Some Aspects of the Triplet Di-π-Methane Rearrangement: Comparison of the Ring Opening of Cyclopropyldicarbinyl and Cyclopropylcarbinyl

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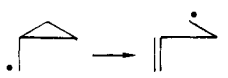
Abstract: Calculations have been performed along the portion of the di-π-methane triplet reaction path which is believed to involve ring opening of cyclopropyldicarbinyl to give dimethylenepropene. For comparison the ring opening of cyclopropylcarbinyl to homoallyl was also studied. The energetics of these two reactions were found to be similar, even though the C_5H_8 rearrangement is complicated by rotations of the methylene groups which do not occur in the C_4H_7 reactions.

The di-π-methane rearrangement is a ubiquitous organic photochemical reaction.[1] The reaction is known to proceed after excitation of the molecule to either the lowest triplet or lowest singlet excited state. Reaction is favored from the triplet state in bicyclic molecules and from the excited singlet in acyclic systems.

Zimmerman has proposed the following mechanism for the rearrangement.

1 2 3 4 5

The step involving ring opening of cyclopropyldicarbinyl (**3**) to the diradical (**4**) has an analogy in monoradical chemistry in the rearrangement of cyclopropylcarbinyl (**6**) to homoallyl (**7**).



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However, on the basis of isotope and substituent effects in bicyclic molecules, Paquette and Bay[2] have suggested that cyclopropyldicarbinyl diradicals may not be intermediates in the di-π-methane rearrangements of these compounds.

In order to investigate the question of whether **3** is a possible intermediate in the triplet di-π-methane rearrangement, we have carried out ab initio calculations on this reaction. For comparison we also report the results of comparable calculations on the cyclopropylcarbinyl to homoallyl radical rearrangement. In the calculations reported here, all geometry optimizations and MCSCF calculations were done with the program GAMESS. Calculations using polarized basis sets and all CI calculations were done with MELD, a set of ab initio molecular orbital programs developed in this laboratory.

It should be noted that the di-π-methane calculations have been performed for 1,4-pentadiene. The ^{3}Hg initiated rearrangement[3] of 1,4-pentadiene yields in addition to **5** the product (**2'**) of a 1,3-allylic shift. For comparison with **3**, we have calculated the energy of **8** which is a possible intermediate in the latter reaction:

2 8 2'

The Cyclopropylcarbinyl–Homoallyl Rearrangement

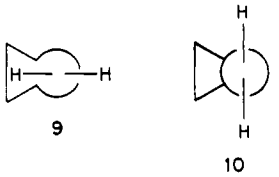
The energetics of the cyclopropylcarbinyl (**6**) to homoallyl (**7**) ring-opening reaction have been determined experimentally. Carter et al.[4] obtained a ΔH of −3.2 kcal/mol for the reaction and a barrier of 9.0 kcal/mol, while Effio et al.[5] obtained a ΔH of −5.2 kcal/mol for the reaction and 5.9 kcal/mol for the barrier.

Table I. Energies for Cyclopropylcarbinyl Ring Opening[a]

	transition state	homoallyl
exptl[b]	9.0	−3.2
exptl[c]	5.9	−5.2
UHF, STO-3G[d]	21.6	7.5
UHF, 4-31G/UHF, STO-3G[d]	8.7	−8.6
UHF, MNDO/3[e]	12.4	−0.5
MCSCF, STO-3G[f]	14.4	−9.2
MCSCF, 3-21G[g]	3.6	−18.5
SCF, SVP[h]	19.6	−5.2
CI, SVP[h,i]	9.2	−3.7

[a] Energies in kcal/mol relative to cyclopropylcarbinyl (**6**). [b] Reference 4. [c] Reference 5. [d] Reference 9. [e] Reference 10. [f] Relative to a GVB, STO-3G/RHF, STO-3G energy for **6**. [g] Relative to a GVB, 3-21G/RHF, STO-2G energy for **6**. [h] Split-valence plus polarization basis set. [i] Extrapolated to include estimates for neglected doubly and quadruply excited configurations.

The ESR spectrum of cyclopropylcarbinyl (**6**) measured by Kochi et al.[6] indicates that the bisected conformation **9** is preferred to conformation **10**. Additional ESR studies by Edge and Kochi[7]



9 10

and Chen, Edge, and Kochi[8] indicate that, in the most stable conformation of the homoallyl radical (**7**), the four carbons are coplanar; but whether the cisoid or transoid conformation is lower in energy has not been experimentally determined.

Hehre[9] has performed partial UHF geometry optimizations of both **6** and **7** using an STO-3G basis set. Cyclopropylcarbinyl was found to prefer the bisected conformation, in concurrence with ESR data. For homoallyl a potential surface with minima at 0° and +/− 120° for the C3–C4–C2–C1 twist angle was found. (A nonstandard numbering scheme has been adopted so that the carbons of twisted homoallyl are superimposable on carbons 1–4

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of dimethylenepropene in Figure 5.) The 120° minimum was about 1 kcal/mol more stable than the 0° cis planar minimum, and the barrier to interconversion was 1–2 kcal/mol.

Hehre located an approximate transition state for the opening of **6** to **7** with the ring-opening bond angle as the reaction coordinate and with partial optimization of other variables. This transition state connected bisected cyclopropylcarbinyl with 120° twisted homoallyl. The STO-3G energy of reaction was +7.5 kcal/mol for ring opening with a barrier of 21.6 kcal/mol. UHF energy evaluations at the STO-3G geometries with an 4-31G basis set gave −8.6 kcal/mol for the energy of reaction and 8.7 kcal/mol for the barrier.

Dewar[10] calculated a reaction path using a spin-unrestricted version of MINDO/3. Homoallyl was calculated to be only 0.5 kcal/mol more stable than cyclopropylcarbinyl. The calculated barrier for ring opening was 12.4 kcal/mol. Table I contains a survey of energies from various sources.

We have optimized the geometry of cyclopropylcarbinyl (**6**) using a STO-3G[11] basis set and a restricted Hartree–Fock (RHF) wave function. The bisected conformation **9** was found to be about 2.5 kcal/mol lower in energy than conformation **10**. The homoallyl radical (**7**) was optimized in the 120° twisted conformation by using the same method. As Hehre found, the STO-3G results indicate that **6** is lower in energy than **7**, which is not the case experimentally. The reason for this erroneous prediction is that the STO-3G basis set describes σ bonds much better than π bonds. Consequently, the energy of the π-bonded isomer is predicted to be artificially high.

The homoallyl radical was reoptimized with the STO-3G basis set and an MCSCF wave function. The active orbitals were the orbital containing the unpaired electron, the π orbital, and the empty π* orbital. The only significant change from the RHF geometry of **7** was a lengthening of the π bond by 0.04 Å.

A similar geometry reoptimization was not done for the cyclopropylcarbinyl sructure, since correlating just the bond to be broken and the half-filled orbital would have destroyed the symmetry. In order to obtain an MCSCF energy to compare with that of homoallyl, a GVB calculation was performed at the RHF geometry. The C2–C3 σ and σ* orbitals were used as a GVB pair, since this σ bond is broken in the reaction. Electron correlation apparently favors homoallyl at this level of approximation, since **7** was found to be 9.2 kcal/mol lower in energy than **6**.

The STO-3G MCSCF transition state was also located, and the barrier to ring opening was calculated to be 14.4 kcal/mol. The normal coordinate corresponding to the one imaginary frequency was composed almost solely of the bond angle opening motion. The necessary 30° methylene rotation was found to be completed before the transition state. The shortening of the C1–C2 bond was also present in the reaction coordinate, but this was a small amplitude displacement of the C1 position compared with the large amplitude motion of C3 during ring opening.

The transition state was relocated with the same type of MCSCF wave function but with a 3-21G basis set. There was very little difference in geometry between the 3-21G and the STO-3G transition states. The MCSCF geometry of twisted homoallyl was also reoptimized with an 3-21G basis set, and this geometry too was nearly identical with that found by using the minimal basis set. In addition, the cis planar geometry of homoallyl was optimized. The energy at this local minimum was calculated to be about 1 kcal/mol higher than that for the twisted form.

With use of the 3-21G basis set, the GVB energy was evaluated for cyclopropylcarbinyl at the RHF STO-3G geometry. Comparison of the MCSCF and GVB energies gave an energy change of −18.5 kcal/mol for ring opening and a barrier of 3.6 kcal/mol.

The internal coordinates shown in Table II for cyclopropylcarbinyl (**6**) and for the transition state are in reasonable agreement with those obtained by Hehre and Dewar. For homoallyl (**7**), the present results find the C3–C4–C2–C1 dihedral angle to be 92°, while both Hehre and Dewar found it to be closer to 120°. The present results agree with Hehre that in **7** the normal to be methylene group is parallel to the C3–C4–C2 plane. Dewar predicted this methylene to be rotated by 90°.

Table II. Internal Coordinates for Cyclopropylcarbinyl Ring Opening[a]

	cyclopropylcarbinyl[b]	transition state[c]	twisted homoallyl[c]	planar homoallyl[c]
C_1C_2	1.498	1.407	1.331	1.334
C_2C_4	1.512	1.504	1.527	1.520
C_4C_3	1.502	1.500	1.522	1.507
$C_1C_2C_4$	119.6	124.3	124.1	125.6
$C_2C_4C_3$	60.2	75.9	111.8	125.6
$C_3C_4C_2C_1$	−109.0	−98.5	−91.8	0
$XC_3C_4H_6$	−72.1	−68.2	−63.9	32.5
$XC_3C_4C_2$	−0.2	0.3	4.3	90
$YC_1C_2C_4$	124.8	91.7	90.5	90
$YC_1C_2C_3$	55.2	31.3	50.9	90

[a] Bond lengths in angstroms, bond angles and dihedral angles in degrees. X is normal to the C_3 methylene plane, Y is normal to the C_1 methylene plane. Numbering is the same as Figures 3–5 with the C_5 methylene removed. [b] STO-3G RHF optimum geometry. [c] 3-21G MCSCF geometry.

As shown in Table I, the 3-21G reaction energetics are not in very good agreement with experiment. The 3-21G calculations give a balanced description of the relative energies of σ and π bonds; but since polarization functions are not included, ring strain is overestimated. This tends to lower the energies of the transition state and homoallyl spuriously relative to that of cyclopropylcarbinyl. Consequently, calculations were performed with a basis set containing polarization functions. The Dunning[12] [3s/2p] split-valence contraction of Huzinaga's (9s/3p) primitive basis augmented with carbon d orbitals was used with a scale factor of 1.2 for hydrogen. The s components of the Cartesian d orbitals were removed thus reducing the number of basis functions from 74 to 70. The K orbital method[13] was used to define virtual orbitals for CI calculations with this basis set. All further calculations were performed at the optimum geometries found with simpler basis sets, i.e., STO-3G RHF for **6** and 3-21G MCSCF for **7** and the transition state.

A preliminary CI, with configurations selected by perturbation theory, was performed at the transition state by using one reference configuration and retaining the lowest four orbitals as core orbitals. Surprisingly, the π–π* single excitation was about as important as the double excitation, so both were included as reference configurations in the final multireference, SDCI calculation. Of the total of 1 969 772 possible spin-adapted configurations, 17 263 were selected by perturbation theory, thus retaining about 54% of the correlation energy in the variational calculation. The resultant energy was extrapolated to approximate the effect of the neglected doubly excited configurations and higher excitations. Equivalent CI's were performed for the initial and final geometries. This led to 17 738 and 19 796 spin-adapted configurations being kept for **6** and **7**, respectively, and to a variational recovery of 72% and 61% of the correlation energy predicted by perturbation theory. These RHF and extrapolated CI energies are included in Table I.

The CI calculations with a SVP basis gave −3.7 kcal/mol for the energy change on ring opening and 9.2 kcal/mol for the barrier. At the RHF level of theory, the computed overall energy change of −5.0 kcal/mol is also reasonable, but there is obviously a large correlation effect on the transition-state energy. It is thus evident that the addition of polarization functions to a split-valence basis set is adequate for approximating the experimental energy difference between homoallyl and cyclopropylcarbinyl at the SCF level. However, a correlated wave function is required to describe

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the energy differences between the transition state and the two minima.

The energy difference between planar and twisted homoallyl at the 3-21G MCSCF geometry was calculated by using a similar CI and the Dunning split valence basis, but with the polarization basis functions omitted. Planar homoallyl was computed to be lower in energy by 3 kcal/mol at the RHF level and by 1 kcal/mol after CI, in contradiction to the 3-21G MCSCF results. Thus, these two conformers of homoallyl are essentially isoenergetic to the accuracy of our calculations.

In order to verify the experimental assignment of the equilibrium conformation of homoallyl, the proton isotropic hyperfine splittings were calculated at both conformations from the best CI wave functions. The splitting of 25.2 MHz computed for the β protons in the cisoid planar form is in good agreement with Kochi's measurement of 28.8 MHz. The calculated splitting of 6.5 MHz for the twisted form was distinctly different.

The β proton hyperfine depends on $\cos^2\theta$, where θ is the dihedral angle between the CH bond to the β proton and the p orbital containing the unpaired electron.[14] This angle should be close to the dihedral angle X–C3–C4–H6 of Table II. As can be seen from the table, $\cos^2\theta$ undergoes a large change between twisted homoallyl ($\theta = -64°$) and planar homoallyl ($\theta = 33°$). Hence, there is no doubt about the experimental assignment of the geometry about the C3–C4 bond.

From the computational results on the opening of cyclopropylcarbinyl (**6**) to homoallyl (**7**), it is evident that a split-valence basis set produces nearly the same geometry predictions as a minimal basis set. However, an SVP basis set combined with CI is needed to approximate the experimental energetics. These results on the ring opening of cyclopropylcarbinyl support the reasonableness of using the above methodology to investigate the ring-opening step in the triplet di-π-methane rearrangement.

The Triplet Di-π-Methane Rearrangement of 1,4-Pentadiene

A diagram showing the triplet excited-state energies for structures along the di-π-methane rearrangement of 1,4-pentadiene has been published by Kirschner and Mussatto[15] based on MINDO/3. Their barrier for ring opening of **3** is 33 kcal/mol, which is much larger than either the experimental or MINDO/3 UHF result for **6**. No further details of the work have been published.

Both spectroscopic studies[16] and ab initio calculations[17] have been done in order to determine the most stable conformation of 1,4-pentadiene. In the gas and liquid phases, C_s and C_2 conformations have been found to be of about equal stability with a third C_1 form at slightly higher energy. To the first approximation rotation around the two CC single bonds is independent with three minima spaced 120° apart for each rotor. If the rotors were completely independent, this would lead to 9 distinct minima. Of these, the planar U form of the molecule turns out not to be a minimum because of high steric interaction of the protons. The other eight, however, are all minima, although, by symmetry, there are only three distinct energies. Thus if the preferred conformation of the starting material is a major influence on the stereochemistry of the cyclopropyldicarbinyl diradical (**3**), the formation of cis and trans isomers seems equally probable.

No experimental or theoretical geometries are available in the literature for structures **2**–**5**. There is extensive literature, however, on some simpler analogues. For example, **2** is expected to have one methylene twisted relative to **1** in analogy to the lowest triplet state of ethylene.[18] This broken symmetry structure is also expected to be lower in energy than a symmetrical triplet state with the excitation delocalized over both vinyl groups.

The preferred orientation of the methylenes in **3** might be like that in the simplest 1,4 diradical, tetramethylene. Borden and Davidson[19] found that for both the transoid triplet and singlet structures the dihedral angles between the normals to the terminal methylene planes and the carbon chain were (0°,0°). Doubleday et al.[20] later showed that, for the singlet surface, this geometry was not a minimum since it dissociated without a barrier into two ground-state ethylenes. The (0°,0°) conformation in **3** would lead to the methylenes being rotated by 60° from the bisected orientation of **6**.

The orientation of the methylenes in **4** might be like that in the simplest 1,3 diradical, trimethylene. Doubleday et al.[21] examined three methylene orientations and concluded the lowest form for the triplet is (90°,90°); that is, the normals to both methylenes are perpendicular to the carbon plane. The (0°,0°) orientation was better for the singlet because this conformation allows some C–C bonding. More recently, Yamaguchi et al.[22] have concluded that the triplet energy is not a minimum for (0°,0°), (0°,90°), or (90°,90°); but they did not search further for the actual minimum. They also concluded that the (0°,0°) singlet collapses without a barrier to cyclopropane. Both Doubleday et al. and Goldberg and Daugherty[23] discussed the (90°,90°) case as a function of central bond angle and concluded that the triplet should be the ground state near the expected tetrahedral equilibrium angle. These results suggest that the preferred conformation of triplet **4** will certainly not be (0°,0°) which would be the analogue to the homoallyl twisted geometry.

Exploratory calculations were performed in which the geometries of all the proposed intermediates in the triplet di-π-methane reaction were optimized with MNDO. The reactant **1** and product **5** geometries were optimized as closed-shell singlets. At the MNDO level, the cis and trans reaction paths were less than 0.5 kcal apart. The adiabatic excitation of **1** to triplet **2** was calculated to require 25 kcal/mol, and ring closure of **2** to **3** was found to be endothermic by another 8 kcal/mol. Ring opening of **3** to form **4** was endothermic by 1 kcal/mol and ring closure of **4** to form **5** was exothermic by 29 kcal/mol.

Compared with the previously computed MINDO/3 surface, the MNDO energy gaps between 1,4-pentadiene and the first two intermediates are considerably smaller. However, **3** is lower in energy than **4**, which seems unreasonable in view of the fact that cyclopropylcarbinyl (**16**) is higher in energy than homoallyl (**7**). The ability of both MINDO/3 and MNDO to describe the ring-opening reaction seems minimal. The MINDO/3 barrier seems excessively large, assuming this step is at all similar to the analogous monoradical reaction.

Ground-state singlet geometries of the two rotamers of vinylcyclopropane and the three rotamers of 1,4-pentadiene were optimized with an STO-3G basis set. With use of the same basis set, the intermediates were optimized as triplets with open-shell restricted Hartree-Fock wave functions. Two geometries for each intermediate were optimized, corresponding to the cis and trans conformations of the starting material. Energies were calculated for the lowest singlet states of the intermediates with GVB wave functions. Along the cis path a few energies were recomputed with the Dunning split-valence plus carbon-d (SVP) basis set. All energies are summarized in Table III.

The energies of cis and trans **3** are very close, as are the energies of the C_s and C_2 forms of 1,4-pentadiene. Thus there should be little or no preference for formation of one isomer over the other. Since the cis and trans path were very close energetically and the conformation of cyclopropyldicarbinyl in bicyclic systems is constrained to be cis, that path was chosen for the transition-state search.

The geometry of the cis 1,3 diradical **4** was reoptimized with an MCSCF wave function in which the four active orbitals were

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Table III. Energies for Triplet di-π-Methane Rearrangement[a]

		RHF, STO-3G[b]	RHF, SVP[e]	CI, SVP
singlet **1**	C_2 (trans)	−35.2		
	C_s (cis)	−35.2	−54.8	
	C_1	−34.1		
triplet **1**	(cis)	59.3[d]	35.0	
	(trans)	59.3[d]		
triplet **2**	(cis)	4.0	−8.2	
	(trans)	3.9		
triplet **3**	(cis)	0	0	0
	(trans)	−0.4		
triplet **4**	**14** (eclipsed)	10.2	−2.8[f]	−6.7[f]
	13 (anti)	8.7		
singlet **5**	**12** (gauche)	−39.4		
	11 (syn)	−41.0	−48.0	
triplet **5**	(gauche)	52.9[d]		
singlet **2**	(trans)	4.9		
singlet **3**	(trans)	−0.6[c]		
	(cis)	−0.2[c]		
singlet **4**	(anti)	9.1[c]		
triplet transition state	(cis, **3**→**4**)		22.4[f]	4.5[f]
triplet **8**		−14.8	−3.6	

[a] Energies in kcal/mol relative to cis cyclopropyldicarbinyl (**3**) triplet state. [b] Reference energy is −191.538504 au. [c] At triplet geometry with GVB wave function. [d] At singlet geometry with $^3\pi\pi^*$ RHF wave function. [e] Reference energy is −193.878946 GVB for cis triplet **3** at RHF, STO-3G geometry. [f] At MCSCF, STO-3G optimum geometry.

Table IV. Internal Coordinates for Triplet Di-π-Methane Rearrangement, Cis Path[b,c]

	1 (cis)	**2** (cis)	**3** (cis)	‡	**4** (eclipsed)	**5** (syn)[a]
C_1C_2	1.309	1.490	1.505	1.396	1.343	1.310
C_2C_4	2.534	2.536	1.514	1.518	1.538	1.511
C_4C_5	1.528	1.530	1.508	1.501	1.527	1.511
C_4C_5	1.309	1.309	1.505	1.516	1.522	1.511
$C_1C_2C_4$	135.1	133.4	119.9	124.9	124.3	125.8
$C_2C_4C_3$	34.0	33.9	59.9	79.5	109.7	121.3
$C_2C_4C_5$	135.1	133.5	119.9	116.9	110.1	121.3
$C_3C_4C_2C_1$	−87.5	−85.3	−109.3	−101.2	−90.5	35.5
$C_5C_4C_2C_1$	0.0	4.8	0.0	15.2	30.6	−35.5
$H_1C_1C_2C_4$	43.0	−65.9	−73.5	4.7	−0.3	0
$H_5C_3C_{C2}$	−120.1	−120.7	−108.6	−100.8	−71.2	−218.9
$H_8C_5C_4C_2$	−43.0	−42.7	73.5	71.0	71.3	2.2
$XC_3C_4C_2$	0.0	−0.3	0.0	−0.1	35.0	−114.4
$YC_1C_2C_4$	132.9	39.4	31.7	93.3	89.8	90.0
$-ZC_5C_4C_2$	−132.9	132.6	−31.7	−34.8	−34.7	−110.4
$XC_3C_4H_5$	−120.9	−118.1	−109.4	−115.1	−86.2	−0.1
$-ZC_5C_4C_3$	−90.1	−89.8	36.6	57.4	86.2	−0.1
$YC_1C_2C_3$	90.1	−1.9	−38.6	33.9	49.4	106.8

[a] Singlet. [b] RHF, STO-3G optimum geometries except ‡ and **4** are MCSCF. [c] See footnote *c*, Table V.

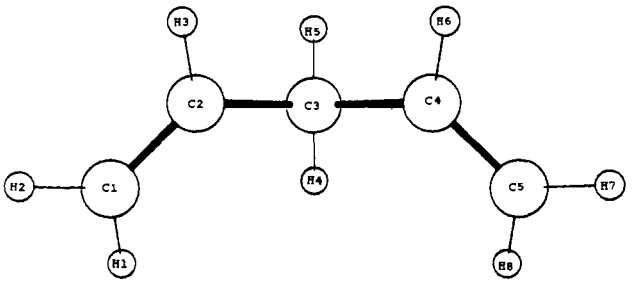


Figure 1. RHF, STO-3G geometry of 1,4-pentadiene (cis path).

the half-filled orbitals and the π and π* orbitals. The same type of MCSCF wave function was used to locate the transition state for the transformation of **3** to **4**. Figures 1–5 depict the changes in geometry along the cis reaction path from **1** to **4**. Tables IV and V give the important geometries along both the cis and trans paths.

The energies of the vertical $^3(\pi-\pi^*)$ excitations were calculated at the SCF level for 1,4-pentadiene and vinylcyclopropane. Initially, the wave function for triplet pentadiene was constrained to retain the symmetry of the molecule which resulted in a very large computed excitation energy compared to that of vinylcyclopropane. The energies of the triplet excitations for both molecules would be expected to be close to each other and comparable to that of ethylene, since all three involve a $\pi-\pi^*$ excitation in a nonconjugated double bond. Relaxing the symmetry con-

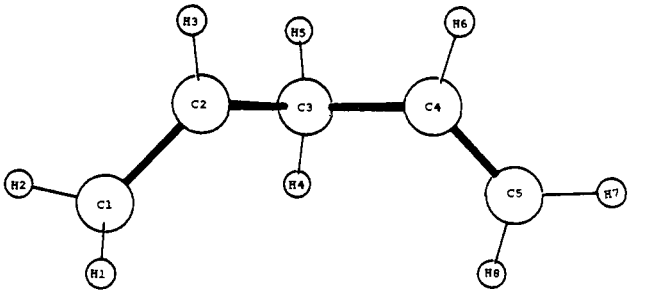


Figure 2. RHF, STO-3G geometry of triplet 1,4-pentadiene (cis path).

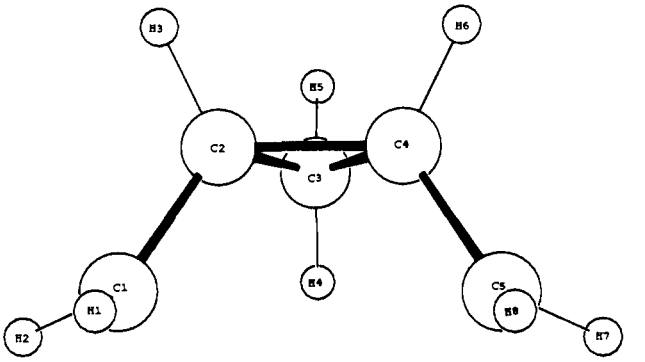


Figure 3. RHF, STO-3G geometry of triplet cyclopropyldicarbinyl (cis path).

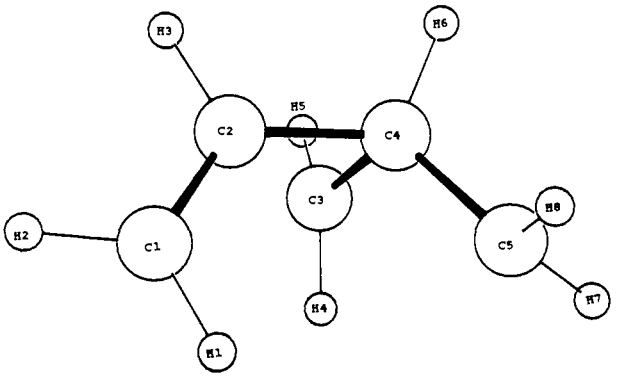


Figure 4. MCSCF, STO-3G geometry of C_5H_8 transition state (cis path).

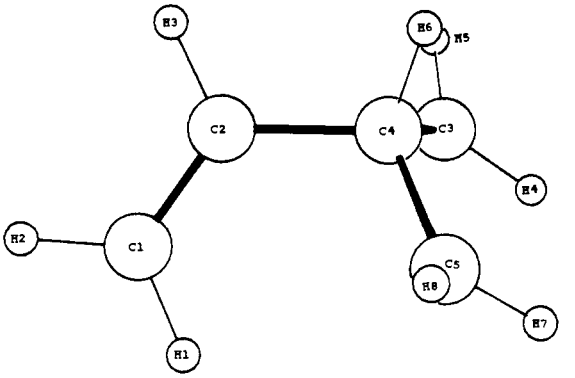


Figure 5. MCSCF, STO-3G geometry of triplet dimethylenepropene (cis path).

Table V. Internal Coordinates for Triplet Di-π-Methane Rearrangement, Trans Path[b,c]

	1[a] (trans)	2 (trans)	3 (trans)	4 (anti)	5 (gauche)[a]
C_1C_2	1.309	1.491	1.506	1.308	1.310
C_2C_4	2.534	2.539	1.509	1.538	1.518
C_4C_5	1.528	1.529	1.507	1.531	1.509
C_4C_5	1.309	1.308	1.505	1.531	1.508
$C_1C_2C_4$	134.2	132.8	119.3	125.4	125.8
$C_2C_4C_3$	34.0	33.8	59.9	109.9	121.7
$C_2C_4C_5$	134.2	135.1	119.6	109.9	123.1
$C_3C_4C_2C_1$	−88.7	−86.3	−109.1	−118.0	−219.9
$C_5C_4C_2C_1$	182.5	186.7	142.0	118.7	68.8
$H_1C_1C_2C_4$	43.1	−66.1	−74.2	0.0	−2.6
$H_5C_3C_4C_2$	−121.4	−122.1	−108.7	−142.8	−220.9
$H_8C_5C_4C_2$	43.1	42.1	−67.1	−70.2	2.9
$XC_3C_4C_2$	−0.7	−0.6	−0.9	−36.0	−113.2
$YC_1C_2C_4$	133.0	39.0	31.0	90.0	87.0
$ZC_5C_4C_2$	133.0	132.0	38.5	36.0	110.8
$XC_3C_4C_5$	118.6	120.4	108.3	86.2	−0.6
$ZC_5C_4C_3$	90.1	89.6	−31.5	−86.2	0.6
$YC_1C_2C_3$	94.6	177.8	−38.9	45.3	119.0

[a] Singlet. [b] RHF, STO-3G optimum geometries. [c] Bond lengths in angstroms, bond angles and dihedral angles in degrees. See figures 1–5 for atom numbering. X is normal to the C_3 methylene plane, Y is normal to the C_1 methylene plane, Z is normal to the C_5 methylene plane.

straint resulted in localization of the excitation and a more reasonable energy gap. As can be seen from Table III, both values are reasonably close to 99 kcal/mol, the experimental value for the lowest $^3(\pi-\pi^*)$ transition of ethylene.

As has been noted for other molecules,[24] RHF with delocalized (symmetry) molecular orbitals is not appropriate for describing an excitation in a molecule containing weakly interacting, but symmetry equivalent, chromophores. If a and b are the delocalized π MO's of 1,4-pentadiene, and a* and b* are the corresponding π* orbitals, then there are four posible singly excited configurations—two of ^3A and two of ^3B symmetry. As all four configurations will have nearly the same energy, the correct wave function will mix the configurations of the same symmetry. Since the Hamiltonian matrix element connecting these configurations is large, the RHF energy of one of them is a poor approximation to the true energy.

In a localized bond orbital picture there is a state corresponding to the local excitation of each π bond. The true lowest states of ^3A or ^3B symmetry will be the sum or difference of these localized states. If the chromophores are weakly interacting, this mixing of localized excitations will produce only a small energy splitting. Hence, an RHF calculation with broken symmetry orbitals may produce a better estimate of the excitation energy than one based on symmetry orbitals.

Because of the tendency of STO-3G to favor σ over π bonds, the calculated energy ordering of the pentadiene and vinylcyclopropane with this basis set is not correct. $\Delta H°_f$ values for gaseous 1,4-pentadiene and liquid vinyl cyclopropane are 25.3 and 29.3 kcal/mol, respectively. Heats of vaporization for C_5H_8 hydrocarbons are in the range of 6–7 kcal/mol, so 1,4-pentadiene should be 10–11 kcal/mol lower in energy than vinylcyclopropane when both are in the gas phase. The SVP RHF energies at the STO-3G geometries are in much better agreement with experiment.

Vinylcyclopropane was found to have two equilibrium conformations:

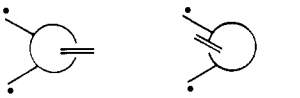
11 (syn) 12 (gauche)

The gauche structure connects to the trans path. The slightly more stable syn structure is on the cis path.

(24) Iwata, S.; Morokuma, K. *Theor. Chim. Acta* **1974**, *33*, 285; **1977**, *44*, 323. Nitzsche, L. E.; Davidson, E. R. *Chem. Phys. Lett.* **1978**, *58*, 171.

The normals to the methylenes in the 1,4 diradical **3** were twisted at (32°,32°) with respect to the two equivalent ring bonds (Y–C1–C2–C3 and Z–C5–C4–C3 in Tables IV and V) in both the cis and trans forms. This structure corresponds to the disfavored orthogonal structure **10** of cyclopropylcarbinyl. In their previous work on tetramethylene Borden and Davidson did not examine such a conformation.

The optimal methylene conformation of the 1,3 diradical **4** was (86°,86°), in agreement with the minimum reported by Doubleday and co-workers for triplet trimethylene and in contrast to Yamaguchi et al.'s conclusion that neither 0° nor 90° is a minimum for triplet trimethylene. Two conformations were found for the remainder of the carbon skeleton:



13 (anti) 14 (eclipsed)

The anti form **13** is slightly lower in energy and lies on the trans path. The cis path connects to the (almost) eclipsed form **14**. The carbon frame twist angles are very similar to the twisted homoallyl analogues.

From the above results it is clear that, while the carbon skeleton rearrangement is quite similar for the monoradical and diradical reactions, the methylene motion is very different. In going from **1** to **5** the following sequence of rotations takes place. First in going from **1** to **2** there is a 90° rotation about C1–C2. Then in going from **2** to **3** there is a 53° rotation about C4–C5. Next, in going from **3** to the transition state there is a 60° rotation about C1–C2 toward the original position, in contrast to the simple 30° methylene rotation in going from **6** to **7**. After the transition state there is a 35° rotation about C3–C4 in getting to **4**. Finally a 90° rotation about both C3–C4 and C5–C4 is necessary to close the triplet **4** to the singlet product **5**.

In spite of the importance of methylene rotations to the triplet di-π-methane reaction, they proceed sequentially and do not seem to contribute much to the reaction coordinate at the transition state for ring opening. The double bond is almost completely formed in the transition state, judging from the C1–C2 bond length and the near coplanarity of H1, H3, H5, C1, and C2. The pyramidalization of the radical at C5 remains almost constant throughout the course of the reaction. No other internal coordinate besides the C1–C2 bond length stands out as being particularly sensitive to changes in the bond angle during geometry optimizations. Since the additional radical center does not contribute significantly to the reaction coordinate, it is not surprising that the carbon framework geometry of this transition state and that for cyclopropylcarbinyl radical ring opening are similar.

The CI calculations performed on the proposed triplet diradical intermediates and transition state were analogous to those done on the monoradical system. The same basis set was used and the s components of the Cartesian d orbitals were again deleted, thereby reducing the number of basis functions from 91 to 86. The carbon inner-shell orbitals were retained as core orbitals and the number of active orbitals was held at 60. Three configurations, analogous to those used for C_4H_7, were chosen as reference configurations.

The CI results are included in Table III. The relative energies are similar to those reported for C_4H_7 in Table I. The effect of configuration interaction on the relative energies of **3** and **4** is to widen the gap slightly, which is opposite to the effect in the C_4H_7 case. The second radical center in **3** appears to lower the barrier for ring opening relative to that in the monoradical **6**. However, these differences may not be particularly significant because the magnitudes of the changes are probably not large relative to the uncertainty introduced by extrapolating the CI energies. As with the monoradical calculation, CI lowers the transition-state energy considerably relative to the energies of the intermediates.

Our best estimates of the energies along the reaction path are summarized in Figure 6 where structures **1** and **5** are minimum energy points on the ground-state singlet surface (S_0) and

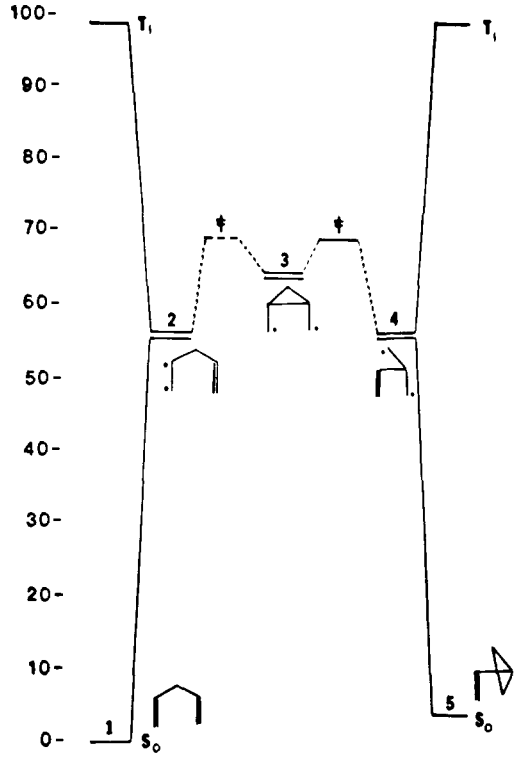


Figure 6. Energies in kcal/mol along the reaction path from the best CI calculations.

structures **2**, **3**, and **4** are minima on the excited triplet surface (T_1). The transition state connecting **3** and **2** has not been calculated, but the reaction is similar to the reaction of **3** to **4** and of **6** to **7**, so the barrier is expected to be similar.

The structure of the triplet diradical **8** was also optimized at the STO-3G RHF level and its RHF energy recomputed with an SVP basis. As expected, **8** seems to be a true intermediate, and it is about 4 kcal/mol more stable than **3**. Hence this diradical could be involved in the ^{3}Hg sensitized 1,3 allylic shift of **2** to **2′**. However, no attempt was made to find the transition states for closing or opening the ring in this species.

Dewar[10] has discussed the analogous ring closure of homoallyl to form the cyclobutyl radical. He also found the four-membered ring to be more stable than the three-membered ring, but the transition-state barrier to ring closure was much higher for cyclobutyl than for cyclopropylcarbinyl. The competition between formation of **8** or **3** from **2** may not be exactly analogous, however, as the terminal carbon of the double bond is being attacked in forming cyclobutyl from homoallyl while an interior carbon is being attacked in forming **8** from **2**.

Conclusion

The monoradical and diradical ring-opening reactions seem quite similar. The cyclopropyldicarbinyl diradical (**3**) does appear to be a true intermediate, and so it could be involved in the triplet di-π-methane rearrangement. Its opening to **4** is predicted to be fairly easy; however. These findings are consistent with Zimmerman's postulated mechanism for the rearrangement.

A much more complete exploration of the triplet potential surface would be necessary to rule out unequivocally a direct 1,2 vinyl shift to form **4** from **2** without the intermediacy of **3**. Needless to say, even if calculations did rule out this direct pathway from **2** to **4** in the triplet di-π-methane rearrangement of 1,4-pentadiene (**1**), they would not preclude the circumvention of a cyclopropyldicarbinyl intermediate in the bicyclic molecules studied by Paquette and Bay. Nevertheless, in light of our computational findings, the results of Paquette and Bay are most economically explained in terms of reversible formation of such an intermediate, which they suggested as an alternative interpretation of their results.

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Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 3. The Valence Isomers of Benzene

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Abstract: Heats of formation and strain energies of the benzene valence isomers Dewar benzene, benzvalene, prismane, and 3,3′-bicyclopropenyl are calculated at the 6-31G*(RMP2) level with use of homodesmic reactions, including the effects of zero-point energies and changes of enthalpy with temperature. Benzvalene and Dewar benzene have similar heats of formation, with the former lower by only 4 kcal/mol. Prismane and bicyclopropenyl have nearly the same heat of formation, with that of prismane lower by ca. 1 kcal/mol. Kekulē benzene is found to be ca. 7–9 kcal/mol higher in energy than benzene.

While benzene and its valence isomers of formula $(CH)_6$ have been of theoretical and experimental interest for many years, their relative energies are incompletely known: heats of formation have been determined experimentally only for benzene (I) and benzvalene (III), that of the latter by its heat of isomerization to benzene in solution. In the present paper we use ab initio molecular orbital theory to compute accurate heats of formation of the $(CH)_6$ benzene isomers Dewar benzene (II), benzvalene (III), prismane (IV), and 3,3′-bicyclopropenyl (V).

We have found that ab initio single-configuration self-consistent-field (SCF) molecular orbital calculations with restricted Møller–Plesset second-order perturbation theory (RMP2) furnish accurate heats of reaction for strained and unstrained hydrocarbons.[1] The basis set should contain d orbitals on carbon

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