A Computational Study of the Factors Controlling Triplet-State Reactivity in 1,4-Pentadiene

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The triplet-state reactions of 1,4-pentadiene have been investigated using density functional theory (UB3LYP) and ab initio (CASSCF) calculations with a 6-31G* basis set. Intramolecular [2 + 2] photocycloadditions and three different reaction pathways leading to vinylcyclopropane have been examined. The computed results are in good agreement with the experimental observations, predicting the dominant product to be vinylcyclopropane produced by a di-π-methane rearrangement, and the favored [2 + 2] cycloaddition product to be bicyclo[2.1.0]pentane. Reaction pathways involving initial C−C or C−H bond cleavage were found to be too high in energy to be significant. Both the [2 + 2] cycloadditions and the di-π-methane rearrangement proceed through cyclic biradical intermediates formed on the triplet surface. The relative rates of formation of these triplet biradicals are found to depend on three factors: biradical stability, the geometry of the transition structure, and orbital interactions through bonds.

Introduction

Triplet sensitization of nonconjugated dienes such as 1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene normally gives rise to a mixture of photoproducts including intramolecular [2 + 2] cycloadducts.[1] The mechanism for the [2 + 2] cycloaddition is illustrated in Scheme 1. The first part of the reaction takes place on the triplet surface and involves the attack of the triplet-excited double bond on the second π bond forming three possible cyclic biradical intermediates. The biradicals formed then undergo intersystem crossing to the ground-state surface and subsequent ring-closure forming cross or parallel products. The final ratio of parallel:cross products depends predominantly on the relative rates of formation of the triplet biradicals, and it varies considerably depending on whether the diene has an even or odd number of carbon atoms: 1,4-pentadiene and 1,6-heptadiene forming mainly parallel products, while 1,5-hexadiene tends to form the cross product (Scheme 2).

Surprisingly, these results are found to be in conflict with the classic rules for ring-closure proposed by Baldwin.[2] Baldwin's rules, based on transition structure geometry, predict that 4- and 5-Exo-Trig should be favored over 5- and 6-Endo-Trig processes (Scheme 3), that is ring formation should occur with cleavage of the π bond exocyclic to the ring. Application of these rules to the 1,4-pentadiene system would suggest that formation of the four-membered ring biradical leading to the cross product should be favored. Other theories have been put forward to explain the alternating trend. Srinivasan suggested that the first bond formed always leads to a five-membered ring; this is commonly referred to as the "Rule of Five".[1] Gleiter and Sander constructed molecular orbital and state correlation diagrams and explained the preference for forming five-membered ring biradicals in 1,4-pentadiene and 1,5-hexadiene in terms of the electronic structures of the transition states involved.[3] Verhoeven also proposed that orbital interactions may be involved.[4] He suggested that reactions leading to the formation of odd-membered rings were "sigma-assisted", whereas those leading to even-membered rings were "sigma-resisted", based on the idea of in-phase and out-of-phase combinations of through-bond and through-space interactions originally discussed by Hoffmann and co-workers.[5] We recently used a similar concept to explain the preference for cleaving three-membered rings relative to four-membered rings in bridged cyclohexanes and alkoxy radicals.[6]

In addition to [2 + 2] cycloadducts, 1,4-pentadiene gives rise to a high yield of vinylcyclopropane on triplet sensitization. The ratio of vinylcyclopropane to cycloadducts is about 9:1, although methyl substitution at the 2- and 4-positions of the diene dramatically reduces this ratio to 2:7 in favor of the cycloadducts. H-transfer and dissociation/recombination processes were originally suggested as possible pathways leading to these cyclopropyl products.[7] Nowadays it is generally believed that 1,4-pentadiene forms vinylcyclopropane by the well-known di-π-methane rearrangement of Zimmerman[8] (Scheme 4)

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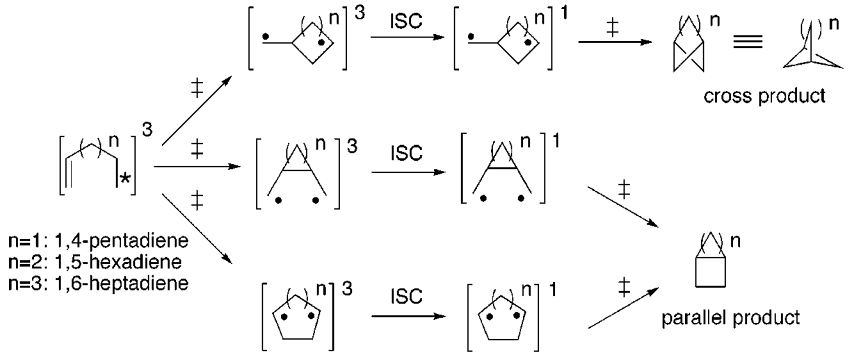
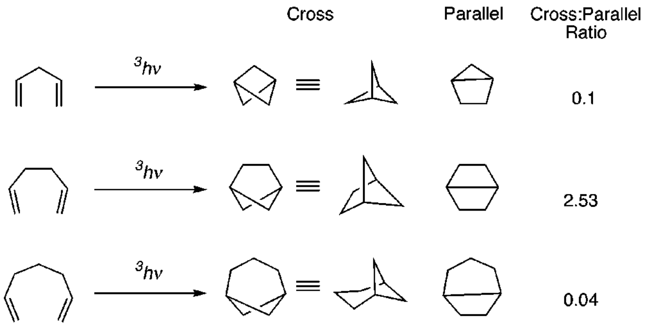
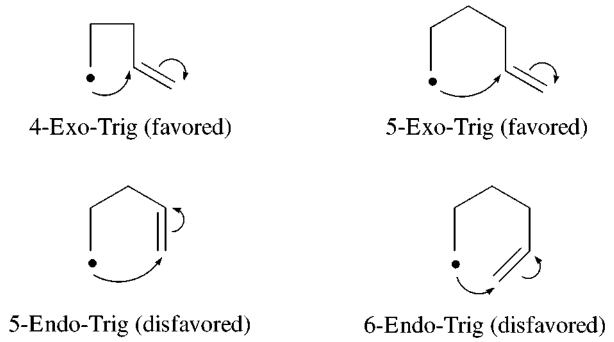
Scheme 1



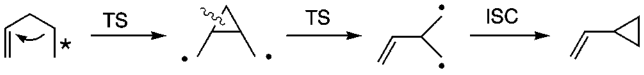
Scheme 2



Scheme 3



Scheme 4



that has been observed on the photosensitization of many different 1,4-dienes.[9] It should be noted that this mechanism is distinct from that of the excited-state singlet reaction which is believed to be quasi-concerted, with decay to the ground-state surface occurring via a conical intersection, bypassing the formation of any stable biradical intermediates.[10]

Some computational work has been carried out previously on 1,4-pentadiene. Ohsaku et al. examined the parallel and cross cycloaddition of 1,4-pentadiene using UHF/6-31G* calculations.[11] They found that a barrier on the triplet surface leading to the four-membered ring biradical which was 22 kcal/mol above that leading to the five-membered ring in qualitative agreement with the 10:1 preference for parallel product formation observed experimentally.[7] They also showed that singlet/triplet crossing points exist close to both biradicals, consistent with the idea that intersystem crossing occurs in these regions.[12]

The triplet di-π-methane rearrangement has also been studied computationally. Davidson and co-workers examined the mechanism using MC−SCF/STO-3G geometry optimizations with single-point energies calculated using SDCI calculations with an SVP (split-valence with polarization functions) basis set.[13] They located two triplet biradical intermediates and a transition structure connecting them, and predicted an activation energy of about 15 kcal/mol for the reaction starting from the cis conformer of triplet pentadiene. A detailed mechanistic study of the related photochemical oxadi-π-methane rearrangement of but-3-enal found analogous stable 1,4- and 1,3-biradicals on the lowest energy triplet surface.[14]

In this paper, a more detailed and complete investigation of the triplet rearrangements of 1,4-pentadiene using UB3LYP/6-31G* and CASSCF/6-31G* calculations is described. The primary aim of the study is to analyze the factors controlling the initial bond formation on the triplet surface. It was shown that orbital interactions through bonds can be used to explain the relative rates of ring cleavage in neutral and radical systems;[6] here the effect of these interactions on the rates of biradical ring formation in triplet 1,4-pentadiene is examined and the factors leading to the breakdown of Baldwin's rules in this system are identified.

Computational Methods

All energies were computed using both the UB3LYP and CASSCF (complete active space self-consistent field) methods and the 6-31G* basis set in GAUSSIAN 94.[15] CASSCF normally reproduces the topology of potential energy surfaces accurately as it includes nondynamic correlation energy and is therefore able to describe homolytic bond cleavage and near-

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Table 1. UB3LYP/6-31G* Energies (Uncorrected and Zero-Point Energy Corrected), ⟨S^2⟩ Values, and Uncorrected CAS(8,8)/6-31G* Energies for the Reactions of Triplet-Sensitized 1,4-Pentadiene

structure	state	UB3LYP Erel (kcal/mol)	⟨S^2⟩	UB3LYP Erel+ZPE (kcal/mol)	CAS(8,8) Erel (kcal/mol)
Reactant					
trans (C_2) min **3a**	S_0	0.0	0.00	0.0	0.0
triplet trans min **3d**	$^3(\pi\pi^*)$	64.2	2.00	60.9	65.9
cis (C_s) min **3b**	S_0	0.7	0.00	0.6	0.5
triplet cis min **3e**	$^3(\pi\pi^*)$	64.3	2.00	61.0	65.9
envelope min **3c**	S_0	0.6	0.00	0.6	0.9
triplet *envelope* min **3f**	$^3(\pi\pi^*)$	64.7	2.00	61.3	66.2
Five-Membered Ring Pathway					
triplet TS (path A) **4a**	$^3(\pi\pi^*)$	78.4	2.04	75.0	87.7
triplet min **4b**	$^3(\pi\pi^*)$	42.6	2.01	40.8	53.5
min **4c**	S_0	43.2	1.01	41.5	54.5
closure TS **4e**	S_0	46.2	0.83	44.5	56.7
cleavage TS **4f**	S_0	64.4	0.76	62.1	74.3
bicyclo[2.1.0]pentane (parallel) **4g**	S_0	11.0	0.00	12.9	25.0
Four-Membered Ring Pathway					
triplet TS (path B) **5a**	$^3(\pi\pi^*)$	97.5	2.05	93.4	105.2
triplet TS (path C) **5b**	$^3(\pi\pi^*)$	80.3	2.03	76.5	90.7
triplet min **5c**	$^3(\pi\pi^*)$	67.2	2.01	64.1	77.2
min **5d**	S_0	67.2	1.01	64.1	77.2
closure TS **5f**	S_0	71.8	0.75	69.9	78.1
cleavage TS **5g**	S_0	72.4	0.81	69.8	81.6
bicyclo[1.1.1]pentane (cross) **5h**	S_0	23.4	0.00	25.7	38.3
Three-membered Ring Pathway					
triplet trans TS (path D) **6a**	$^3(\pi\pi^*)$	75.5	2.03	71.6	85.4
triplet cis TS (path D) **6b**	$^3(\pi\pi^*)$	75.5	2.03	72.3	85.5
triplet trans min **6c**	$^3(\pi\pi^*)$	66.2	2.01	62.8	75.9
	S_0	65.2[a]	0.97		75.6[a]
triplet cis min **6d**	$^3(\pi\pi^*)$	66.8	2.01	63.2	76.2
	S_0	65.6[a]	0.97		74.1[a]
Di-π-methane Pathway					
triplet trans C2−C3 cleavage TS **7a**	$^3(\pi\pi^*)$	76.5	2.03	72.1	86.3
triplet cis C2−C3 cleavage TS **7b**	$^3(\pi\pi^*)$	77.5	2.03	73.1	87.0
triplet trans C2−C3 cleavage min **7c**	$^3(\pi\pi^*)$	68.0	2.01	63.7	69.3
	S_0	68.5[a]	1.01		70.5[a]
triplet cis C2−C3 cleavage min **7d**	$^3(\pi\pi^*)$	69.0	2.01	64.9	70.4
	S_0	69.4[a]	1.00		71.5[a]
vinylcyclopropane (trans) **7e**	S_0	3.8	0.00	4.5	13.8
vinylcyclopropane (cis) **7f**	S_0	5.4	0.00	6.1	14.7
Dissociation/Recombination Pathway					
triplet trans cleavage TS **8a**	$^3(\pi\pi^*)$	96.8	2.03	91.6	100.8
triplet cis cleavage TS **8b**	$^3(\pi\pi^*)$	97.0	2.03	91.8	100.7
triplet trans cleavage TS **8c**	$^3(\pi\pi^*)$				100.9
triplet cis cleavage TS **8d**	$^3(\pi\pi^*)$				101.7
allyl **8e** + vinyl **8f** radicals	$D_0 + D_0$	85.5		78.6	80.0
cyclopropyl **8g** + vinyl radicals	$D_0 + D_0$	114.9		108.5	113.6
H-Transfer Pathway					
triplet trans H-transfer TS **9a**	$^3(\pi\pi^*)$	99.3	2.02	93.2	111.8
triplet cis H-transfer TS **9b**	$^3(\pi\pi^*)$	99.1	2.02	93.2	112.0
triplet trans minimum **9c**	$^3(\pi\pi^*)$	48.2	2.03	44.7	52.7
	S_0	48.4[a]	1.02		53.2[a]
triplet cis minimum **9d**	$^3(\pi\pi^*)$	49.2	2.03	45.8	54.2
	S_0	49.5[a]	1.02		55.2[a]
trans closure TS **9e**	S_0	49.1	1.03	45.3	53.9
cis closure TS **9f**	S_0	50.0	1.03	46.4	
vinylcyclopropane (trans)	S_0	3.8	0.00	4.5	11.1
vinylcyclopropane (cis)	S_0	5.4	0.00	6.1	12.3

[a] Ground-state energy computed at triplet-optimized geometry.

degeneracy effects correctly. In addition, algorithms are available in GAUSSIAN 94 to optimize singlet/triplet crossing points and to compute spin−orbit coupling constants which are of particular interest in this system. However CASSCF is known to lack dynamic correlation energy that can lead to errors in the energies, and frequency calculations can be prohibitively expensive with large active spaces. UB3LYP, on the other hand, has been shown to give remarkably good energetics for many different ground-state reactions and is cheap enough to carry out analytical vibrational frequency analyses. The main controversy surrounding the DFT method concerns the fact that the wave functions are not exact eigenfunctions of the S^2 operator. This often causes the energies of ground-state biradicaloid species to be spin contaminated as the triplet surface becomes close in energy. The expectation values of the S^2 operator provide a measure of this spin contamination, and these are given alongside the DFT energies in Table 1. Although some of the ground-state biradicaloid species in this system are affected by spin contamination, the central arguments of the paper are concerned with the barriers on the triplet surface, so these effects will not be discussed further.

For the CASSCF calculations, an active space comprising eight electrons in eight orbitals was used including the four π orbitals, and the σ orbitals in the C2−C3 and C3−H bonds

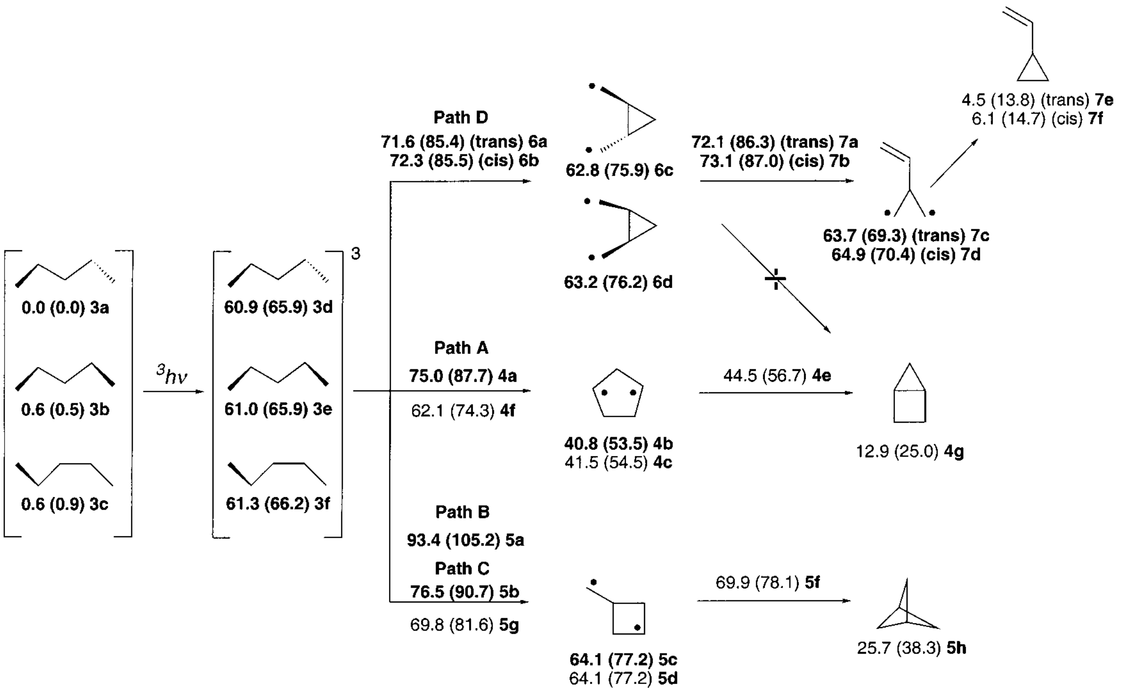

Figure 1. Reaction pathways for triplet 1,4-pentadiene leading to intramolecular [2 + 2] cycloaddition products (parallel and cross) and di-π-methane rearrangement product (vinylcyclopropane). The UB3LYP/6-31G* energies (with zero-point energy corrections) are shown in kcal/mol relative to the energy of ground-state *trans*-pentadiene, with the uncorrected CAS(8,8)/6-31G* energies given in parentheses. Triplet energies are shown in bold text and singlet energies in plain text. The corresponding figure numbers are given after each energy.

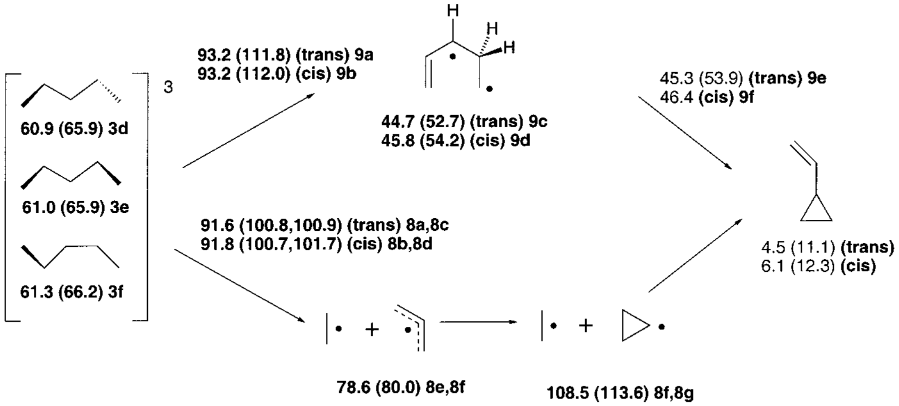

Figure 2. Alternative reaction pathways (H-transfer and dissociation/recombination) leading to vinylcyclopropane. The UB3LYP/6-31G* energies (with zero-point energy corrections) are shown in kcal/mol relative to the energy of ground-state *trans*-pentadiene, with the uncorrected CAS(8,8)/6-31G* energies given in parentheses. Triplet energies are shown in bold text and singlet energies in plain text. The corresponding figure numbers are given after each energy.

that are broken in the di-π-methane rearrangement and H-shift pathways, respectively. Singlet/triplet crossing points were optimized using CAS(6,6)/6-31G* calculations without the C2−C3 σ orbitals. These were located using the algorithm in GAUSSIAN 94 which optimizes the lowest energy point on an n-1-dimensional singlet/triplet crossing seam where the two surfaces are degenerate (n is the number of degrees of freedom in the molecule).[16] Spin−orbit coupling constants were also computed at these points using a one-electron approximation with the effective nuclear charges of Koseki et al.[17]

Results

Four different types of triplet-state reaction were examined: (i) intramolecular [2 + 2] cycloadditions, (ii) the di-π-methane rearrangement, (iii) a dissociation/recombination mechanism involving initial C2−C3 bond cleavage, and (iv) a H-transfer mechanism. The overall results are illustrated in Figures 1 and 2, and a complete listing of the energies can be found in Table 1. The UB3LYP and CASSCF results are in good agreement with each other although the CASSCF results are generally 5−10 kcal/mol higher in energy. The surface topologies are very similar with only a few minor differences that will be discussed below. The energies given in the following text are the zero-point energy corrected UB3LYP energies unless stated otherwise.

1,4-Pentadiene has several low-energy ground-state conformers. The three lowest energy structures differ in

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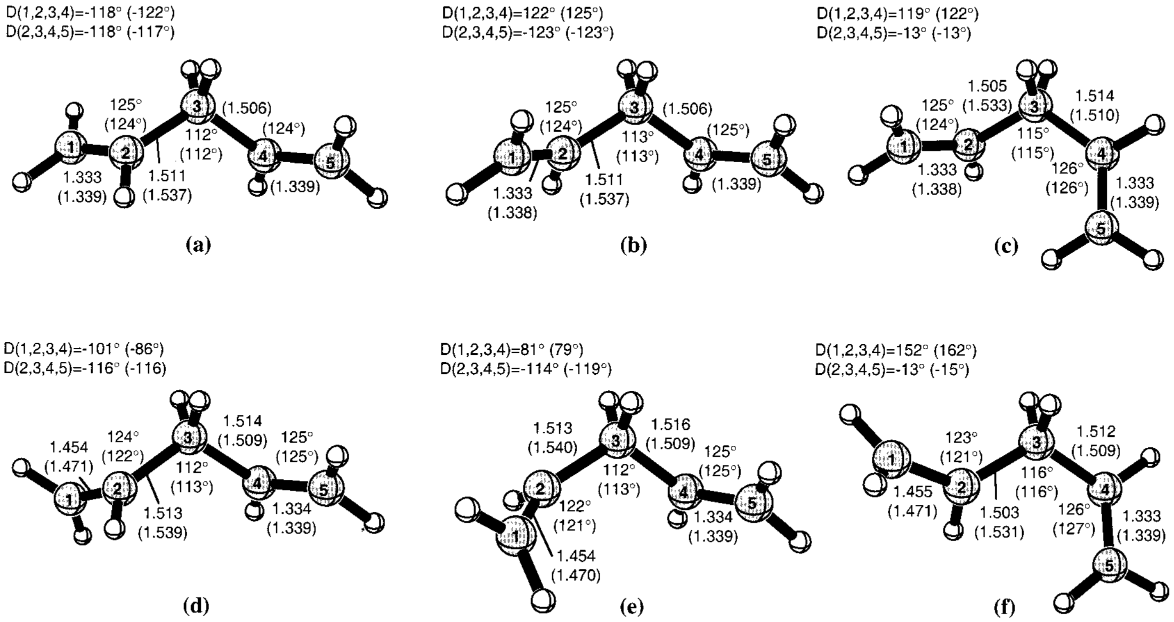
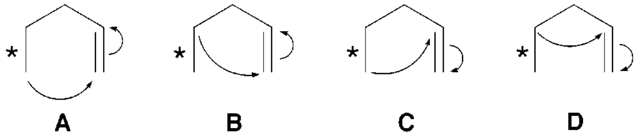


Figure 3. UB3LYP/6-31G*-optimized geometries of the ground-state and triplet-state reactants, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) S_0 trans conformer (C_2 symmetric), (b) S_0 cis conformer (C_s symmetric), (c) S_0 *envelope* conformer, (d) T_1 trans conformer, (e) T_1 cis conformer, and (f) T_1 *envelope* conformer.

Scheme 5



energy by less than 1 kcal/mol and are shown in Figure 3a–c. The trans conformer (Figure 3a) has C_2 symmetry and is the lowest in energy; the energies in Table 1 and Figures 1 and 2 are given relative to this structure. The C_s cis conformer (Figure 3b) and the *envelope* conformer (Figure 3c) both lie 0.6 kcal/mol higher in energy, respectively. The corresponding triplet ($\pi\pi^*$) conformers (Figure 3d–f) are structurally similar but the triplet excited double bond is longer (about 1.46 Å) and the terminal methylene group is twisted. These structures lie some 61 kcal/mol higher in energy than their ground-state counterparts. The structures shown in Figures **3e**, **3f** were located previously by Ohsaku and co-workers at the UHF level.[11]

(i) [2 + 2] Photocycloadditions. The first step in the photocycloadditions involves the attack of the triplet excited double bond on the second π bond forming a triplet biradical intermediate. Scheme 5 shows the four possible ways (A–D) in which initial bond formation can occur leading to five- (A), four- (B and C), or three-membered (D) rings. The transition structures, biradical intermediates, and singlet/triplet crossing points corresponding to each of these paths have been located and the optimized geometries can be found in Figures 4–6.

The transition structure (Figure 4a) corresponding to the formation of a C1–C5 bond from *cis*-pentadiene (path A) lies 14.0 kcal/mol above the cis triplet conformer. The five-membered ring biradical formed is a stable intermediate on both the triplet and ground-state surfaces, and the optimized geometries (Figure 4b,c) are similar to the UHF/6-31G* structures.[11] At both the UB3LYP and CASSCF levels of theory, the singlet and triplet biradicals differ by only 1 kcal/mol and have similar geometries. The lowest energy point on the singlet/triplet crossing seam was optimized using CASSCF, and the geometry is shown in Figure 4d. The computed spin–orbit coupling at the crossing point is zero, indicating that the five-membered ring corresponds to an almost "perfect" biradical where there is no interaction between the two radical centers, i.e., the triplet and singlet biradicals differ only by the relative spins of the two unpaired electrons. The negligible spin–orbit coupling implies intersystem crossing will be slow,[18] although the presence of minima on both the triplet and the ground-state surfaces will increase the probability of a transition occurring.

Once on the ground-state surface, closure to form the parallel product, bicyclo[2.1.0]pentane (Figure 4g), competes with C1–C5 bond cleavage back to 1,4-pentadiene. The transition structures for these two processes (shown in Figure 4e,f) lie 3.0 and 20.6 kcal/mol above the singlet biradical, respectively, indicating that ring closure will be strongly favored over C1–C5 cleavage after intersystem crossing to the ground-state surface has occurred.

There are two possibilities for forming a four-membered ring biradical, shown as paths B and C in Scheme 5. These correspond to 4-Endo-Trig and 4-Exo-Trig processes, respectively, using the terminology coined by Baldwin.[2] The transition structure for path B leading from the *envelope* conformer of pentadiene to the four-membered ring biradical was previously optimized at the UHF level and the UB3LYP- and CASSCF-optimized geometries for this transition structure are shown in Figure 5a. At the UB3LYP level, this transition structure lies 18.4 kcal/mol above the five-membered ring transition structure. However, as predicted by Baldwin's rules, the 4-Exo-Trig process (path C) is the favored pathway for four-membered ring formation. The transition structure leading to the four-membered ring from *cis*-cyclo-

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[18] The probability of intersystem crossing can be related to the spin–orbit coupling constant using the form of the Landau–Zener formula adapted by Yarkony, see: Yarkony, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5406.

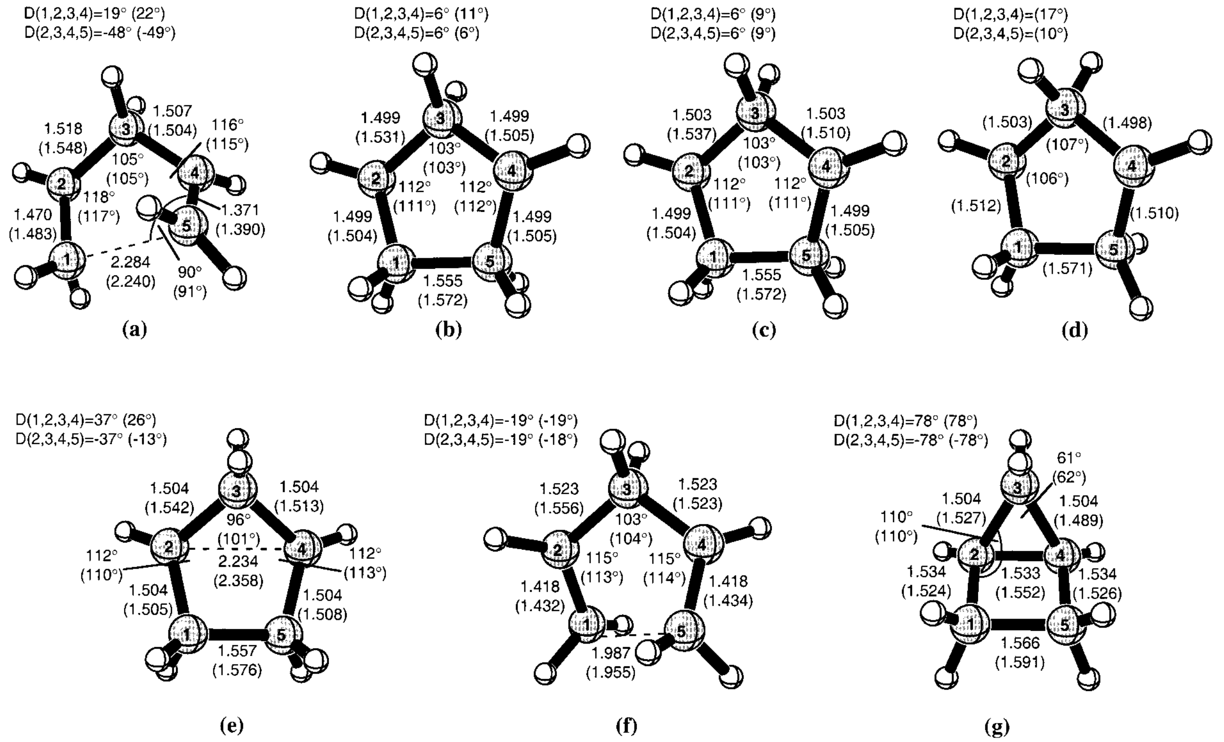

Figure 4. UB3LYP/6-31G*-optimized geometries for the five-membered ring pathway, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) T_1 transition structure for forming the C1−C5 bond, (b) T_1 five-membered ring biradical intermediate, (c) S_0 five-membered ring biradical intermediate, (d) T_1/S_0 crossing point (optimized using CAS(6,6)/6-31G*), (e) S_0 transition structure for closure to form the parallel product, (f) S_0 transition structure for cleaving the C1−C5 bond, and (g) S_0 parallel product (bicyclo[2.1.0]pentane).

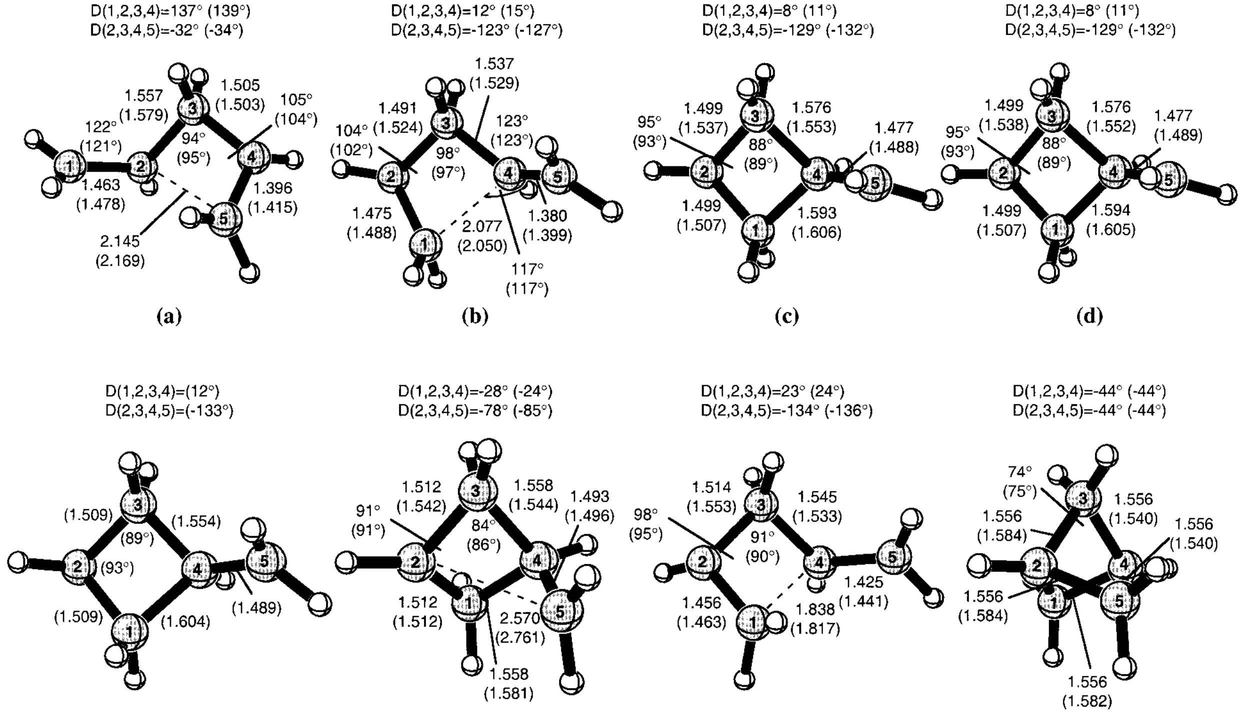

Figure 5. UB3LYP/6-31G*-optimized geometries for the four-membered ring pathway, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) T_1 transition structure for forming the C2−C5 bond, (a) T_1 transition structure for forming the C1−C4 bond, (c) T_1 four-membered ring biradical intermediate, (d) S_0 four-membered ring biradical intermediate, (e) T_1/S_0 crossing point (optimized using CAS(6,6)/6-31G*), (f) S_0 transition structure for closure to form the cross product, (g) S_0 transition structure for cleaving the C1−C4 bond, and (h) S_0 cross product (bicyclo[1.1.1]pentane).

pentadiene via pathway C (Figure 5b) lies 16.9 kcal/mol below the transition structure for path B, and only 1.5 kcal/mol above the transition structure leading to the five-membered ring biradical. This energy difference is

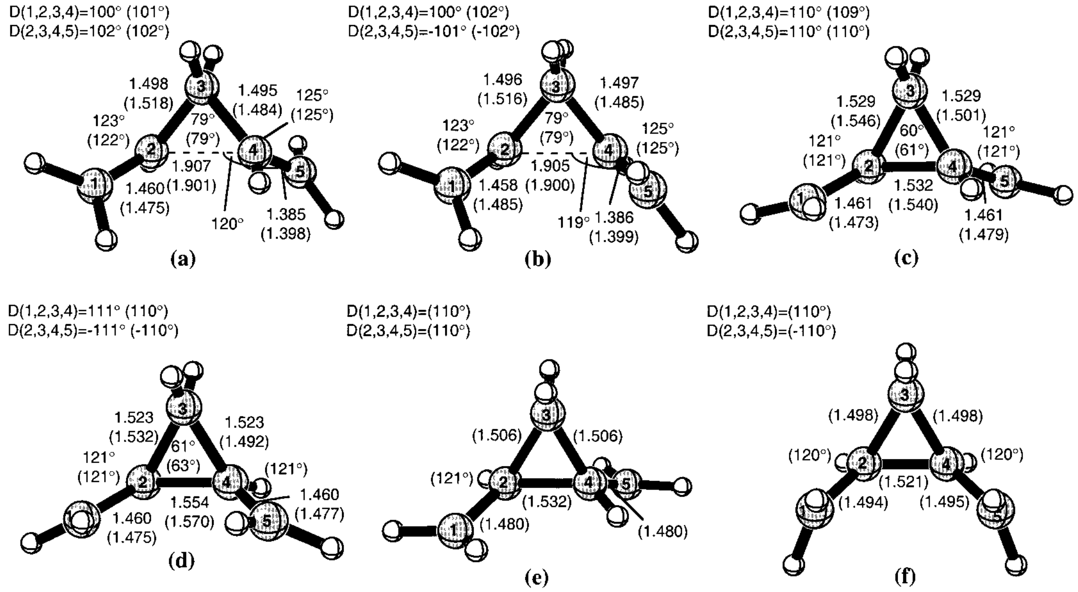

Figure 6. UB3LYP/6-31G*-optimized geometries for the three-membered ring pathway, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) T_1 transition structure for forming the C2−C4 bond (trans), (b) T_1 transition structure for forming the C2−C4 bond (cis), (c) T_1 three-membered ring biradical intermediate (trans), (d) T_1 three-membered ring biradical intermediate (cis), (e) T_1/S_0 crossing point (trans) (optimized using CAS(6,6)/6-31G*), and (f) T_1/S_0 crossing point (cis) (optimized using CAS(6,6)/6-31G*).

in good agreement with the 10:1 ratio of parallel:cross products observed experimentally.

Both transition structures lead to formation of the four-membered ring triplet biradical shown in Figure 5c. Like the five-membered ring biradical, the four-membered ring triplet biradical is degenerate with a stable intermediate on the ground-state surface (Figure 5d) and the CASSCF-optimized singlet/triplet crossing point is shown in Figure 5e. As before, the computed spin−orbit coupling at the crossing point is very small (0.1 cm^{-1}) such that the probability of intersystem is expected to be low, but may be increased by the topologies of the triplet and the ground-state surfaces which parallel each other over a wide range of geometries. The ground-state biradical can close to form the cross product, bicyclo[1.1.1]pentane (Figure 5h), or cleave the C1−C4 bond to reform the ground-state diene. The optimized transition structures for these two processes are shown in Figure 5f,g and correspond to barriers of 5.8 and 5.7 kcal/mol, respectively, indicating a small preference for reversion to the reactant molecule. The uncorrected CASSCF/6-31G* barriers are smaller (0.9 and 4.4 kcal/mol) and favor ring closure.

Formation of a three-membered ring biradical (path D) can occur from either *trans*- or *cis*-pentadiene via the transition structures shown in Figure 6a,b. The barriers for C2−C4 bond formation are only 10.7 and 11.3 kcal/mol leading to trans (Figure 6c) and cis biradicals (Figure 6d), respectively. Path D is in fact the lowest energy pathway of the four reaction paths considered; the transition structures lie 2−3 kcal/mol below the transition structure for forming the five-membered ring, and 4−5 kcal/mol below the transition structure for forming the four-membered ring. However, although the three-membered biradicals are stable intermediates on the triplet surface, they are not stable species on the ground-state surface. Singlet/triplet crossing points were optimized (Figure 6e,f), but the calculations indicate that intersystem crossing would lead directly back to the reactant diene and not to parallel products as might be expected. Again the computed spin−orbit coupling constants at the crossing points are small (0.1 and 0.2 cm^{-1}). Intersystem crossing in this case is expected to be less favorable than at the five- and four-membered ring biradicals as there is no minimum on the ground-state surface such that the triplet and singlet surfaces are degenerate over a smaller range of geometries.

(ii) Di-π-methane Rearrangement. Two types of bond cleavage in the trans and cis three-membered ring triplet biradicals (Figure **6c**, **6d**) compete with intersystem crossing to the ground-state surface. Cleavage of the C2−C4 bond via the structures shown in Figure **6a**, **6b** would lead back to the triplet reactant. Alternatively the C2−C3 bond can break (via the transition structures in Figure **7a**, **7b**) leading to trans and cis triplet 1,3-biradicals (Figure 7c,d) where the unpaired electrons are located on C3 and C5 and a new double bond has formed between C1 and C2. The barriers for these two processes are similar as predicted by Davidson,[13] 8.8 kcal/mol (trans) and 9.1 kcal/mol (cis) for C2−C4 cleavage, and 9.3 kcal/mol (trans) and 9.9 kcal/mol (cis) for C2−C3 cleavage. The triplet 1,3-biradicals lie 1−2 kcal/mol above the three-membered ring biradicals. At these geometries the ground-state surface lies about 1 kcal/mol above the triplet surface which implies that intersystem crossing will occur in this region although a singlet/triplet crossing point could not be fully optimized. The ground-state biradicals formed are unstable with respect to torsions of the methylene groups and will readily close to form *trans*- and *cis*-vinylcyclopropane (Figure 7e,f).

(iii) Dissociation/Recombination Mechanism. An alternative pathway leading to vinylcyclopropane involves initial cleavage of the C2−C3 bond followed by radical recombination (Figure 2). There are four possible transition-state conformations for cleaving the C2−C3 bond depending on the C1C2C3C4 dihedral angle and the orientation of the H atom on C2. At the UB3LYP level only two of these conformers are stable; these are the

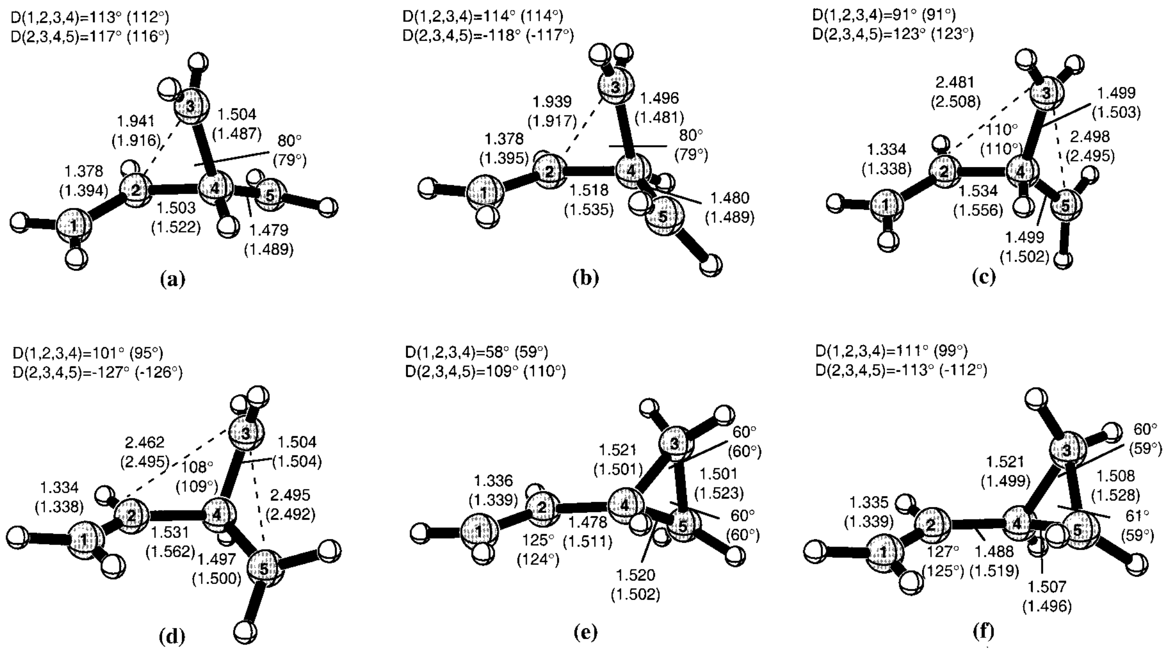

Figure 7. UB3LYP/6-31G*-optimized geometries for the di-π-methane pathway, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) T_1 transition structure for cleaving the C2−C3 bond (trans), (b) T_1 transition structure for cleaving the C2−C3 bond (cis), (c) T_1 biradical intermediate (trans), (d) T_1 biradical intermediate (cis), (e) S_0 *trans*-vinylcyclopropane, and (f) S_0 *cis*-vinylcyclopropane.

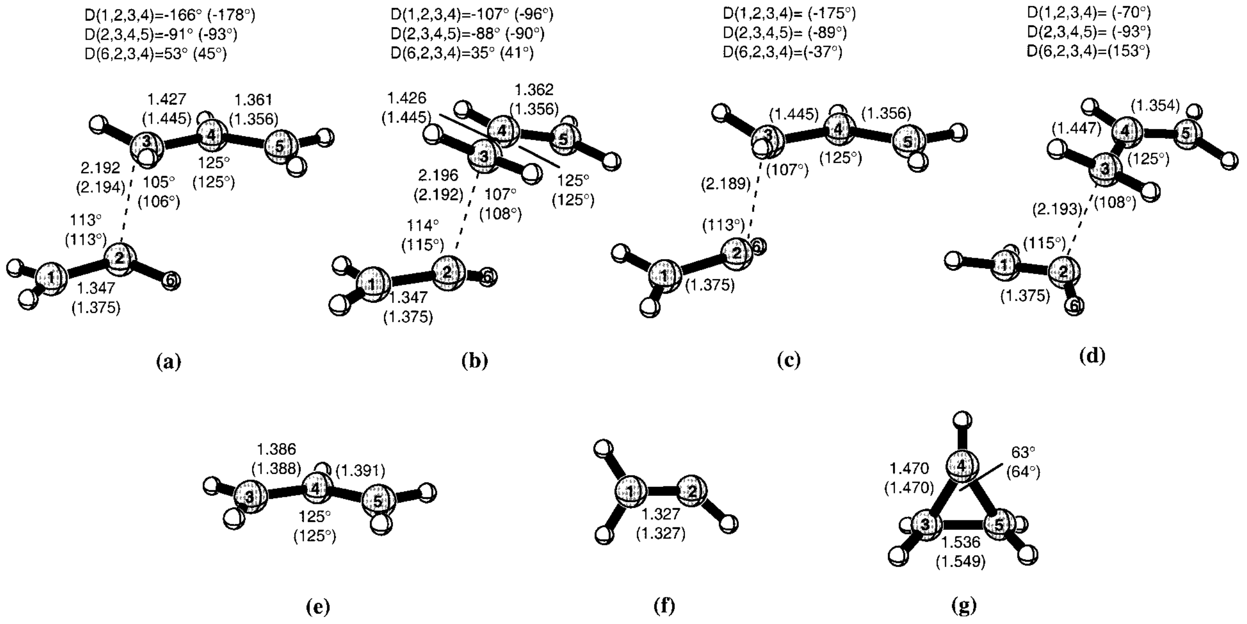

Figure 8. UB3LYP/6-31G*-optimized geometries for the dissociation/recombination pathway, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) T_1 trans transition structure for cleaving the C2−C3 bond, (b) T_1 cis transition structure for cleaving the C2−C3 bond, (c) T_1 trans transition structure for cleaving the C2−C3 bond, (d) T_1 cis transition structure for cleaving the C2−C3 bond, (e) allyl radical, (f) vinyl radical, and (g) cyclopropyl radical.

trans and cis transition structures shown in Figure 8a,b, respectively. At the CASSCF level all four conformers were optimized (Figure 8a−d) and were found to lie within 1 kcal/mol of each other.

The cleavage transition structures lie 20 kcal/mol above the transition structures leading to formation of the three-membered ring biradical so this reaction is unlikely to compete effectively. Bond cleavage would lead to the formation of allyl (Figure **8e**) and vinyl (Figure **8f**) radicals. These radicals could recombine to reform ground-state pentadiene with no barrier, or the allyl radical could close to form a cyclopropyl radical (Figure **8g**) which could recombine with a vinyl radical to form vinylcyclopropane.

(iv) H-Transfer Mechanism. Figure 2 shows a third possible pathway leading to vinylcyclopropane that involves a hydrogen atom transfer from C3 to C2, followed by intersystem crossing and ring closure. Two transition structures (trans and cis) for the H-transfer were optimized, and these are shown in Figure 9a,b. They have carbon skeletons that are nearly planar, and the bridging H atom has bond-breaking and bond-forming bond lengths

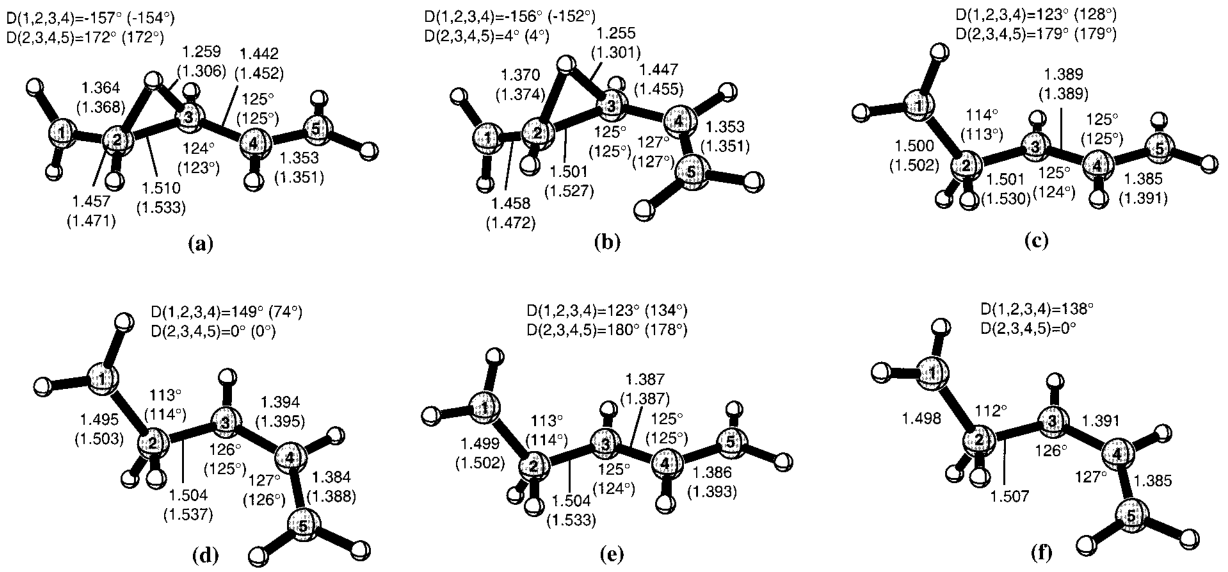

Figure 9. UB3LYP/6-31G*-optimized geometries for the H-transfer pathway, with CAS(8,8)/6-31G*-optimized geometries shown in parentheses: (a) T_1 transition structure for H-transfer from C3 to C2 (trans), (b) T_1 transition structure for H-transfer from C3 to C2 (cis), (c) T_1 biradical intermediate (trans), (d) T_1 biradical intermediate (cis), (e) S_0 closure transition structure (trans), and (f) S_0 closure transition structure (cis).

of 1.26 and 1.37 Å, respectively. However, the computed activation energy for this process is 21 kcal/mol higher than that of the di-π-methane rearrangement, and it is therefore also strongly disfavored.

The transition structures would lead to 1,3-biradicals where the triplet and ground-state surfaces lie within 1 kcal/mol of each other and intersystem crossing to the ground state could occur. Both cis and trans transition structures would lead to the cis biradical shown in Figure 9c, while only the trans transition structure would lead to the biradical shown in Figure 9d. The structures of the triplet biradicals differ somewhat according to the method used. At the UB3LYP level, the trans and cis structures are similar with C1C2C3C4 torsional angles of 123° and 149°, respectively, whereas at the CASSCF level the cis structure has a much smaller C1C2C3C4 torsional angle (74°). No stable biradical intermediate could be located on the ground-state surface in this region as the biradicals are unstable with respect to torsion about the C1−C2 bond. However, trans and cis closure transition structures (Figure 9e,f) were fully optimized at the UB3LYP level, with imaginary frequencies corresponding predominantly to this methylene torsion. Intrinsic reaction coordinate calculations initiated at these geometries indicated that these were vinylcyclopropane isomerization transition structures, leading to different isomeric forms of vinylcyclopropane depending on the initial direction of the methylene torsion. Only a trans closure transition structure could be located at the CASSCF level.

The cis structures located here resemble those involved in the ground-state [1,3]-shift pathway between vinylcyclopropane and cyclopentene. Our findings are consistent with the results of Davidson[19] and Houk[20] who both showed that no stable biradical intermediate exists along this reaction path. They located a transition structure for a concerted [1,3]-shift and several other transition states leading to isomerization.

Discussion

It is often found that for similar reactions the activation energy is linearly related to the stability of the products formed.[21] The results presented here clearly show that the energies of the transition structures for biradical formation in this system are not governed by the stability of the biradical alone. The three-membered ring biradicals are some 21−22 kcal/mol less stable than their five-membered counterpart, but the transition structures leading to them are favored by 3 kcal/mol. In fact, the three-membered ring transition structures are the lowest energy transition structures of the four pathways (A−D) considered, although the biradical formed leads to the di-π-methane product, vinylcyclopropane, rather than to a [2 + 2] cycloaddition product. The cross and parallel [2 + 2] cycloaddition products are formed via the four- and five-membered ring pathways, respectively. These have transition structures separated by only 1.5 kcal/mol, despite a 22.6 kcal/mol difference in the energies of the biradicals.

One of the aims of this study was to examine the effect of through-bond interactions on the intramolecular [2 + 2] photocycloadditions of dienes. In previous work it was shown that the cleavage of three-membered rings is favored over that of four-membered rings in both neutral and radical systems.[6] This was explained in terms of the interactions between the orbitals in the σ-framework of the ring and those of the breaking bond in the transition structures (Scheme 6). In the transition structures for cleaving three-membered rings, the lowest unoccupied σ^* orbital of the σ framework is of the correct symmetry to mix with the σ orbital of the breaking bond leading to a stabilizing interaction. In contrast, in the transition structures for cleaving four-membered rings,

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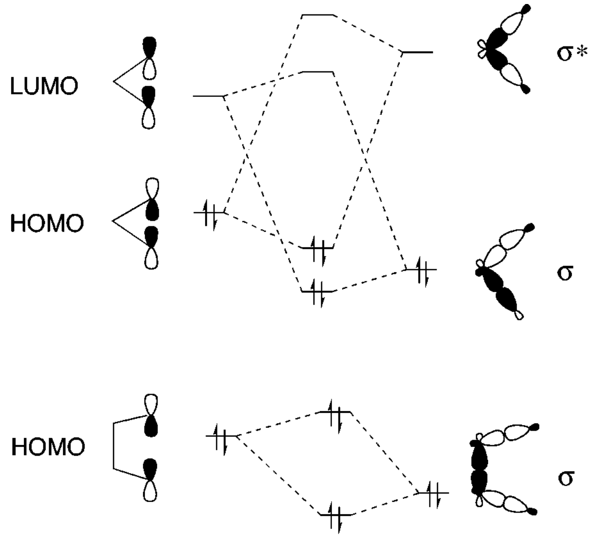
(19) Davidson, E. R.; Gajewski, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543.

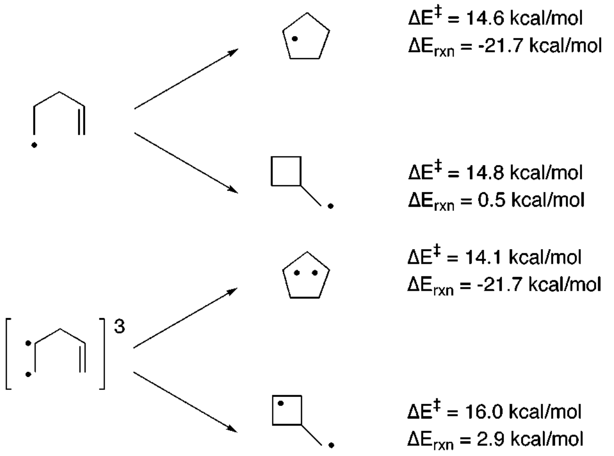
(20) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. *J. Am. Chem. Soc.* **1997**, *119*, 10545.

(21) (a) Ogg, R. A.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 604. (b) Evans, A. G.; Evans, M. G. *Trans. Faraday Soc.* **1935**, *31*, 1401. (c) Evans. M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11. (d) Evans. M. G.; Warhurst, E. *Trans. Faraday Soc.* **1938**, *34*, 614.

Scheme 6



Scheme 7



it is the highest occupied σ orbital of the σ framework that is of the correct symmetry to mix with the σ orbital of the breaking bond; this is a "filled−filled" interaction leading to destabilization of the transition structure. Similar through-bond interactions are apparent in the 1,4-pentadiene system; the four-membered ring biradical is only 1 kcal/mol higher in energy than the three-membered ring biradicals but the corresponding transition structure is 4−5 kcal/mol higher in energy. This difference in energy is similar to that obtained for the alkoxy radical cleavage reactions studied previously.[6b] Although these reactions were studied in the reverse direction to the ones described here, cyclopropoxy ring formation is predicted to be favored over cyclobutoxy formation by 5.5 kcal/mol, even though the cyclobutoxy reaction is only 0.6 kcal/mol more endothermic than the cyclopropoxy reaction.

However, the effects of through-bond interactions are fairly small, and it is obvious that other factors have a much greater influence on the transition state energies in this system. The five-membered ring biradical is favored by 22 kcal/mol relative to the other two biradicals which have a high degree of ring strain, but very little of this stability shows up in the transition structure. The effect is not related to interactions between the two radical centers; the uncorrected UB3LYP/6-31G* results for the analogous radical reactions are found to be remarkably similar to those of the triplet systems (Scheme 7). In all cases reaction is assumed to occur from the cis conformer. The only significant difference is between the energies of the four-membered rings (2.4 kcal/mol), most probably due to the additional ring strain imposed by having an sp^2-hybridized radical center in the ring of the biradical.

The dominant effect must be the geometry of the transition structure as predicted by Baldwin.[2] This is reinforced by the relative energies of the transition structures computed for paths B and C that indicate the 4-Exo-Trig process is favored over the 4-Endo-Trig process by a massive 16.9 kcal/mol. The optimum angle of attack on a π bond in a trigonal system is expected to be 109° as this is the angle that will be adopted in the product; for the pentadiene system the angle of attack for the five-membered ring is only 90°, while it is 117° and 119−120° for the four- and three-membered rings, respectively. The poor transition structure geometry is enough to destabilize the five-membered ring transition structure so that it is of comparable magnitude to the other transition structures, although not enough to make the five-membered ring the disfavored biradical.

In summary, several effects operate simultaneously in these systems which make predicting the outcome of these reactions very difficult. It is clear that Baldwin's rules fail in this system because the five-membered ring formed is so stable that even destabilizing the transition structure by 17 kcal/mol is not enough to make it the disfavored biradical. Likewise, the rates of formation of the biradicals cannot be predicted solely on the basis of their stability. Ring strain is the primary factor in determining the stability of the biradical, but it is the combination of biradical stability, transition structure geometry, and through-bond interactions that control their rates of formation.

Conclusions

The triplet and singlet potential surfaces of 1,4-pentadiene have been mapped using UB3LYP/6-31G* and CAS(8,8)/6-31G* calculations in order to examine the factors controlling the triplet-sensitized photoreactions. Intramolecular [2 + 2] cycloadditions, the di-π-methane rearrangement, a dissociation/recombination pathway, and a H-transfer mechanism were all examined. The results indicate that for the parent system the lowest energy pathway is the trans di-π-methane rearrangement, the [2 + 2] cycloadditions leading to parallel and cross products lie 3.4 and 4.9 kcal/mol higher in energy, respectively. This is in good agreement with the experimental product yields. Both the dissociation/recombination and H-transfer pathways are too high in energy to compete effectively.

The product yields depend primarily on the energies of the transition structures leading to the biradical intermediates on the triplet surface. In previous work, biradical stability,[1] transition structure geometry,[2] and through-bond interactions[3,4] have all been proposed as factors affecting the heights of these transition structures. The results presented here indicate that all of these play a role. A consideration of biradical stability alone would predict the five-membered ring to be the favored biradical by the "Rule of Five" and the parallel product to be formed exclusively. However, the transition structures for the three-membered rings are lower in energy than the five-membered ring transition structure, and the four-membered ring transition structure is only 1.5 kcal/mol higher in energy. Baldwin's rules predict that 4-Exo-Trig is favored over 5-Endo-Trig[2] suggesting the cross product should be dominant, but the five-membered ring biradical is so stable that, despite the unfavorable geometry of the transition structure, it is still formed preferentially over the four-membered ring. Finally, although there is only a 1 kcal/mol energy difference between the three- and four-membered ring biradicals, interactions between the orbitals in the σ framework and those in the breaking bond, cause the three-membered ring transition structures to be stabilized by 4 kcal/mol relative to the four-membered ring transition structure. This is enough to cause the di-π-methane pathway to be the lowest in energy and vinylcyclopropane to be the dominant photoproduct.

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Supporting Information Available: A list of the Cartesian coordinates and energies of the structures reported in the paper, optimized at both the UB3LYP and CASSCF levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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