according to BWH[1]). However, we have found that, unlike the ethylene-extrusion reactions (6b and 6d), both of the reactions (6a and 6c) in which H_2 is extruded occur with reverse activation energy. Consequently, the barriers to H_2 loss from **6** and **7** will be greater than the corresponding reaction energies (131 and 76 kJ mol^{-1}, respectively) shown in Table II.

In order to gain some measure of the reliability of our calculated energies for the extrusion fragmentations, we have performed higher-level calculations for the simplest reaction of this type, $H_2S{\cdots}SH_2^{\bullet+}$ (**6**) $\rightarrow$ $H_2SS^{\bullet+}$ (**11**) + H_2. These were carried out at the same level of theory as used previously[5,6] to calculate the hemibond energy (vide supra), namely MP4/6-311G(MC)(d,p)//MP2/6-31G(d) plus zero-point vibrational correction. The extrusion energy calculated in this manner (148 kJ mol^{-1}) is slightly higher than the value (131 kJ mol^{-1}) obtained at the highest level of theory used for the remaining systems in this paper (MP2/6-31G(d)//HF/6-31G(d) + ZPVE, Table II).

Our theoretical results appear to rationalize both the ease with which the sulfur-transfer reaction 1 takes place and the facile formation (reaction 3) of the thiirane dimer radical cation **5**. However, the finding[3a] that **5** is apparently thermally unstable in some matrices at only 105 K is somewhat puzzling in the light of our moderately large calculated barrier (160 kJ mol^{-1}) for extrusion of ethylene. It is possible that the observed behavior may be associated with a matrix effect, a suggestion supported by the fact that the decomposition is strongly matrix dependent.[3a] Alternatively, it is possible that there may be a lower-energy pathway for production of ethylene that we have not yet investigated.[22]

Conclusions

In this paper, we have demonstrated that the experimental report of the formation of the hemibonded dimer radical cation of thiirane (**5**) is consistent with the theoretical prediction that sulfur–sulfur hemibonds of the type found in **5** are generally rather strong. Although fission of the sulfur–sulfur hemibond is probably the lowest-energy fragmentation pathway (127 kJ mol^{-1}), our calculations indicate that an alternative, and only slightly more energetically costly, unimolecular fragmentation is the recently observed ethylene-extrusion decomposition (160 kJ mol^{-1}). Both of these processes are predicted to occur without reverse activation energy. The mixed H_2S–thiirane dimer cation (**7**) is predicted to be a much less stable species than either the thiirane dimer cation (**5**) or the hydrogen sulfide dimer cation (**6**), principally because of the comparatively low barrier (47 kJ mol^{-1}) to the fission of its hemibond.

Acknowledgment. We thank Professor Ffrancon Williams for a preprint of ref 3a and gratefully acknowledge the award of an ANU Vacation Scholarship to P.W. and a generous allocation of time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

Registry No. **1**, 420-12-2; **2**, 119273-76-6; **3**, 119273-77-7; **4**, 74-85-1; **8**, 7783-06-4; **9**, 26453-60-1; **10**, 1333-74-0; **11**, 119273-78-8.

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[22] For example, in related gas-phase experiments involving thiirane *anions*, the proposed mechanism for extrusion of ethylene involved *ring-opened* sulfur-containing species: de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1988**, *110*, 2066.

Ab Initio Studies of the C_3H_4 Surface. 2. MCSCF and CI Study of Structures of Vinylmethylene and Ring Opening of Cyclopropene

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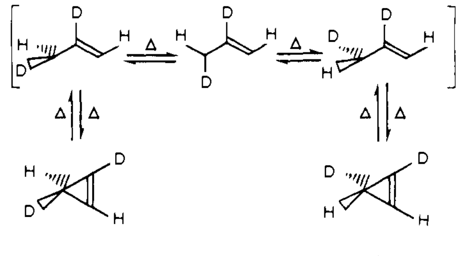
Received August 1, 1988

Abstract: MCSCF and CI calculations have been performed to investigate the potential energy surface of vinylmethylene and rearrangement paths from cyclopropene to vinylmethylene and propenylidene. The results show that triplet vinylmethylene has two isoenergetic minima (trans and cis) that have allylic planar structures and lie 45.9 kcal/mol above the X $^1A_1$ state of methylacetylene. Singlet vinylmethylene has four isoenergetic local minima (two for cis and two for trans) that have allylic-like nonplanar structures and lie 12 kcal/mol above triplet vinylmethylene. These singlet species are rather unstable with respect to the ring closures to cyclopropene, with potential energy barriers of 1.3 and 4.7 kcal/mol for the cis and trans species, respectively. It is found that a direct reaction path from cyclopropene to *cis*-vinylmethylene exists with the potential energy barrier of 36.5 kcal/mol while the barrier for the cyclopropene to *trans*-vinylmethylene is 40.2 kcal/mol. The rearrangement of cyclopropene to propenylidene is a concerted reaction with the potential energy barrier of 41.5 kcal/mol, in which ring opening is accompanied by a 1,2-hydrogen migration, and the barrier for the reverse reaction is 20.5 kcal/mol, indicating that this ring-opening process is product forming. We also found a surface crossing between the singlet excited and ground states of C_3H_4 occurring in the vicinity of the singlet vinylmethylene structure, providing a mechanism for radiationless decay of excited cyclopropene species.

I. Introduction

In the first paper of this series[1] (hereafter referred to as paper 1), we reported SCF and CI calculations for the structures and relative energies of the C_3H_4 isomers. In this paper we report MCSCF and CI calculations on the reaction paths among various vinylmethylene structures, which are sketched in Figure 1, and reaction paths for the reversible ring closure to cyclopropene (**1**).[2] In addition we present a study on the reaction path for the ring opening of cyclopropene to propenylidene (**2**), which has been proposed in paper 1 as a possible low-energy path to methylacetylene.

Scheme I



It has been suggested that vinylmethylene plays a central role in the thermal interconversions on the C_3H_4 surface. The in-

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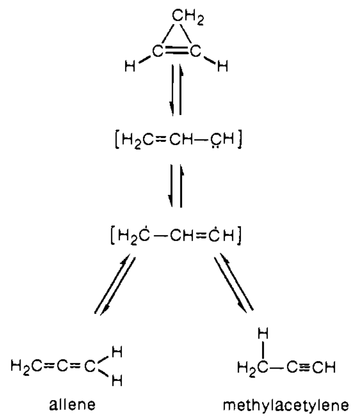
Scheme II



terconversion mechanisms involving vinylmethylene as a reactive intermediate have recently been reviewed by Steinmetz et al.[3] We briefly summarize those thermal interconversion mechanisms pertinent to the potential surface under consideration. First, the mechanism proposed for racemization of cyclopropene (**1**) involves vinylmethylene as indicated in Scheme I.[4] As shown in Scheme II, cyclopropene has also been implicated in the reversible thermal allene to methylacetylene isomerization.[5] In the mechanism proposed, vinylmethylenes were introduced as reactive intermediates, which, in effect, mandates that the allene to methylacetylene interconversion proceed by two consecutive 1,2-H shifts, with the highly reversible ring closure to cyclopropene as a competitive process. The diradical species were introduced to account for the fact that the cyclopropene to methylacetylene isomerization is faster than the conversion to allene. This could then be explained on the basis that the hydrogen migration in the diradical to form methylacetylene is over a single bond while to form allene hydrogen migration must occur over the double bond, resulting in an obviously strained situation. However, as Steinmetz et al.[3] have pointed out, the experimental evidence for the involvement of vinylmethylene is indirect, and their structures are not well established experimentally due to the possibility of equilibration among various structures and electronic states possible for vinylmethylene. Thus, theoretically calculated structures and electronic states for vinylmethylene have been exclusively employed in describing these mechanisms.

Previous theoretical calculations on the structures of vinylmethylene and the ring-opening reaction of cyclopropene have also been reviewed.[3] The main conclusions forwarded by these studies are as follows. The most stable form of vinylmethylene is the localized carbene structure with a $^3A''$ state (**7** or **8**).[6-8] The closed-shell $^1A'$ state of the carbene structure (**7**) is the most stable singlet species.[6-8] The ground-state potential surface for the ring opening of cyclopropene is considered as a concerted reaction path of a ring opening and the methylene group rotation to reach a trans-planar carbene species (**7**).[8] The involvement of *cis*-vinylmethylene (**4**, **6**, **8**) is considered secondary in nature because a relatively high barrier was calculated for the cis–trans isomerization for planar carbene.[7] It was also suggested that singlet planar diradical species (**5**, **6**) may be involved only in the photochemical process since it is strongly correlated with the excited state of cyclopropene.[8] However, because of either the quality of the wave function employed or the limited range of geometries examined, the results of these calculations are still qualitative and might not represent a true picture of the potential surface. For example, vinylmethylene has various low-lying states with different structures that can be connected by the methylene rotation. Once the methylene rotation takes place, then all these low-lying electronic states should have avoided crossings, leading to a rather complex potential surface. Furthermore, there exists a possibility of resonance phenomena between various structures (i.e., between the carbene and diradical), which should make bond reorganization a less energy-demanding process. To account for these points, a more sophisticated wave function than those used in these previous calculations must be employed.

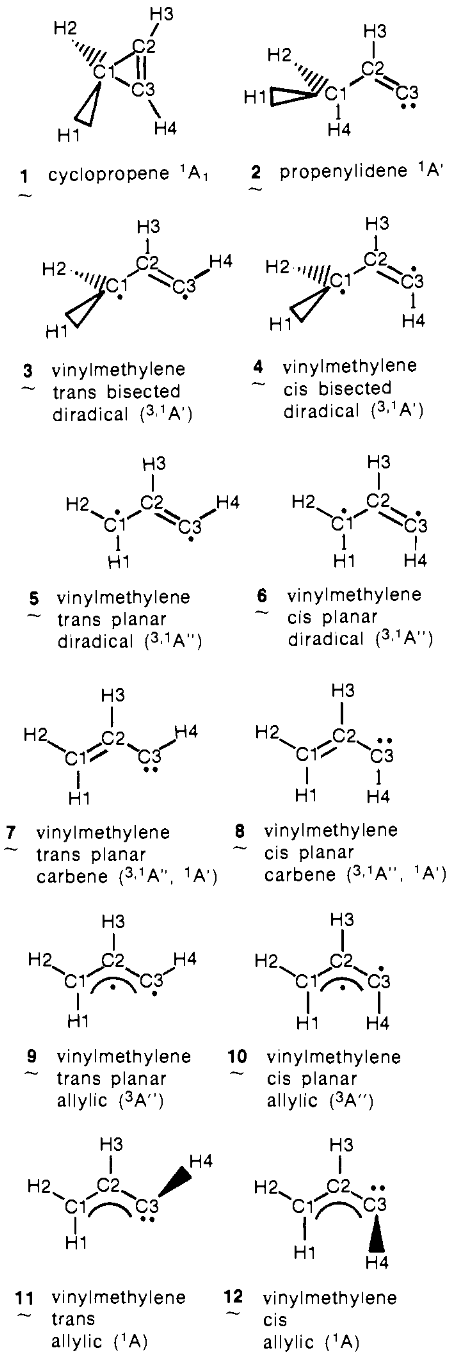


Figure 1. Possible structures for cyclopropene, propenylidene, and vinylmethylene.

With these points in mind we have performed MCSCF and CI calculations for the ground-state potential surface relevant to the ring-opening reaction of cyclopropene to vinylmethylene and that

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to propenylidene. We should mention that the latter reaction has not been considered previously in connection with the cyclopropene ring opening, but it has important consequences for the thermal interconversions on the C_3H_4 surface.[2]

We present first the results for the structure of the triplet ground state of vinylmethylene in section II. These predict that the most stable geometry has an allylic (resonance) structure. In addition, some discussion is given regarding a minimum requirement for the MCSCF wave function that properly describes the resonance phenomena. In section III, the singlet vinylmethylene results are presented. Here the resonance effects are also important and lead to an allylic-like structure for the lowest singlet state. Furthermore, it is pointed out that the excited- and ground-state potential surfaces meet in the vicinity of the local minima for singlet vinylmethylene. In section IV, the reaction paths are presented for the ring closure of *trans*- and *cis*-vinylmethylene to cyclopropene. For this case, the barrier for the closure of the cis species is much smaller than that of the trans species, contrary to the previous results indicating that the involvement of the cis species in the ring closure is secondary in nature.[7] In section V, the reaction path and energy profile for the cyclopropene–propenylidene isomerization are presented and the results for the ring-opening mechanism are summarized.

In this study structures and reaction paths were in general determined by MCSCF wave functions with the 4-31G basis using the program GAMESS.[9] Our best energy profile of the resultant path is evaluated by multireference CI wave functions with the double-ζ polarization function basis using the programs ALCHEMY I and II.[10]

Before we embark on a detailed discussion on the C_3H_4 surface, a few comments on the notation used are pertinent. Since we are studying a fairly large number of species with a variety of ab initio methods, we must use a consistent notation that at least attempts to organize the results. First, general structures for a particular species will be referred to by their common names and a number in parentheses; e.g., trans-planar diradical (**5**) refers to structure **5** in Figure 1 (which also contains descriptions for all of the systems reported herein). Note that no specific geometric parameters are specified and the label, trans-planar diradical (**5**), loosely refers to a species with the electronic configuration and geometry shown in Figure 1. The actual equilibrium geometry or the best geometry obtainable for a particular species is written in capitalized italic form. For example, *TPD* denotes a point on the potential surface whose geometry and electronic configuration provide the best description for the trans-planar diradical (**5**).

A number of points are computed along reaction paths and are listed in tables and discussed in the text. These are labeled by a capitalized italic letter for a particular reaction path followed by a number indicating the particular point on the path. Thus, the points computed along the path listed in Table VIII are *A1* for the first, *A2* for the second, etc. Lastly, transition states on a reaction path's coordinates are labeled as TS1, TS2, etc. In addition, acronyms are used to specify a particular ab initio method (e.g., SCF, MCSCF). As with the notation for the transition states, these are also capitalized in nonitalicized letters to distinguish them from the computed structures.

II. Triplet Vinylmethylene

The ground electronic configuration of vinylmethylene is known to be a triplet state.[11] The discussion is centered over whether the triplet ground state may best be described as a delocalized carbene with an allylic π structure and equivalent C–C bonds or a localized carbene with single and double C–C bonds. The former view was promulgated as a result of ESR measurements,[11a] while the latter was consistent with the results of theoretical calculations.[7,8] Although the debate may seem moot, nevertheless, the underlying theme of localization versus delocalization (or resonance) is an important and very useful concept in chemistry.

Scheme III

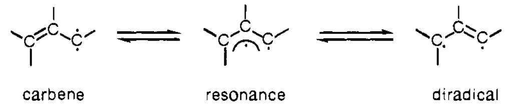

Table I. Active Orbitals and Number of CSF's for MCSCF Wave Functions (MC4) for Triplet Vinylmethylene

state	active orbitals	no. of CSF's	structure
$^3A''$	10a′, 1,2,3a″	9	planar
$^3A'$	9,10a′, 1,2a″	7	bisected
^3A	10,11,12,13a	15	transition state

Our results reported in paper 1 revealed that the carbene structure (**7** or **8**) had a lower energy in the SCF and SDCI levels. However, a study on the path between bisected diradical (**3**, **4**) and carbene structures revealed the possibility that an allylic structure (**9**, **10**) could be lower in energy than both planar carbene and diradical structures. We have carried out MCSCF and multireference CI calculations (MRCI) to further investigate the triplet vinylmethylene structure. The calculations and results will be described in detail below.

A. Computational Details. Resonance between the planar carbene and diradical structures shown in Scheme III can be accomplished by delocalization of π electrons. To properly describe the resonance phenomenon, we used an MCSCF wave function that includes all configurations generated by distributing three electrons in the valence σ-orbital space. The space consists of two SCF occupied π orbitals (1, 2a″) and one antibonding π orbital (3a″) as shown in Table I, where active orbitals for other states are also listed. Assuming a planar symmetry, this MCSCF wave function has nine configuration state functions (CSF), which will be called MC4. Similar MCSCF wave functions are used for the bisected diradical (structures **3** and **4** in Figure 1) and cis–trans transition-state structures.

Geometry optimization was carried out by using the MC4 wave functions with the 4-31G basis[12] (MC4(431G)) and the gradient technique.[13] In addition, several points in the vicinity of the MC4(431G) equilibrium geometry are determined by keeping the C1–C2 bond length fixed and relaxing all other geometrical parameters. The C1–C2 bond lengths studied range from 1.30 to 1.47 Å, which include carbene and diradical structures.

In order to measure the polarization function and correlation energy effects on the structure and energy, MC4 calculations with the double-ζ polarization basis[14] (MC4(DZP)) were carried out at some selected MC4(431G) geometries to produce a set of natural orbitals. MC4(DZP) calculations with the natural orbitals were repeated to produce a unique set of configuration weights (CW). Three dominant electronic configurations, which generate five configuration state functions (CSF), listed in Table II, were then selected as the reference configurations for subsequent multireference CI calculations (MRCI(DZP)). Table II also lists orbital maps that are used in generating MRCI(DZP) wave functions for the $^3A''$, $^3A'$, and ^3A states. The number of CSF's generated ranges from 367 926 to 739 185, where a partial interacting space method is used for the double excitations from orbitals in the inactive orbital set such that only the singlet couplings between electrons in the inactive and external orbital sets are retained.

A convergence of the energy against the number of reference configurations was also investigated by deleting less dominant configurations one at a time. This was done to estimate an energy that could be calculated if all the configurations in the MC4 wave function were to be included as reference configurations in the

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Table II. Reference CSF's, Orbital Maps, and Number of CSF's for MRCI Wave Functions for Triplet Vinylmethylene

state	$^3A''$				$^3A'$				^3A			
reference CSF												
active	a′	a′	a″	a″	a′	a′	a″	a″	a	a	a	a
orbital	10	1	2	3	9	10	2	3	10	11	12	13
occupation	1	2	0	1	1	1	2	0	2	1	1	0
	1	0	1	2	1	1	0	2	0	1	1	2
	1	1	1	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1	1	1	1
orbital map												
orb sym		a′	a″			a′	a″			a		
core		3	0			3	0			3		
inactive		6	0			5	1			6		
active		1	3			2	2			4		
external		39	13			36	16			52		
core complt		3	0			3	0			3		
total		52	16			49	19			68		
no. of CSF's		367 926				382 283				739 185		

Table III. MC4(431G) Geometrical Parameters and Energies Calculated in Various Approximations for Selected Points near the Equilibrium Structures of Triplet *trans*- and *cis*-Vinylmethylenes

	point							
	1	2	3	4	5	6	7	8
			Geometrical Parameters[a]					
C1C2	1.300	1.374	1.403	1.476	1.300	1.375	1.400	1.476
C2C3	1.414	1.394	1.386	1.367	1.413	1.393	1.387	1.367
C1H1	1.073	1.072	1.071	1.070	1.074	1.072	1.073	1.070
C1H2	1.072	1.071	1.070	1.070	1.072	1.071	1.071	1.070
C2H3	1.079	1.078	1.077	1.076	1.077	1.075	1.074	1.075
C3H4	1.071	1.069	1.068	1.069	1.071	1.071	1.070	1.071
C1C2C3	125.4	124.8	124.4	123.8	125.9	125.2	125.2	124.1
H1C1C2	122.2	121.4	121.1	120.5	122.3	121.7	121.4	120.6
H2C1C2	122.0	121.3	121.1	120.4	122.0	121.3	121.0	120.3
H3C2C3	115.5	117.1	117.8	119.3	114.9	116.5	117.0	118.8
H4C3C2	130.7	131.3	131.7	132.3	130.6	131.5	132.0	132.0
			Total Energies (hartrees)[b]					
MC4(431G)	.67882	.68399	.68339	.67773	.67873	.68403	.68361	.67796
C1C2 grad.	−.0800	−.0003	.0210	.0580	−.0809	−.0004	.0178	.0568
MC4(DZP)	.86551	.87124	.87096	.86580	.86546	.87130	.87107	.86604
MRCI(DZP)	.20117	.20812	.20819	.20366	.20062	.20815	.20830	.20403
NORM	.99635	.99850	.99932	.99980	.99636	.99850	.99924	.99983
MRCI*(DZP)	.20190	.20842	.20833	.20370	.20135	.20845	.20845	.20406
			Relative Energies (kcal/mol)[c]					
MRCI*(DZ)	50.1	46.0	46.0	48.9	50.4	46.0	46.0	48.7

[a] Bond lengths are in angstroms and bond angles are in degrees. [b] Only fractional parts are given; the integer parts are −115. and −116. for MC4 and MRCI results, respectively. See the text for the definitions of the wave functions. [c] These are given with respect to the $^1A_1$ state of methylacetylene, for which MRCI*(DZP) is estimated to be −116.28168.

CI calculations. These results will be designated as MRCI*(DZP) and estimated as

$$\text{MRCI*(DZP)} = \text{MRCI(DZP)} - 0.2(1.0 - \text{NORM}) \quad (1)$$

where NORM is the sum of the squares of the MC4 SCF coefficients. More detailed discussion on eq 1 will be given in section III, where the MRCI*(DZP) relative energy estimates with respect to the X $^1A_1$ state of methylacetylene will also be discussed.

B. **Results and Discussion. Ground-State Structure.** The geometries determined by the MC4(431G) wave function and energies calculated in various approximations for the ground $^3A''$ state are given in Table III, where points 1–4 are for *trans*-vinylmethylene and points 5–8 are for *cis*-vinylmethylene.

We note first that the MC4(431G) calculation already gives an allylic-like structure with C–C bond lengths of 1.374 and 1.394 Å for the trans system and 1.375 and 1.393 Å for the cis system (points 2 and 6 in Table III). As the level of approximation improves, the equilibrium C–C bond lengths tend to become equivalent. Since all the geometrical parameters vary smoothly from the carbene to diradical structure (e.g., points 1–4 in Table III), the linearly interpolated geometrical parameters according to the MRCI*(DZP) energies (see Figure 2) are expected to be reasonably reliable. The estimated geometrical parameters and energies are listed in Table IV, and the energies for *trans*-vinylmethylene are plotted as a function of the C1–C2 bond length in Figure 2. A transition state for the cis–trans isomerization was also determined with the MC4(431G) wave function, and the results are also given in Table IV (point 11) and Figure 2. Thus, our best results predict that triplet vinylmethylene has two isoenergetic minima (trans and cis) that have allylic planar structures with ΔR of −0.006 and −0.001 Å, respectively. Furthermore, these lie 45.9 kcal/mol above the X $^1A_1$ state of methylacetylene and are separated by a potential energy barrier of 5.7 kcal/mol.

Feller et al. recently reported an MCSCF study for the triplet vinylmethylene structure.[15] Their best MCSCF calculation (8-orbital/8-electron σ/π MCSCF) gave C1–C2 and C2–C3 bond lengths of 1.400 and 1.413 Å with ΔR = −0.013 Å. Compared

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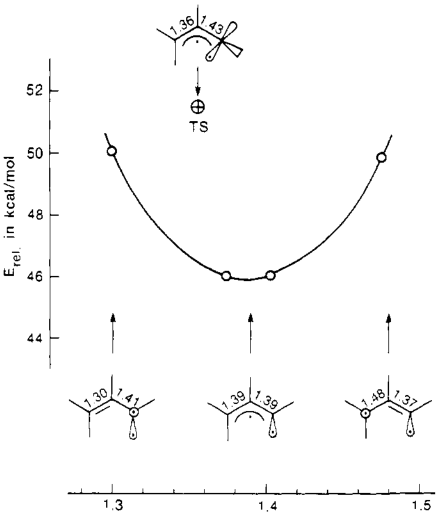

Figure 2. MRCI*(DZP) potential energy curve for $^3A''$ *trans*-vinylmethylene between the carbene (**7**) and diradical (**5**) structures. The cis–trans transition-state energy is indicated by TS, and the energies are relative to that of the $^1A_1$ state of methylacetylene.

Table IV. Structures and Energies for Triplet *trans*- (**9**) and *cis*-Vinylmethylene (**10**) and the Trans–Cis Transition State (**11**)

	geometry		
	9	**10**	**11**
	Geometrical Parameters[a]		
C1C2	1.385	1.389	1.356
C2C3	1.391	1.390	1.430
C1H1	1.072	1.073	1.073
C1H2	1.071	1.071	1.072
C2H3	1.078	1.074	1.078
C3H4	1.069	1.070	1.068
C1C2C3	124.6	125.2	124.4
H1C1C2	121.3	121.5	121.6
H2C1C2	121.2	121.1	121.4
H3C2C3	117.4	116.8	117.1
H4C3C2	131.5	131.8	135.8
H1C1C2C3			3.2
H2C1C2C3			177.1
H3C2C3C1			175.6
H4C3C2C1			90.8
	Total Energies (hartrees)[b]		
MC4(431G)			.67401
C1C2 grad			−.0005
MC4(DZP)			.86101
MRCI(DZP)			.19801
NORM			.99288
MRCI*(DZP)	.20853	.20857	.19943
	Relative Energies (kcal/mol)[c]		
MRCI*(DZ)	45.9	45.9	51.6

[a] Bond lengths are in angstroms and bond angles are in degrees. [b] Only fractional parts are given; the integer parts are −115. and −116. for MC4 anf MRCI results, respectively. See the text for the definitions of the wave functions. [c] These are given with respect to the $^1A_1$ state of methylacetylene, for which MRCI*(DZP) is estimated to be −116.28168.

to these our MRCI*(DZP) C–C bond lengths are slightly shorter but are much closer (ΔR = −0.006 or −0.001 Å for the trans and cis systems, respectively). This implies that the correlation energy effect not included in the MCSCF is to make ΔR smaller. This can be explained in part by the fact that for the $^3A''$ state the correlation energy contribution is larger at the diradical structure than at the carbene; the SDCI(DZP) calculations in paper 1 gave a 3 kcal/mol difference in favor of the diradical structure.

The MC4(431G) structure for the cis–trans transition state indicates that the isomerization path can be described as a rotation of the carbene hydrogen along the C2–C3 bond. The geometrical parameters show a sign of the resonance effect such as a noticeable decrease of the difference between C–C bond lengths (0.135 and 0.074 Å for SCF and MC4, respectively). The barrier height of 5.7 kcal/mol is increased by 1 kcal/mol from the SDQCI result of 4.6 kcal/mol, which reflects the resonance effects on the $^3A''$ state.

Table V. CI Weights for $^3A''$ State MC4(DZP) Wave Functions

point structure				2 trans	6 cis
10a′	1a″	2a″	3a″		
1	2	1	0	0.96001	0.96012
1	0	1	2	0.14592	0.14546
1	1	1	1	0.20095	0.10206
1	1	1	1	0.11596	0.17273
1	1	1	1	0.04203	0.12348

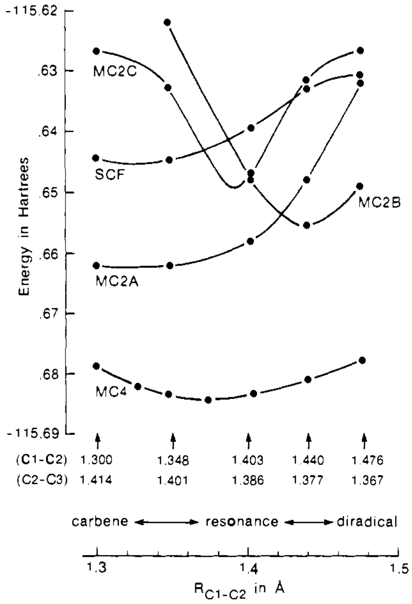

Figure 3. Potential energy curves for the $^3A''$ *trans*-vinylmethylene between the carbene (**7**) and diradical (**5**) structures calculated by various two-configuration MCSCF(431G) wave functions. See the text for description of the wave functions employed.

Although the vinylmethylene structures represented by bisected diradicals (**3**, **4**) do not correspond to minima on the potential energy surface, and hence are most likely not stable species, nevertheless, one can still determine a lowest energy structure in C_s symmetry. We have carried out an MC4(431G) geometry optimization which yielded a structure similar to the SCF structure except for a slight lengthening of the C2–C3 bond by about 0.02 Å for both the trans and cis diradicals. The energy results calculated by MRCI*(DZP) show that these bisected diradicals are isoenergetic and located 17 kcal/mol above the $^3A''$ of planar diradical (**5**, **6**). The MRCI*(DZP) relative energy is close to the SCF(431G) energy of 15 kcal/mol. These indicate the SCF(431G) path from the $^3A'$ state of the bisected diradical to the $^3A''$ state of the planar diradical, reported in paper 1, is reasonable. Thus, the triplet bisected diradical structures are only inflection points on the lowest triplet surface of vinylmethylene.

Two-Configuration MCSCF Calculations. As shown in Table V, there are three dominant configurations in the MC4 wave function for the $^3A''$ state (the third configuration generates three CSF's). The sum of the squares of the coefficients of the first two configurations is about 0.94, and these two configurations should at least conceptually be capable of describing the resonance phenomenon between the carbene and diradical structures. We have carried out two-configuration SCF calculations (MC2) at several points on the MC4(431G) path, and the results are summarized in Figure 3 together with the SCF and MC4 results. These calculations were done with the 431G basis.

The results indicated that the MC2 wave function does not adequately describe the configuration space and that depending on the input orbitals, different solutions can be obtained. The MC4 calculations, however, produce a unique solution regardless of the input orbitals.

The three solutions shown in Figure 3 are obtained as follows: At the carbene geometry (C1–C2 = 1.300 Å), the lowest energy MC2 solution has a carbene-like, localized orbital structure. Using these orbitals as input to the MC2 calculations for the next point, say at C1–C2 = 1.348 Å, one obtains a solution whose orbital structure is still carbene-like. If one repeats this process, the curve designated MC2A in Figure 3 can be obtained. If one starts at the diradical geometry (C1–C2 = 1.476 Å), where the lowest energy solution has a diradical orbital structure, and uses a similar process for the next point, the MC2B curve in Figure 3 is obtained. The third curve, MC2C, results when delocalized orbitals are used as input. Since orbitals are delocalized, the MC2C curve has a minimum at the resonance geometry although its energy is higher than that of the MC2A solution. We note that even if we trace the lowest energies of the MC2 solutions, the resultant curve is essentially the same as the SCF curve. This indicates that at least the third configuration shown above is necessary for an MCSCF wave function to be able to describe a resonance phenomenon.

The results of the MC2 calculation discussed above give an indication as to why the GVB calculations[7] failed to predict the allylic structure for triplet vinylmethylene. Furthermore, it supports the adequacy of the MC4 wave function for describing vinylmethylene structures.

III. Singlet Vinylmethylene

Singlet vinylmethylene has six possible conformations (structures **3**–**8** in Figure 1). SCF and SDCI studies reported in paper 1 indicated that trans- and cis-planar carbenes (**7** and **8**) should be the most stable conformations followed by trans- and cis-planar diradicals (**5** and **6**). Both trans and cis bisected diradicals (**3** and **4**) not only are higher in energy but also are unstable with respect to the CH_2 rotation along the C1–C2 bond and are transformed without any potential energy barriers to planar diradicals (**5** and **6**).

For the triplet states of vinylmethylene, as discussed in the previous section, it was found that resonance energy arising from the interaction between the carbene and diradical electronic structures plays an important role in stabilization of the triplet structure. For singlet vinylmethylene, this resonance phenomenon does not occur since the symmetry of the lowest state of carbene differs from that of the diradical although their energies are close (60.2 and 62.6 kcal/mol for the $^1A'$ state of trans-planar carbene and the $^1A''$ state of the trans-planar diradical, respectively). Thus, a reaction path connecting these two states must lie in C_1 symmetry. The purpose of the MCSCF study of singlet vinylmethylene was to determine the lowest energy reaction path between the $^1A'$ state of planar carbene and the $^1A''$ state of diradical to see whether a barrier exists and hence determine if these structures really represent local minima.

The MCSCF and MRCI calculations, which will be described in detail below, yielded rather unexpected results such that neither of these two states represents local minima and ring-closure mechanisms for *trans*- and *cis*-vinylmethylene differ considerably. First we shall describe the computational models employed. Subsequently, the potential surfaces for *trans*- and *cis*-vinylmethylenes will be presented and discussed, respectively.

A. Computational Details. Two types of MCSCF wave functions were employed in this study. The first includes all configurations generated by distributing four electrons in four orbitals, which shall be designated as the MC4 wave function. The configurations included in the second are generated by distributing eight electrons in eight orbitals (MC8). The symmetry, active orbitals involved, and the numbers of configuration state functions (CSF) are listed in Table VI for various states. The MC4 wave function meets the minimum requirement for describing reaction paths among the planar carbene and the diradicals, and bisected diradicals. For the carbene to diradical path the C1–C2 π bond will be broken and the C2–C3 π bond will be formed. To take this into account, bonding and antibonding π orbitals are included in the active orbitals. The other two active orbitals would be two open-shell orbitals (π at C1 and σ at C3) for the diradical and a closed-shell σ and π orbital at C3 for the carbene to account for the near-degeneracy effect. Two additional C–C bonds are correlated in the MC8 wave function with two pairs of σ bonding and antibonding orbitals in order to properly describe the conversion of vinylmethylene in C_s to cyclopropene in C_{2v} symmetry.

Table VI. Active Orbitals and Number of Configuration State Functions for Various MCSCF Wave Functions for Singlet Vinylmethylene

WF	state	active orbitals	no. of CSF's	structure
MC4	$^1A'$	10a′, 1,2,3a″	12	planar carbene
MC4	$^1A''$	10a′, 1,2,3a″	8	planar diradical
MC4	$^1A'$	9,10a′, 2,3a″	12	bisected diradical
MC4	^1A	10,11,12,13a	20	other points
MC8	$^1A'$	6,...,10a′, 1,2,3a″	900	planar carbene
MC8	$^1A''$	6,...,10a′, 1,2,3a″	864	planar diradical
MC8	$^1A'$	5,...,10a′, 2,3a″	924	bisected diradical
MC8	^1A	6,...,13a	1764	other points

For structure and reaction path determinations MC4 or MC8 wave functions with the 4-31G basis (MC4(431G) or MC8(431G)) were used, and the results will be called the MC4(431G) or MC8(431G) structures or paths. These 431G paths appear to be a reasonable approximation to the actual paths, but the energy profiles are not correct due to lack of polarization functions and correlation energy corrections. To remedy this, configuration interaction (CI) calculations were performed on the 431G paths, which will be described in detail below.

In order to obtain sets of orbitals and dominant configurations to be used as reference configurations, MC4(DZP) calculations and natural orbital transformations were carried out at some selected points on the paths to determine a unique set of CI coefficients of MC4 wave functions. Reference configurations are then selected according to the CI coefficients. Table VII lists reference CSF's chosen for various CI wave functions and also includes orbital maps and numbers of CSF's generated. The numbers of reference CSF's are 6 and 7 for C_s and C_1 symmetry. These reference CSF's are chosen so that the sum of the squares of the coefficients is greater than 0.99 for all points studied. We shall refer to this quantity as NORM. With these reference CSF's, CI wave functions are constructed that include MC4 configurations and those generated by single and double excitations from the reference CSF's. The core orbitals (1s orbitals of three carbons) are kept frozen and three core complement orbitals are excluded from the external orbital space. We shall call these CI wave functions MRCI.

Because the NORMs of reference CSF's are not constant along the path, the MRCI(DZP) energy profile may not be smooth. We expect that if all MC4 configurations are used as reference configurations, the resultant MRCI(DZP) energy profile should be in general consistent and should also be smooth. An attempt was made therefore to improve the quality of the energy profile by extrapolating MRCI(DZP) results to a limit where all the CSF's in the MC4 wave function are included. For some points on the surface we have investigated a convergence pattern for the MRCI energy as a function of NORM. The results are shown in Figure 4, where one least important configuration is deleted one at a time. The results revealed that a linear extrapolation may be sufficient for the cases where NORMs are greater than 0.99 and linear coefficients appear to vary little, with a mean value of −0.2. Thus, the extrapolation formula, eq 1, given in section II, is used for all points on the surface studied, including the triplet surface. The extrapolated values are designated MRCI*(DZP) and are our best estimates of the energies.

It is instructive to express the energies of these isomers relative to the $^1A_1$ state of methylacetylene, which is the isomer with the lowest energy of the C_3H_4 system. It is difficult to design an MCSCF wave function for methylacetylene equivalent to the MC4 wave function employed here. We have instead matched the MRCI* potential energy surface with the SDQCI surface at the

Table VII. Reference Configurations, Orbital Maps, and Number of CSF's for Various CI Wave Functions for Singlet Vinylmethylene

state	$^1A'$				$^1A''$				$^1A'$				^1A			
orbitals	a′ 10	a″ 1	a″ 2	a″ 3	a′ 10	a″ 1	a″ 2	a″ 3	a′ 9	a′ 10	a″ 2	a″ 3	6a 10	a 11	a 12	a 13
configuration																
1	2	2	0	0	1	2	1	0	2	0	2	0	2	2	0	0
2	2	0	2	0	1	0	2	1	2	0	0	2	2	0	2	0
3	2	0	1	1	1	1	0	2	0	2	2	0	0	2	0	2
4	0	2	2	0	1	0	1	2	0	2	0	2	0	0	2	2
5	0	2	0	2	1	1	1	1	1	1	1	1	0	1	2	1
6	0	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1
7													1	1	1	1
orbital map																
orb sym		a′	a″			a′	a″			a′	a″			a		
core		3	0			3	0			3	0			3		
inactive		6	0			6	0			5	1			6		
active		1	3			1	3			2	2			4		
external		39	13			39	13			36	16			52		
core complt		3	0			3	0			3	0			3		
total		52	16			52	16			49	19			68		
no. of CSF's		324 348				342 641				339 784				718 196		

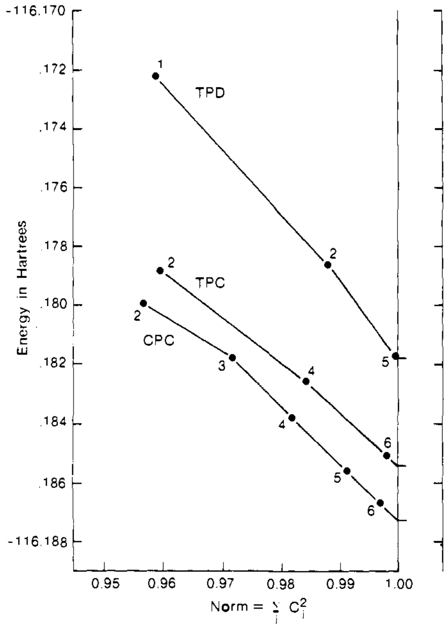

Figure 4. Convergence patterns of MRCI(DZP) energies with respect to NORM (the sum of the squares of the MCSCF CI weights of those used as reference configurations). The numerals indicate the number of reference configurations used.

SCF(DZP) geometry of the $^1A'$ state of trans-planar carbene. Thus, the MRCI*(DZP) energy (−116.28168 hartrees) of methylacetylene is estimated by subtracting the SDQCI(DZP) relative energy of 0.09595 hartree from the MRCI*(DZP) energy of −116.18573 hartrees calculated at the SCF(DZP) geometry of trans-planar carbene. In a similar manner, the MRCI*(DZP) energies of −116.24576 and −116.21223 hartrees are estimated for cyclopropene and propenylidene.

B. *trans*-Vinylmethylene. To start out this MCSCF study, geometries of trans-planar carbene (*TPC*) and diradical (*TPD*) were optimized by using the MC4(431G) wave functions constrained to C_s symmetry. The resultant geometries shown in Table VIII (points *A1* and *A4*) are close to the SCF results except for slight lengthening of the C2–C3 bond (<0.02 Å). The energy levels are still reversed; that is, *TPC* is 3.6 kcal/mol higher in energy than *TPD* although it is considerable improvement from the SCF(431G) result of 11.5 kcal/mol.

Geometries of two points on the reaction path between *TPC* and *TPD* were determined by relaxing all geometrical parameters except the C1–C2 bond length. The bond lengths chosen are 1.375 and 1.400 Å, and the calculations were carried out in C_1 symmetry.

Table VIII. Geometrical Parameters and Energies for Selected Points on the MC4(431G) Singlet Trans-Planar Carbene to Trans-Planar Diradical Path

point	*A1* *TPC*	*A2*	*A3*	*A4* *TPD*
state	$^1A'$	^1A	^1A	$^1A''$
	Geometrical Parameters[a]			
C1C2	1.348	1.375	1.403	1.461
C2C3	1.469	1.384	1.352	1.331
H1C1	1.072	1.071	1.071	1.070
H2C1	1.073	1.072	1.070	1.069
H3C2	1.078	1.080	1.080	1.079
H4C3	1.101	1.081	1.072	1.068
C1C2C3	118.2	122.9	124.2	125.0
H1C1C2	119.8	120.7	120.7	120.6
H2C1C2	122.6	121.6	121.1	120.7
H3C2C3	122.9	118.8	118.1	118.2
H4C3C2	108.8	120.6	129.1	135.5
H1C1C2C3	0.0	0.4	1.3	0.0
H2C1C2C3	180.0	173.1	171.6	180.0
H3C2C3C1	180.0	178.6	178.3	180.0
H4C3C2C1	180.0	147.1	154.8	180.0
	Total Energies (hartree)[b]			
MC4(431G)	.64625	.64937	.65059	.65206
MC4(DZP)	.85092	.84698	.84400	.84253
NORM	.99691	.99905	.99743	.99958
MRCI(DZP)	.18511	.18810	.18489	.18178
MRCI*(DZP)	.18573	.18827	.18540	.18186
	Relative Energies (kcal/mol)[c]			
MRCI*(DZP)	60.2	58.6	60.4	62.7

[a] Bond lengths are in angstroms and bond angles are in degrees. [b] Only fractional parts are given; the integer parts are −115. and −116. for MC4 and MRCI results, respectively. See the text for the definitions of the wave functions. [c] These are given with respect to the $^1A_1$ state of methylacetylene, for which MRCI*(DZP) is estimated to be −116.28168.

The results (listed under *A2* and *A3* in Table VIII) indicate that structures at these points are essentially planar except that the terminal hydrogen H4 is out of the plane of three carbon atoms.

For singlet *trans*-vinylmethylene, structures and paths between *TPC* and *TPD* were also investigated by the MC8(431G) wave function. The results are given in Table IX (points *B1* to *B4*). We note that the MC8(431G) C–C bonds are noticeably longer than the SCF(431G) C–C bonds (as much as 0.04 Å) for both *TPC* and *TPD*. In fact, the MC8(431G) optimization of cyclopropene revealed that it would give artificially longer C–C bonds; the MC8 bond lengths are 1.533 and 1.322 Å, while the experimental values are 1.509 and 1.296 Å. Points between *TPC* and *TPD* are also determined in the same manner, with C1–C2 bond lengths of 1.403 and 1.440 Å.

Table IX. Geometrical Parameters and Energies for Selected Points on the MC8(431G) Singlet Trans-Planar Carbene via Trans-Planar Diradical to Cyclopropene Path

point	*B1*	*B2* *STV*	*B3*	*B4*	*B5* *TS2*	*B6*
symmetry	$^1A'$	^1A	^1A	$^1A''$	^1A	$^1A'$
Geometrical Parameters[a]						
C1C2	1.369	1.403	1.440	1.482	1.509	1.482
C2C3	1.491	1.401	1.352	1.349	1.336	1.305
H1C1	1.072	1.071	1.071	1.069	1.071	1.070
H2C1	1.071	1.071	1.070	1.069	1.074	1.070
H3C2	1.076	1.078	1.079	1.078	1.075	1.070
H4C3	1.102	1.082	1.068	1.068	1.065	1.060
C1C2C3	117.0	121.2	125.0	124.8	115.0	90.0
H1C1C2	122.5	121.2	120.7	120.4	118.5	120.5
H2C1C2	119.4	120.1	120.6	120.4	119.2	120.5
H3C2C3	123.8	120.4	117.7	118.2	124.6	137.4
H4C3C2	107.5	119.4	135.3	134.9	139.3	156.3
H1C1C2C3	0.0	1.7	1.8	0.0	37.2	91.9
H2C1C2C3	180.0	169.7	175.9	180.0	117.9	91.9
H3C2C3C1	180.0	179.1	179.5	180.0	176.3	180.0
H4C3C2C1	180.0	146.1	173.9	180.0	164.6	180.0
Total Energies (hartrees)[b]						
MC8(431G)	.69962	.70073	.70232	.70328	.70266	.72717
MC4(DZP)	.85044	.84763	.84229	.84215	.84295	.86675
NORM	.99714	.99911	.99443	.99957	.99851	.99978
MRCI(DZP)	.18497	.18902	.18200	.18132	.18127	.20989
MRCI*(DZP)	.18554	.18920	.18311	.18132	.18157	.20993
Relative Energies (kcal/mol)[c]						
MRCI*(DZP)	60.4	58.1	61.9	62.9	62.8	45.0

[a] Bond lengths are in angstroms bond angles are degrees. [b] Only fractional parts are given; the integer parts are −115. and −116. for MC4 and MRCI results, respectively. See the text for the definitions of the wave functions. [c] These are given with respect to the $^1A_1$ state of methylacetylene, for which MRCI*(DZP) is estimated to be −116.28168.

No further optimization of the path itself is performed. However, the energy profile of the path was improved by inclusion of polarization function and correlation energy corrections. The MC4(DZP), MRCI(DZP), and MRCI*(DZP) energy results for the MC4 and MC8 paths are listed in Tables VIII and IX, respectively. We first note that at the MC4(DZP) level *TPC* is lowest in energy and no barriers exist for these two paths. In fact, these potential curves are similar in shape except the MC8 curve is shifted toward the longer C1–C2 bond lengths. The energy difference between *TPC* and *TPD* also appears to be too large in comparison to the SDQCI results. This is mainly due to the σ- and π-orbital near-degeneracy effect at *TPC* being overestimated. However, the MRCI calculations correct this overestimate so that the MRCI*(DZP) energy difference between *TPC* and *TPD* is 2.5 kcal/mol while the SDQCI(DZP) is 3.2 kcal/mol, indicating that the SDQCI(DZP) surface is a reasonable one at least in the vicinity of *TPC* and *TPD* structures. Furthermore, the MRCI*(DZP) energy profiles show that there is no barrier between the *TPC* and *TPD* structures and a local minimum is located between them. Although *TPC* and *TPD* are no longer stable points on the surface, our best approximation to the reaction path between these two points is a composite path consisting of points *A1*, *A2*, *B2*, *B3*, and *A4* in Tables VIII and IX and its MRCI*(DZP) energy profile is shown in Figure 5.

Therefore, the point with lowest energy on this path (*B2*) most likely represents a local minimum for singlet *trans*-vinylmethylene. It has C–C bond lengths of 1.403 and 1.401 Å, and the terminal hydrogen is out of the plane of C1, C2, and C3. Since it is nonplanar, singlet *trans*-vinylmethylene has two local minima; one structure is represented by *B2* and the other is its stereoisomer; we desginate these structures *STV* and *STV'*. These two minima are isoenergetic, lying 58.1 kcal/mol above the $^1A_1$ state of methylacetylene and separated by a potential barrier of 2.1 kcal/mol on a reaction path that is via trans-planar carbene (*TPC*).

As the geometry of *STV* indicates, a resonance between the carbene and diradical structures may be a stabilizing factor here. However, unlike the triplet states discussed in the previous section, the resonance does not occur on the planar conformation for the singlet system because states of different symmetries are involved. A resonance can occur, however, in the lowest symmetry (this case in C_1 symmetry); it is the pseudo-Jahn–Teller effect.[16] The SCF(DZP) calculations at the *A2* geometry clearly show this effect. The open-shell SCF ($10a^2$, 11a, 12a) and the closed-shell SCF ($10a^2$, $11a^2$) give similar energies of −115.79536 and −115.79596 hartrees, respectively. Compared to the energy of −115.80766 hartrees for the trans-planar carbene (*TPC*), these diabatic states are 0.01170 hartree higher in energy, but when these are allowed to interact, lowering of the energy results. More detailed discussion will be given on this point later in section D

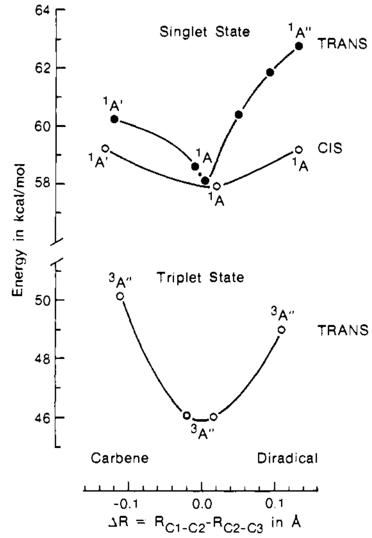

Figure 5. MRCI*(DZP) potential energy curves for vinylmethylene between the planar carbene and planar diradical structures. The energies are relative to the $^1A_1$ state of methylacetylene. The $^3A''$ cis curve is almost identical with the $^3A''$ curve and is not shown here.

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(16) Opik, U.; Pyrce, M. H. L. *Proc. R. Soc. London, A* **1957**, *A238*, 425. Murrell, J. N. *Quantum Theory of Chemical Reactions*, Daudel, R., Pullman, A., Salem, L., Veillard, A., Eds.; D. Reidel: Dordrecht, Holland, 1980; Vol. 1, pp 161–176.

Table X. Geometrical Parameters and Energies for Selected Points on the MC4(431G) Singlet Cis-Planar Carbene to Cyclopropene Path

point	*C1*	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*
	CPD	*CPC*	*SCV*	*TS1*		*CBD*			
symmetry	$^1A''$	$^1A'$	^1A	^1A	^1A	$^1A'$	$^1A'$	$^1A'$	$^1A'$
				Geometrical Parameters[a]					
C1C2	1.465	1.349	1.397	1.467	1.462	1.463	1.452	1.452	1.488
C2C3	1.331	1.473	1.378	1.338	1.344	1.333	1.317	1.317	1.265
H1C1	1.069	1.074	1.069	1.067	1.079	1.073	1.071	1.071	1.076
H2C1	1.070	1.073	1.077	1.083	1.071	1.073	1.071	1.071	1.076
H3C2	1.076	1.074	1.079	1.075	1.070	1.068	1.066	1.066	1.070
H4C3	1.069	1.103	1.081	1.074	1.077	1.073	1.059	1.059	1.140
C1C2C3	125.1	124.6	122.9	122.2	120.9	106.9	92.5	90.0	78.8
H1C1C2	120.5	121.4	120.6	117.9	119.7	120.0	120.8	120.8	119.5
H2C1C2	120.9	122.2	123.1	119.4	116.3	120.0	120.8	120.8	119.5
H3C2C3	118.1	116.7	118.0	119.6	119.3	126.1	132.6	132.6	142.8
H4C3C2	136.3	107.4	120.2	132.5	129.8	133.4	151.2	170.0	173.7
H1C1C2C3	0.0	0.0	9.1	6.8	14.8	79.8	89.5	89.5	99.5
H2C1C2C3	180.0	180.0	162.8	143.7	128.2	79.8	89.5	89.5	99.5
H3C2C3C1	180.0	180.0	167.9	169.2	168.5	180.0	180.0	180.0	180.0
H4C3C2C1	0.0	0.0	41.9	27.1	26.4	0.0	0.0	0.0	180.0
				Total Energies (hartrees)[b]					
MC4(431G)	.65041	.64403	.65088	.65421	.65592	.66543	.66246	.66393	.67194
MC4(DZP)	.84042	.84905	.84769	.84703	.84922	.85876	.85984	.86127	.87514
NORM	.99918	.99678	.99828	.99668	.99714	.99976	.99974	.99979	.99982
MRCI(DZP)	.18006	.18670	.18907	.18676	.18896	.19907	.20545	.20820	.22390
MRCI*(DZP)	.18022	.18735	.18942	.18742	.18953	.19912	.20550	.20824	.22393
				Relative Energies (kcal/mol)[c]					
MRCI*(DZP)	63.7	59.2	57.9	59.2	57.8	51.8	47.8	46.1	36.3

[a] Bond lengths are in angstroms and bond angles are in degrees. [b] Only fractional parts are given; the integer parts are −115. and −116. for MC4 and MRCI results, respectively. See the text for the definitions of the wave functions. [c] These are given with respect to the $^1A_1$ state of methylacetylene, for which MRCI*(DZP) is estimated to be −116.28168.

in connection with the excited-state surface.

C. *cis*-Vinylmethylene. MC4(431G) geometries for cis-planar diradical (*CPD*) and cis-planar carbene (*CPC*) are given in Table X, and their energies are similar to those for the corresponding trans species. However, when geometry optimization of points on a reaction path between *CPC* and *CPD* was carried out in the same manner as in the trans case, a bisected diradical structure with substantially lower energy resulted, suggesting that a local minimum for *cis*-vinylmethylene may have a bisected diradical structure (**4** in Figure 1).

We have therefore attempted to optimize the geometry of *cis*-vinylmethylene by starting from a slightly perturbed geometry of *cis*-planar carbene (the terminal hydrogen was placed slightly out of the molecular plane). In this way we should obtain not only an equilibrium geometry but also an approximate reaction path from *CPC*. It eventually converged to a cis bisected diradical structure with the angle (C1C2C3) of 107° (see point *C6* in Table X). The MC4(431G) energy profile (Figure 6a) and the maximum gradients (Figure 6b) as a function of the optimization steps are shown in Figure 6. We note that, although the energy profile shows a monotonic decrease to *C6*, the maximum gradient curve has an interesting feature. In particular, the gradients become small (<0.01) at steps 12 and 16, indicating extrema of some sort. The MRCI*(DZP) energy profile shown in Figure 6c reveals that the structure at the 12th step (geometrical parameters listed under *C3* in Table X) corresponds to a local minimum with a resonance-like structure and that at the 16th step (*C4* in Table X) corresponds to a transition state with a diradical structure. Thus, the path may be divided into two parts. The first corresponds to breaking of the C1–C2 π bond and subsequent forming of the C2–C3 π bond with a local minimum in between. We also note that in this part the plane of H1C1H2 remains reasonably close to the C1C2C3 plane but the terminal hydrogen on C3 (H4) subsequently comes out of the plane; this situation closely resembles that of the *trans*-vinylmethylene system. In the second part a major change occurs in the rotation of the CH_2 group along the C1–C2 bond to reach a bisected position and H4 returns to the C1C2C3 plane.

The MRCI*(DZP) energy profile (see Figure 6c) indicates the existence of a local minimum also for singlet *cis*-vinylmethylene; we designate this *SCV*, and its geometrical parameters are listed under *C3* in Table X. Since it is nonplanar, singlet *cis*-vinylmethylene also has two local minima; one is represented by *C3* and the other by its stereoisomer. These two minima are isoenergetic, lying 57.9 kcal/mol above the $^1A_1$ state of methylacetylene and separated by a potential barrier of 1.3 kcal/mol on a reaction path via the cis-planar carbene structure.

Figure 5 summarizes the results for the low-lying states of vinylmethylene. We have located six minima in total, all of which have a resonance structure with equivalent C–C bond lengths. The most stable are the $^3A''$ states of *trans*- and *cis*-vinylmethylene, which lie 46 kcal/mol above the $^1A_1$ state of methylacetylene and are most likely global minima. The remaining four are local minima, belong to the singlet ground-state surface of C_3H_4, and have the same energy, lying 12 kcal/mol above triplet vinylmethylene. These singlet species are reactive intermediates that can easily be converted to cyclopropene by ring closure. The calculated reaction paths and potential energy barriers for ring closure will be presented and discussed in section IV. In the remaining part of this section a part of the surface of a low-lying excited state of vinylmethylene that is connected to the ground-state surface is discussed.

D. Surface Crossing. The present and previous[1,7] studies have shown that when vinylmethylene is in a planar conformation, the $^1A'$ state favors a carbene structure while the $^1A''$ state favors a diradical structure; furthermore, the energies of these two electronic states are close. This implies that in planar symmetry the potential energy surface of the $^1A'$ state intersects that of the $^1A''$ state somewhere between the carbene and diradical structures; there is a curve of intersection where two states have the same energy. As stated above, singlet vinylmethylene has equilibrium geometries with nonplanar C_1 symmetry, and those of the lowest $^1A'$ and $^1A''$ states belong to the lowest singlet surface (see Figure 5). Therefore, the curve of intersection represents points where the first excited (S_1) and the lowest singlet (S_0) surfaces meet, and the surface below belongs to the lowest state while the surface above belongs to the excited state. We note that the lowest singlet surface (S_0) of vinylmethylene is connected to the singlet ground-state surface of methylacetylene, allene, and cyclopropene.[2] The location of the curve is of considerable interest because it is where an interconversion of the excited- and ground-state species most likely takes place.

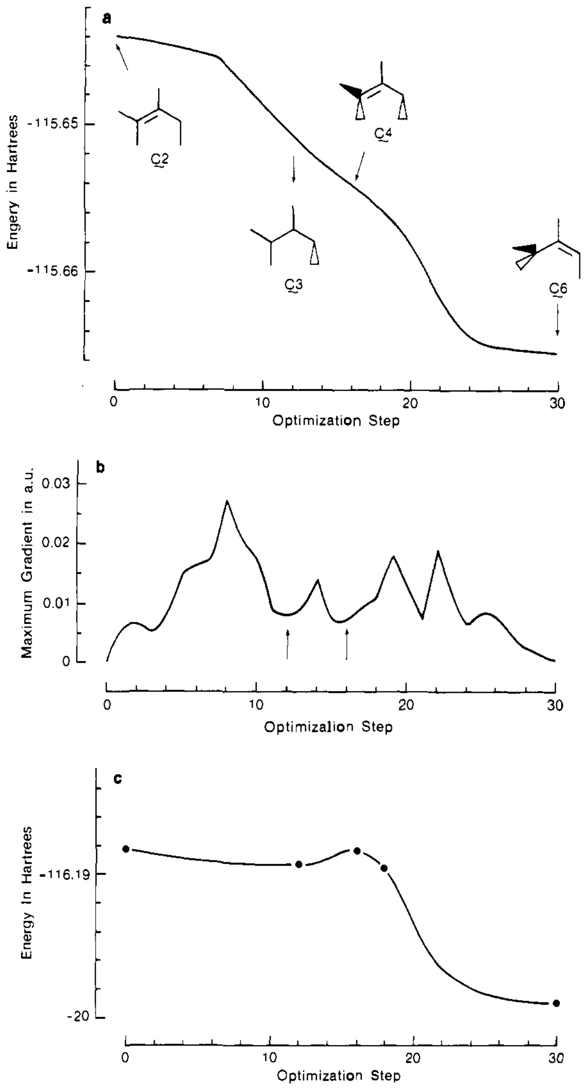


Figure 6. Potential energy profiles and maximum gradients for the singlet cis-planar carbene to bisected diradical reaction path obtained with the MC4(431G) wave function. A unit of the reaction coordinate corresponds to one step in the optimization procedure. (a) Energy profile calculated by the MC4(431G) wave function. (b) Maximum gradients calculated by the MC4(431G) wave function. (c) MRCI*(DZP) energy profile calculated at the same geometries.

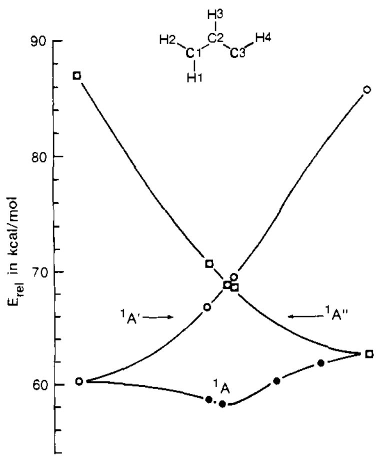
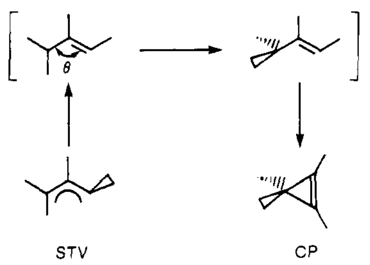
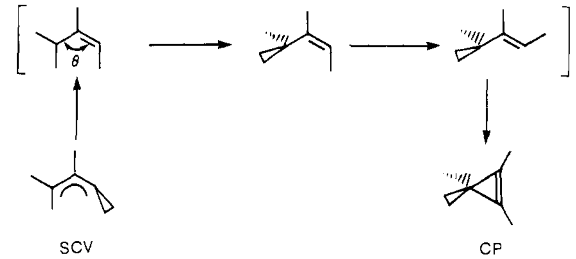


Figure 7. Potential curves for the $^1A'$, $^1A''$, and ^1A states between the trans-planar carbene (*TPC*) and diradical (*TPD*) structures. Energies are given relative to that of the $^1A_1$ state of methylacetylene.

Scheme IV



Scheme V



We located a point on the curve of intersection for the *trans*-vinylmethylene surface, and the results are shown in Figure 7. First, we converted the nonplanar *A2* and *A3* geometries in Table VIII to planar structures and left all bond lengths and angles at their initial values. By linear interpolation of the energies at these two points, we are able to locate a point with $\Delta R = 0.008$ Å where the energies agree within 0.0005 hartree in the MRCI* approximation. This point is believed to be reasonably close to the minimum on the curve of intersection and lies only 12 kcal/mol above the lowest singlet-state vinylmethylene (*STV*). We have not investigated *cis*-vinylmethylene but here we also expect a similar curve of intersection.

The fact that S_1 and S_0 of C_3H_4 meet on the vinylmethylene potential surface has a significant implication on the photochemistry of cyclopropene. Sevin and Arnaud-Danon[8] noted that the $^1A''$ state (S_1) of vinylmethylene should correlate with the valence excited state ($^1B_1$) of cyclopropene and predicted no barrier for its path. Thus, photoracemization of cyclopropene most likely proceeds via planar vinylmethylene and should be efficient. Furthermore, this provides a reaction mechanism for radiationless decay of excited cyclopropene species via vinylmethylene. This also suggests that interconversions to methylacetylene and allene most likely occur on the ground-state surface of C_3H_4 upon photolysis of cyclopropene.

We may note further that there seems to be no other region on the C_3H_4 surface where S_1 and S_0 meet. For example, Lam and Johnson[17] reported calculations on the excited states of allene, and their results indicated that the closest approach of S_0 and S_1 occur at planar geometries separated by 0.76 eV (17.5 kcal/mol). Therefore, the fact that S_0 and S_1 meet on the vinylmethylene surface gives strong evidence for the pivotal involvement of vinylmethylene in not only the thermal isomerization but also the photoisomerization occurring on the C_3H_4 surface.

IV. Ring Closure: Vinylmethylene to Cyclopropene

Both singlet *trans*- and *cis*-vinylmethylenes have equilibrium geometries with equivalent bond lengths; the structures are planar except for a terminal hydrogen protruding out of the CCC plane. Thus, it is reasonable to expect their rearrangement to cyclopropene to involve (1) formation of the C2–C3 double bond, (2) rotation of the CH_2 group, and (3) ring closure. This mechanism is illustrated in Schemes IV and V for singlet *trans*- and *cis*-vinylmethylene, respectively.

The reaction path from *trans*-vinylmethylene to cyclopropene appears to go through a planar diradical structure; the transition state along this reaction path, however, is most likely located in the vicinity of the planar to bisected part of the path. The fact

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(17) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.

that the bisected structure converts to cyclopropene, a process requiring no barrier, strongly suggests that the transition state should indeed be located in the planar to bisected segment of the reaction path.

The path for the *cis*-vinylmethylene to cyclopropene conversion involves an additional step: the inversion of the C3–H4 bond from the cis to the trans position in the bisected structure. Since it was found that *cis*-vinylmethylene transforms to a cis bisected structure with only a 1 kcal/mol potential energy barrier, the factor for the *cis*-vinylmethylene to cyclopropene ring-closure mechanism may be the energetics for the inversion of the C3–H4 bond. We present below the results for these path determinations and discuss the difference between the *cis*- and *trans*-vinylmethylene ring closures.

A. Ring Closure: *trans*-Vinylmethylene to Cyclopropene. In order to locate a transition state for the trans-planar diradical to cyclopropene reaction path, the angle $\Theta = \angle C1C2C3$ (see Scheme V) was used as a reaction coordinate. Structures for several points on this path were determined by relaxing all other geometrical parameters except Θ. The MC8(431G) wave function was used for this investigation since it is capable of transforming vinylmethylene in the C_s symmetry to cyclopropene in the C_{2v} symmetry. The geometrical parameters and energies for Θ = 115 and 90° are listed in Table IX as points *B5* and *B6*.

In the MC8(431G) calculation, the transition state was found to be at Θ = 115° and the barrier height for the trans-planar diradical to cyclopropene conversion is 0.4 kcal/mol. At the transition state the CH_2 group is rotated halfway to a bisected position and it becomes a bisected structure in the C_s symmetry when Θ reaches 110°.

The energy profile was improved by the MC4(DZP) and MRCI(DZP) calculations. The MC4 and MRCI wave functions are employed since these are well defined for vinylmethylene and computationally feasible. Although these wave functions are not well defined for cyclopropene, they are reasonable on the path until Θ reaches 80°. The energies are listed in Table IX and the MRCI*(DZP) energy profile for this path is shown in Figure 8 as a function of $\Theta = \angle C1C2C3$; Figure 8a shows a part of the path from *STV* through *TPD* to the trans bisected diradical potential surface, and Figure 8c shows the whole energy profile (the path for the *cis*-vinylmethylene to cyclopropene ring closure is also included). In addition, we have investigated the trans bisected diradical surface at Θ = 95, 107, 115, and 125°. The geometries are determined by the MC4(431G) wave function, relaxing all other parameters except Θ; the MRCI*(DZP) results are also shown in Figure 8a as a dotted line. Also included in Figure 8a is the trans-planar diradical potential surface, which has been estimated from the MC4(DZP) calculation carried out at Θ = 120 and 125°; these structures are the same as that of *TPD* except Θ is reduced.

The MRCI* results indicate that the *trans*-vinylmethylene to cyclopropene conversion most likely proceeds via the trans-planar diradical with a potential energy barrier of 5 kcal/mol. The transition state (TS2) appears to be located at Θ = 115° (see point *B5* in Table IX for the structure), and the ring closes smoothly once a bisected diradical structure is reached. However, the energy profile for the transition from the trans-planar to bisected diradical structure is found to be quite flat (the difference in the *TPD* and TS2 energies is 0.1 kcal/mol), and it is difficult to determine the exact location of the transition state. However, the chemically meaningful quantity, the barrier height, is believed to be correct.

Of particular interest is the geometry of TS2, which is halfway between those of the bisected and planar diradicals. At Θ = 115° the bisected surface lies 1 kcal/mol above and the planar surface lies even higher. This means that the pathway between the bisected and the planar diradicals along the angle Θ = 115° has a shallow well, and a similar situation also exists at Θ = 120°. Because of these wells, a very flat energy profile results for the planar to bisected transition when it is coupled with the ring closure. It is possible, however, that there exists a direct path from *STV* to cyclopropene that does not go through a trans diradical structure; this would be a concerted path of bond reorganization coupled with the CH_2 rotation. As discussed above, the geometry of TS2 and the feature of the potential surface around it strongly suggest that this path must also go through TS2 or at least a TS2-like structure. This implies then that a barrier on the concerted path should be equal to or higher than 5 kcal/mol. This gives additional support for our conclusion that the singlet *trans*-vinylmethylene ring-closure reaction proceeds via the planar diradical structure.

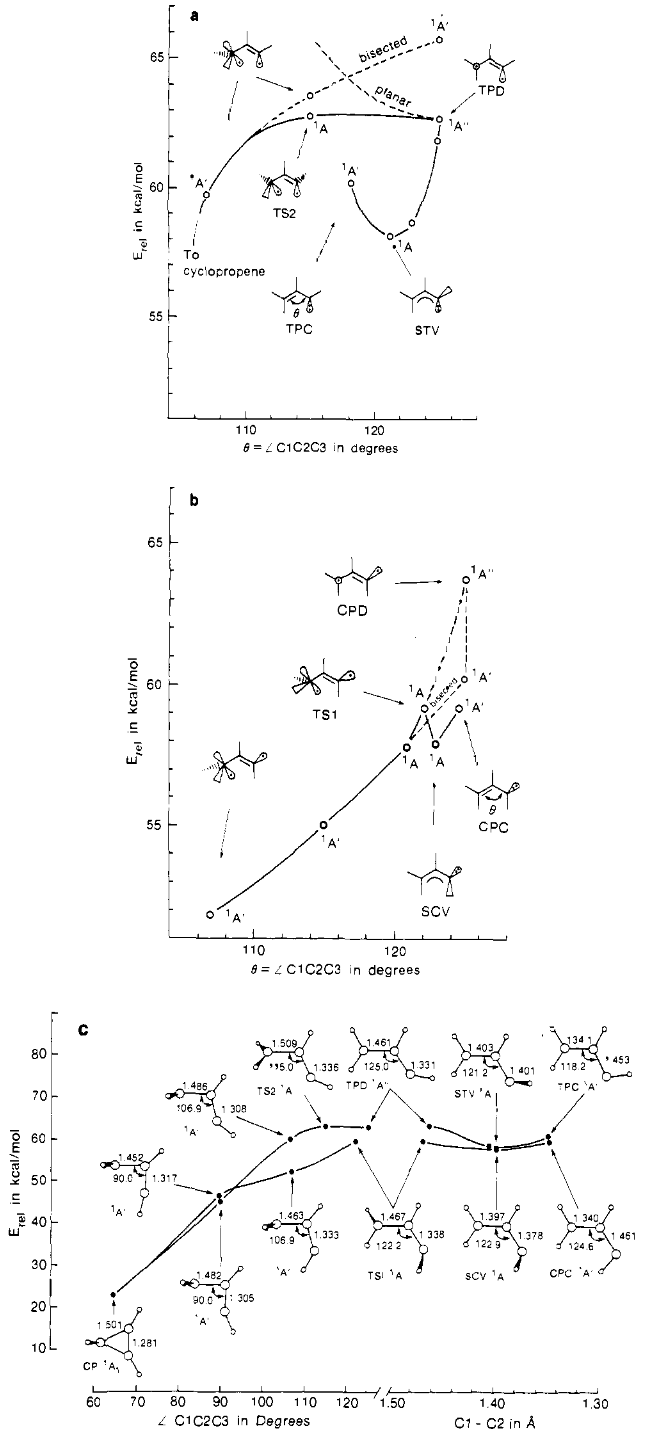


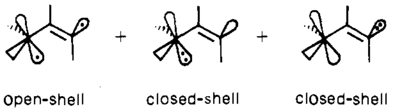
Figure 8. MRCI*(DZP) energy profiles for the *trans*- and *cis*-vinylmethylene to cyclopropene rearrangement paths. The energies are relative to that of the $^1A_1$ state of methylacetylene. (a) Upper part of the energy profile for the trans-vinylmethylene to cyclopropene path as a function of the angle (C1C2C3). Also shown are the potential curves for the trans bisected and planar diradical structures. (b) Upper part of the energy profile for the *cis*-vinylmethylene to cyclopropene path as a function of the angle (C1C2C3). The potential curve for the cis bisected diradical structure is also shown. (c) The complete energy profiles for the *trans*- and *cis*-vinylmethylene to cyclopropene paths.

Table XI. Calculated Geometrical Parameters and Energies for Selected Points on the SCF(431G) Cyclopropene (CP) to Propenylidene (PD) Reaction Path

point	*CP*	*D1*	*D2* *TS3*	*D3*	*PD*	*D1**
symmetry	$^1A_1$	$^1A'$	$^1A'$	$^1A'$	$^1A'$	$^1A'$
			Geometrical Parameters[a]			
C1C2	1.500	1.458	1.474	1.510	1.510	1.446
C2C3	1.281	1.312	1.320	1.317	1.298	1.304
H1C1	1.084	1.072	1.077	1.090	1.084	1.079
H3C2	1.070	1.059	1.061	1.073	1.085	1.068
H4C3	1.070	1.203	1.364	1.698	2.686	1.166
H4C1	2.456	1.566	1.472	1.303	1.083	1.525
C1C2C3	64.7	84.4	85.4	87.6	127.2	80.9
H1C1C2	119.7	120.4	119.7	117.8	110.1	120.8
H3C2C3	150.1	137.5	136.6	135.5	112.5	138.9
H4C3C2	209.9	107.7	101.1	91.2	52.3	110.7
H1C1C2C3	105.6	99.2	101.6	107.5	120.2	99.5
			Total Energies (hartrees)[b]			
SCF(431G)	.64257	.55135	.55190	.55377	.63271	
SCF(DZP)	.84946				.83086	.77166
MC4(DZP)		.83392	.82550	.83160		.83237
NORM		.99924	.99919	.99768		.99926
MRCI(DZP)		.18658	.17944	.18261		.18615
MRCI*(DZP)	(.24576)	.18673	.17961	.18307	(.21223)	.18630
			Relative Energies (kcal/mol)[c]			
MRCI*(DZP)	(22.6)	59.6	64.1	61.9	(43.6)	59.9

[a] Bond lengths are in angstroms and bond angles are in degrees. [b] Only fractional parts are given; the integer parts are −115. and −116. for MC4 and MRCI results, respectively. See the text for the definitions of the wave functions. [c] These are given with respect to the $^1A_1$ state of methylacetylene, for which MRCI*(DZP) is estimated to be −116.28168.

Scheme VI



B. Ring Closure: *cis*-Vinylmethylene to Cyclopropene. For *cis*-vinylmethylene we found a path from the cis-planar carbene structure to cis bisected diradical structure while searching for a local minimum. The MRCI*(DZP) energy profile along this path is plotted as a function of ∠C1C2C3 in Figure 8b. A cis bisected diradical potential curve was also calculated in a similar manner as done for the trans case, and the MRCI*(DZP) energy profile is also shown in Figure 8b.

First, we note that the cis bisected diradical curve lies about 6 kcal/mol below the trans bisected diradical curve between $\Theta = 107°$ and $\Theta = 125°$. The single-configuration SCF and CI study reported in paper 1 indicated that cis and trans bisected diradical structures have the same energy at $\Theta = 125°$. This implies that closed-shell singlet electronic states shown in Scheme VI exist nearby for the cis bisected structures but not for the trans bisected structures. These three electronic structures must then interact strongly to lower the energy for the cis case but apparently not so strongly for the trans case.

Second, because of the low-lying cis bisected diradical potential surface, the transition from *SCV* to the cis bisected structures occurs essentially before the ring closure with the small barrier of 1 kcal/mol. In contrast to the trans case, it is a concerted process of a double-bond formation and the rotation of the CH_2. The transition state (see point TS1 in Table X) is located at $\Theta = 122°$ and it has a diradical structure. In contrast to the trans case, TS1 lies slightly above the cis bisected surface at $\Theta = 122°$ (see Figure 8b).

As noted above, the cis bisected diradical structure at $\Theta = 107°$ appeared to be a local minimum at the MC4(431G) level. In order to complete the path to cyclopropene, we first determined a transition state in the MC4(431G) approximation, which was located at $\Theta = 92.5°$. The rest of the path was calculated by perturbing this structure slightly and performing the MC4(431G) geometry optimization; it converged to a cyclopropene structure although it is not exactly in the C_{2v} symmetry. MC4(DZP) and MRCI(DZP) calculations were performed at selected points on this MC4(431G) path to get a better energy profile; the structures and energies of these points are given in Table X. As the MRCI*(DZP) energy profile plotted in Figure 8c shows, the cis bisected diradical structure at $\Theta = 107°$ is no longer a local minimum and the cis–trans transition has no barrier when coupled with the ring closure. It is of interest to note that the structure at ∠C1C2C3 = 78.8° (*C9* in Table X) is trans, indicating that the trans and cis ring-closure paths merge around this point.

It has been conjectured that the *cis*-vinylmethylene ring-closure reaction must go through *trans*-vinylmethylene.[3] The present study revealed, however, that singlet *cis*-vinylmethylene does directly transform itself to cyclopropene. In fact, the barrier for the ring closure is less than that for the *trans*-vinylmethylene closure. Furthermore, the barriers for the ring-opening reaction of cyclopropene to vinylmethylene were determined to be 36.6 and 40.2 kcal/mol for cis and trans species, respectively. Therefore, not only *trans*- but also *cis*-vinylmethylene must actively be involved in the thermolysis of cyclopropene.

V. Ring Opening of Cyclopropene

In this section we first present the results for the cyclopropene to propenylidene rearrangement, which has not been previously studied. Afterward, the results of the present study on the ring-opening mechanisms of cyclopropene will be summarized and discussed.

A. Ring Opening to Propenylidene. The SCF and SDCI study for relative energies of various possible isomers of C_3H_4 reported in paper 1 showed that propenylidene should be lower in energy than vinylmethylene by 16 kcal/mol. This suggested that a potential energy barrier for the ring opening of cyclopropene to form propenylidene could compete with other types of ring-opening reactions, i.e., the cyclopropene to vinylmethylene that was discussed in the previous section. In order to further investigate this possibility, we have determined a reaction path for the cyclopropene to propenylidene rearrangement.

A search for the transition state (TS) was carried out in two steps. In the first step we assumed Φ = ∠H4C3C2, shown in Scheme VII, as a reaction coordinate and calculated an approximate transition-state structure by optimizing geometries for several values of Φ with the SCF(431G) wave function. In the second step the SADDLE POINT program of GAMESS[9] was used to locate an accurate transition-state structure at least at the SCF(431G) level starting from the previously obtained approximate structure. The structural parameters are listed in Table XI as point *D1*, and we shall label this structure as the SCF(431G) TS

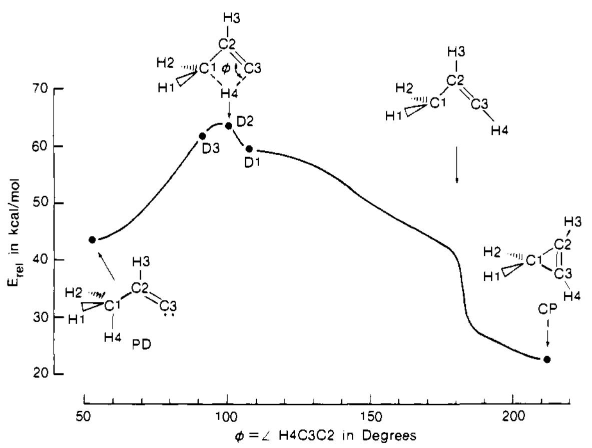
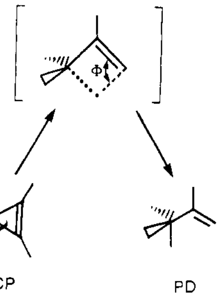


Figure 9. MRCI*(DZP) potential energy profile for the cyclopropene to propenylidene isomerization path as a function of the angle (H4C3C2).

Scheme VII



structure. At this structure the maximum gradient was less than 0.0005 au and a vibrational analysis yielded a large negative eigenvalue. To see the polarization function effect on the structure, we also determined in a similar manner a transition-state structure with the SCF(DZP) wave function, which will be referred to as the SCF(DZP) TS structure; its geometrical parameters are also listed in Table XI as *D1**. These two structures are reasonably close; Φ are 107.7 and 110.7° and the ring-opening angles, ∠C1C2C3, are 84.4 and 80.9° for the SCF(431G) and SCF(DZP) TS structures, respectively. However, the migrating hydrogen H4 is still attached to C3 (bond lengths C1H4 and C3H4 are 1.5659 and 1.2032 Å, respectively, for the SCF(431G) TS structure).

Paths from the transition state to cyclopropene and propenylidene were investigated with the SCF(431G) wave function. A path to cyclopropene was determined by increasing Φ by 2° to 109.7° and optimizing the geometry, which converged smoothly to cyclopropene in 22 steps. A path to propenylidene was also obtained in the same manner by decreasing Φ by 2°, which converged to propenylidene in 18 steps.

The SCF(431G) energy profile along the path thus determined is not energetically correct. This can be seen from the fact that the energy differences between cyclopropene and propenylidene are 7 and 21 kcal/mol in the SCF(431G) and SDQCI(DZP) approximations, respectively. The correlation energy effect must be substantial on the energy profile, especially on the potential energy barrier. In order to take into account the polarization and correlation corrections, we have carried out MC4(DZP) and MRCI(DZP) calculations at several points in the vicinity of the SCF(431G) TS structure on the SCF(431G) path. The MC4 and MRCI wave functions are the same as those used for the bisected diradicals described in the previous section, and the geometrical parameters and energies are also given in Table XI. Figure 9 gives the MRCI* energy profile of the SCF(431G) path from cyclopropene to propenylidene as a function of the angle Φ, where solid dots are calculated energies and the rest of the profile is obtained from the SCF(431G) profile by scaling it to match at those points where the MRCI(DZP) calculations are done.

We may make two observations from the MRCI*(DZP) energy profile. The first observation is that the transition state is much closer to the point *D2* than the SCF(431G) or SCF(DZP) structures. Thus, our best estimate for the transition-state structure (TS3) is that of the point *D2*, where H4 is essentially halfway between C3 and C1 (bond lengths H4–C3 and H4–C1 are 1.364 and 1.472 Å, respectively). The second observation is that the energy profile from the transition state to cyclopropene has a shoulder at Φ = 180°, implying that the transition occurs roughly in two steps. In the first step H4 moves to a position to make H4C3C2 collinear, keeping ∠C1C2C3 close to 85°, and then the second step is to close the ring while keeping H4C3C2 collinear. The energy profile to propenylidene is smooth. At point *D3*, H4 is already attached to C1 and the ring opening follows.

Table XII. Barrier Heights (kcal/mol) for the Cyclopropene to Propenylidene Isomerization Calculated in Various Approximations

approx	cyclopropene to propenylidene	propenylidene to cyclopropene
SCF(431G)	57.3	51.1
SCF(DZP)	48.8	37.2
SDQ(DZP)	41.5	20.4
MRCI(DZP)	41.2	20.2
MRCI*(DZP)	41.5	20.5

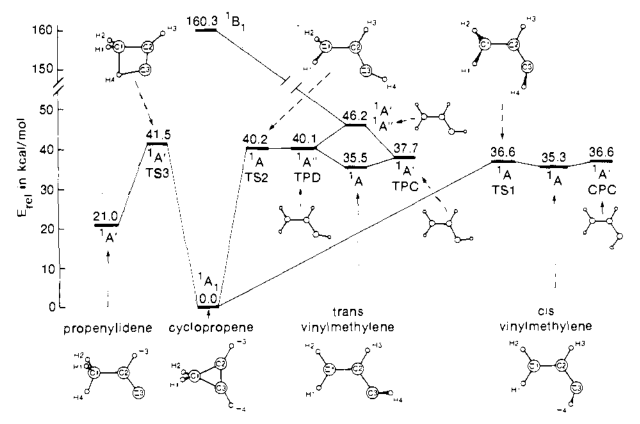


Figure 10. Schematic potential energy profiles showing rearrangement pathways from cyclopropene to propenylidene, *trans*-vinylmethylene, and *cis*-vinylmethylene.

Our best estimates for potential energy barriers for the cyclopropene to propenylidene and reverse rearrangements are 41.5 and 20.5 kcal/mol, respectively. These are the MRCI*(DZP) results and the estimated MRCI*(DZP) energies, discussed in section III, are used for cyclopropene and propenylidene. To illustrate the substantial effects of the polarization function and of the correlation energy, the barrier heights calculated in various approximations are given in Table XII. These effects are quite large and can be as much as 30 kcal/mol.

B. Summary of the Intermediates Involved in the Ring Opening of Cyclopropene. The pertinent results for three ring-opening reaction mechanisms of cyclopropene are summarized in Figure 10. The first two are for isomerizations to *cis*- and *trans*-vinylmethylenes, and the third is for isomerization to propenylidene. The calculated potential energy barriers for these reactions are close, ranging from 36.5 to 41.5 kcal/mol, indicating that they are competitive processes.

The ring opening to *cis*-vinylmethylene has the lowest potential energy barrier, 36.5 kcal/mol, and involves ring cleavage, moving of a hydrogen to a cis position, and rotation of the methylene group to form *cis*-vinylmethylene. The trans–cis transition occurs early and has no barrier. The transition state is located 36.5 kcal/mol above cyclopropene and its structure resembles cis-planar diradical but the CH_2 group is slightly rotated. A resonance stabilization between carbene and diradical structures lowers the energy of *cis*-vinylmethylene somewhat but the barrier for reclosure is only 1.3 kcal/mol, indicating that this reaction would be highly reversible. The isomerization to *trans*-vinylmethylene proceeds in a similar manner but it goes through a planar diradical structure. Thus, the transition state occurs in a bisected to planar transition and is located 40.2 kcal/mol above cyclopropene. The resonance stabilization also lowers its energy in this case by 4.7 kcal/mol. It is still small enough so that its ring-closure reaction would also be fast.

The third reaction of isomerization to propenylidene is of considerable interest because it is product forming, unlike the other two just discussed. This mechanism involves a concerted reaction of ring cleavage and a 1,2-hydrogen shift resulting in a tight transition-state structure. Although its barrier of 41.5 kcal/mol is close to those of the other two reactions, a barrier of 20.5 kcal/mol for its ring closure makes the reverse reaction very slow. Furthermore, it has been determined that propenylidene would isomerize itself readily to methylacetylene,[2] the most stable isomer of the C_3H_4 system. Therefore, this ring-opening reaction of cyclopropene would not participate in racemization of cyclopropene, which will be discussed below.

York and co-workers[4] reported that on pyrolysis in the gas phase, optically active 1,3-diethylcyclopropene undergoes racemization (E_a = 32.6 kcal/mol) considerably faster than it is converted to a mixture of substituted diene and acetylene products. Thermochemical analysis of this system by them had led to a mechanism that a vinylcarbene is an intermediate in this process and the barrier for reclosure is 6 kcal/mol. The present study on unsubstituted cyclopropene strongly supports their mechanism although details are somewhat different. According to our results, both *cis*- and *trans*-vinylmethylenes would be involved in the racemization as an intermediate. The potential energy barriers of 36.5 and 40.2 kcal/mol are reasonably close to the activation energy of 32.6 kcal/mol for 1,3-diethylcyclopropene. Planarization needed for racemization is achieved by going through a planar diradical structure for the trans case, and for the cis case a planar carbene structure is energetically accessible for it.

As mentioned earlier, vinylmethylene may also be involved in photolysis of cyclopropene since the electronically excited state $^1B_1$ of cyclopropene is directly connected, without a potential barrier, to the lowest singlet state of vinylmethylene as shown in Figure 10. Thus, this excited state can spontaneously yield a vinylmethylene species by synchronous ring opening and methylene rotation.[8] Furthermore, it is a ground-state species of C_3H_4 that possesses an excess of energy and consequently is able either to reclose (photochemical racemization) or to lead to further reactions, e.g., isomerizations on the ground-state surface of C_3H_4. One isomerization pathway accessible is to allene via a transition state lying 46.5 kcal/mol above cyclopropene[2] and another is an indirect pathway to methylacetylene via cyclopropene and propenylidene as discussed above. Therefore, photolysis of cyclopropene most likely produces methylacetylene and allene in addition to racemization products.

VI. Conclusion

From the results discussed above, we draw the following conclusions about structures of vinylmethylene and the ring-opening mechanisms of cyclopropene.

1. The structure that has been loosely referred to as "vinylmethylene" corresponds to six minima on the C_3H_4 surface. As a consequence, the present theoretical studies have brought some organization to mechanistic discussions dealing with 1,3-diradicals and vinyl carbenes. For example, the bisected 1,3-diradicals (**3**, **4**) have been identified as not having stable geometries while the singlet and triplet states with allylic geometries do correspond to minima on the potential energy surface. Hence, the allylic structures of vinylmethylene are reactive intermediates while the bisected species are only points along a reaction coordinate.

2. The $^3A''$ states of *trans*- and *cis*-vinylmethylene have an allylic structure and are isoenergetic, lying 46 kcal/mol above the ground $^1A_1$ state of methylacetylene with a potential energy barrier of 5.7 kcal/mol between them.

3. For the singlet states of vinylmethylene, allylic-like structures with the terminal hydrogen above or below the plane of the three carbon atoms represent local minima for both the trans and cis species. These four minima are isoenergetic, lying 12 kcal/mol above the triplet states, but the barriers to ring closure differ considerably; 4.7 and 1.3 kcal/mol are our best estimates for the trans and cis systems, respectively. No other planar or bisected structures are found to be stable points on the singlet surface.

4. The singlet excited state C_3H_4 surface touches the ground singlet state surface in the vicinity of the singlet vinylmethylene structures, indicating that vinylmethylene may play a pivotal role as a reactive intermediate in not only thermal but also photochemical isomerizations occurring on the C_3H_4 surface.

5. Not only *trans*- but also *cis*-vinylmethylene species are involved in the ring opening of cyclopropene, in particular racemization, as reactive intermediates with the potential energy barriers of 40.2 and 36.5 kcal/mol, respectively.

6. The cyclopropene–propenylidene isomerization is also a ring-opening reaction with a comparable barrier of 41.5 kcal/mol. It is not reversible and produces methylacetylene via propenylidene.

7. The last conclusion is on the computational method; for those paths where resonances of some kind are occurring, MCSCF wave functions may be sufficient for determining a qualitative reaction path, but they may not be flexible enough to yield a quantitatively correct energy profile. For example, the equilibrium geometries of singlet *trans*-vinylmethylene were obtained only after MRCI calculations were used; MCSCF calculations merely indicated a barrier may not exist on the path between the trans-planar carbene and diradical structures.

As stated above, the detailed examination of the potential surface for vinylmethylene and cyclopropene has revealed several important and significantly new facts about the ring-opening mechanism of cyclopropene. The other part of the C_3H_4 surface has also been investigated and detailed mechanisms for various thermal isomerizations occurring on the C_3H_4 surface will be presented in a subsequent paper.

Registry No. 1, 2781-85-3; **2**, 70277-78-0; vinylmethylene, 19527-08-3.