrons in five orbitals. [c] Single point calculation using the CASSCF geometries. [d] Reference 12. [e] Reference 11.

These values can be compared with the potential energy barriers corresponding to the formation of the different conformers of **t1** (see Table 2). For the acyclic systems, these barriers are much larger than the energy necessary to reach the $^3(\pi-\pi^*)/S_0$ intersection point. Intersystem crossing from **t1** to **s1** is therefore strongly favored over addition of ethylene to give **t2** for acyclic systems, in agreement with experiment. On the other hand, for 2-cyclohexenone the energy barrier corresponding to the formation of **t2g-in** (1.8 kcal mol^{-1}) is similar to the energy necessary to reach the $^3(\pi-\pi^*)/S_0$ intersection (1.5−1.4 kcal mol^{-1}). Although both magnitudes are not strictly comparable, these results seem to indicate that the different behavior of cyclic and acyclic α,β-unsaturated carbonyl compounds in photochemical [2 + 2]-cycloadditions can be directly related to the lifetime of the corresponding $^3(\pi-\pi^*)$ transient intermediate.

Concluding Remarks

We have studied the ground and first triplet excited-state potential energy surfaces for the [2 + 2]-cycloadditons of 2-cyclohexenone, methyl acrylate, and methyl crotonate to ethylene. The attack of ethylene to the $^3(\pi-\pi^*)$ α,β-unsaturated carbonyl compound leads to the formation of a triplet 1,4-biradical intermediate, which evolves to the ground-state potential energy surface. This intermediate has three possible conformers arising from the rotation around the new C−C bond: *anti*, *gauche-in*, and *gauche-out*.

The evolution of these biradicals to the ground state is expected to be favorable. Once in the ground state, there are two possible reaction paths: ring closure or fragmentation. Ring closure requires a *gauche* conformer and is expected to be faster than fragmentation or *gauche/anti* rearrangement. For *anti* biradicals, fragmentation competes with the *anti/gauche* rearrangement. For 2-cyclohexenone the formation of a *gauche* 1,4-biradical is more favorable than the formation of the *anti* conformer, while for the acyclic systems there is no such preference.

However, the competition between ring-closure and fragmentation paths in the ground state potential energy surface is not enough to fully understand the experimentally observed behavior of cyclic and acylic α,β-unsaturated carbonyl compounds. The outcome of the reaction is governed by the competition between the deactivation of the $^3(\pi-\pi^*)$ α,β-unsaturated carbonyl compound and its reaction with ethylene to form the triplet 1,4-biradical. The competition between these two processes has been explicitly considered for the first time. For 2-cyclohexenone the potential energy barrier corresponding to the formation of the triplet 1,4-biradical is lower than for the acyclic systems. On the other hand, the energy necessary to reach the crossing point between the $^3(\pi-\pi^*)$ and the ground-state potential energy surfaces is much lower for the acyclic sytems than for 2-cyclohexenone. For methyl acrylate and methyl crotonate (and for acrolein[13]), deactivation of the $^3(\pi-\pi^*)$ to the ground state is expected to be faster than the formation of the 1,4-biradical, so that the [2 + 2]-cycloaddition will not take place as is experimentally observed. On the other hand, for 2-cyclohexenone the formation of the triplet 1,4-biradical is expected to be more favorable, and the process will lead to the formation of the corresponding cyclobutane.

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Supporting Information Available: Total energies and geometries of energy minima and transitions states. This material is available free of charge via the Internet at http://pubs.acs.org.

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