

correspond to saddle points on the potential surface, i.e. to possible TSs.

In such situations, where a molecule is depicted as a hybrid of two different structures, the effect of the resonance between them depends on the difference in geometry and the magnitude of the corresponding interaction ("resonance integral").

If the difference in geometry is large or the interaction small, the ARO and BR structures will correspond to separate stationary points on the potential surface. This seems to be the situation in the case of the Diels-Alder reaction between ethylene and butadiene and in most of the Cope rearrangements. Exceptions are expected only in cases where the two TSs differ greatly in energy. The TS of higher energy may then cease to be a stationary point.

If the difference in geometry is small and the interaction large, the two structures will merge into a single hybrid whose geometry will depend on the relative contributions of the ARO and BR wave functions. This is the situation envisaged by Gajewski where the TS can have structures varying between the BR and ARO extremes. According to our calculations, the Claisen rearrangement is an example. While pairs of TSs were found for some of the reactions we studied, the differences between them were essentially negligible, being indeed well within the uncertainties of AM1. The merging of mechanisms in the CLR is due to its large exothermicity. The TSs consequently have structures intermediate between the reactants and the aromatic or biradicaloid intermediates. The structures of the TSs are consequently much more alike than those of the intermediates.

Synchronous multibond mechanisms are expected⁹ to be favored in reactions involving migration of hydrogen,⁹ due to the propensity

of hydrogen to form three-center bonds.⁹ An allowed pericyclic reaction involving migration of hydrogen is therefore likely to be synchronous. Sigmatropic rearrangements involving migration of hydrogen, and ene reactions, are obvious examples.

Pericyclic reactions with small heats of reaction are likely to proceed by alternative BR and ARO paths. If a TS is located for such a reaction, it cannot be assumed to be the "true" TS unless and until the other TS has been located or shown not to exist. It is also necessary to use procedures able to distinguish reliably between the two mechanisms. Reasonably reliable conclusions can be derived from calculations on their own only if a very high level ab initio procedure is used. Such calculations can usually be carried out only for the simplest example of a reaction, an unfortunate limitation since the simplest example of *any* reaction is often untypical. The alternative is to combine calculations with experiment for a number of examples of a reaction where experimental data are available. Here, a less accurate treatment can suffice because it is much easier to predict relative activation parameters, etc., for a series of related reactions than their absolute values. AM1 is the obvious choice in this connection, particularly in cases where the usual RHF version can be used. The conclusions reached in this way are usually reliable. Problems arise in the case of BR mechanisms where the intermediates are truly biradical-like, due to the weaknesses of current open-shell versions of AM1.

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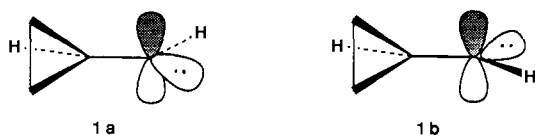
A Theoretical Investigation of the Intramolecular Reactions of Cyclopropylmethylene

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Abstract: An ab initio investigation of the energetics of the intramolecular reactions of cyclopropylmethylene (**1**) has been carried out. Geometries were fully optimized at the HF/3-21G levels, and single point calculations were made at the MP2/6-31G* and MP4SDQ/6-31G levels and combined in order to approximate relative energies at the MP4SDQ/6-31G* level. Carbene **1** exists in two conformers in which the empty p orbital overlaps the antisymmetric Walsh orbital on the three-membered ring. The conformer with the carbene and cyclopropyl hydrogens cis, **1a**, is calculated to be more stable than the trans conformer, **1b**, by 1.8 kcal/mol and separated from it by a barrier of 14.9 kcal/mol. The most favorable reaction of **1a** is the ring expansion to give cyclobutene (**2**; $\Delta H^\ddagger = 5.0$ kcal/mol). Ring expansion of conformer **1b** is less favorable ($\Delta H^\ddagger = 20.4$ kcal/mol) and the most rapid reaction of **1b** should be fragmentation to ethylene and acetylene. The fragmentation of **1** may involve a nonsynchronous pathway with an estimated barrier of 8.0 kcal/mol (from **1b**). Ring expansion may predominate in **1a** while fragmentation is favored in **1b**. The triplet carbene is calculated to lie slightly below the singlet in energy and should undergo facile cleavage to a triplet biradical. This triplet carbene may be involved in the gas-phase chemistry of **1** at high pressures.

The cyclopropyl carbene **1** occupies a unique position in the chemistry of divalent carbon intermediates. This carbene exists in two conformers, **1a** and **1b**, in which there is an expected and



calculated barrier to interconversion.^{1,2} It is one of the few

carbenes to prefer to rearrange via a C-C insertion, to give cyclobutene (**2**) to the exclusion of the more common insertion into a β C-H bond which could yield methylenecyclopropane (**3**).³ This ring expansion is interesting in that the least substituted bond migrates,⁴ leading to stereospecific cyclobutene formation,^{5,6} thus

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Table I. Absolute Energies (hartrees) of Species on the C₄H₆ Potential Energy Surface

	mol symm	3-21G	6-31G*	MP2/6-31G ^a	MP2/6-31G* ^a	MP4SDQ/6-31G ^a	ZPE/NEV ^b
1a^c	C _s	-153.93080	-154.804 41	-155.070 15	-155.295 60	-155.111 05	56.08 (0)
1b	C _s	-153.927 91	-154.802 10	-155.067 07	-155.292 39	-155.108 22	56.02 (0)
3	C _{2v}	-154.018 73	-154.886 95	-155.175 04	-155.395 07	-155.213 39	57.81 (0)
2	C _{2v}	-154.030 72	-154.898 31	-155.185 89	-155.407 75	-155.224 59	58.38 (0)
4 + 5		-153.996 95	-154.849 44	-155.154 43	-155.348 75	-155.190 82	53.43 (0)
6	C _{2v}	-153.986 64	-154.869 59	-155.146 18	-155.387 11	-155.181 77	58.44 (0)
	C _{2h}	-154.059 45	-154.919 61	-155.212 43	-155.420 69	-155.252 33	57.77 (0)
TS1a-1b	C ₁	-153.908 70	-154.782 41	-155.043 85	-155.266 75	-155.087 67	54.69 (1)
TS1-3	C ₁	-153.874 50	-154.759 98	-155.033 10	-155.267 15	-155.071 38	53.44 (1)
TS1a-5	C _s	-153.896 55	-154.755 05	-155.047 08	-155.260 08	-155.084 97	54.33 (1)
TS1b-5	C _s	-153.898 37	-154.758 27	-155.052 70	-155.266 69	-155.090 19	54.49 (1)
TS1b-2	C ₁	-153.874 29	-154.749 69	-155.035 36	-155.265 12	-155.072 72	55.15 (1)
TS1a-2	C ₁	-153.908 89	-154.783 96	-155.062 24	-155.291 94	-155.098 77	56.05 (1)
TS1a-6	C ₁	-153.863 36	-154.747 30	-155.033 91	-155.276 44	-155.067 50	54.20 (1)
TS1b-6	C ₁	-153.851 48	-154.736 99	-155.018 55	-155.262 50	-155.053 68	54.51 (1)
³1a	C _s	-153.964 17	-154.830 59	-155.085 62	-155.298 53	-155.123 23	55.35 (1)
³1b	C _s	-153.964 36	-154.831 13	-155.086 34	-155.299 28	-155.125 46	55.59 (0)
³TS1a-7	C ₁	-153.950 29	-154.811 13	-155.071 50	-155.279 99	-155.112 31	53.78 (1)
³TS1b-7	C ₁	-153.949 59	-154.810 45	-155.070 75	-155.279 24	-155.111 55	53.80 (1)
³7	C _s	-153.973 00	-154.831 43	-155.085 27	-155.287 54	-155.129 22	53.17 (0)

^a Projected-MP (PMP) value; frozen core approximation is used. For the projected-MP4SDQ/6-31G energy, the correction at the MP3/6-31G level is subtracted from the MP4SDQ level. ^b Zero-point energy (kcal/mol) and number of negative eigenvalues of force constant matrix in parentheses. ^c The last five entries in this column are for the triplet electronic state.

Table II. Relative Energies (kcal/mol) of Species on the C₄H₆ Potential Energy Surface at Various Levels

molecule	3-21G	6-31G*	MP2/6-31G	MP2/6-31G*	MP4SDQ/6-31G	[MP4SDQ/6-31G*] (+ZPC)
1a	0.0	0.0	0.0	0.0	0.0	0.0 (0.0)
1b	1.81	1.45	1.93	2.01	1.78	1.86 (1.80)
3	-55.19	-51.81	-65.84	-62.44	-64.24	-60.84 (-59.11)
2	-62.72	-58.94	-72.65	-70.40	-71.27	-69.02 (-66.72)
4 + 5	-41.52	-28.26	-52.90	-33.36	-50.07	-30.53 (-33.18)
6	-35.05	-40.91	-47.72	-57.44	-44.39	-54.11 (-51.75)
	-80.75	-72.31	-89.31	-78.52	-88.68	-77.89 (-76.20)
TS1a-1b	13.87	13.81	16.51	18.11	14.68	16.28 (14.89)
TS1-3	35.34	27.89	23.26	17.86	24.90	19.50 (16.86) ^a
TS1a-5	21.50	30.98	14.48	22.30	16.37	24.19 (22.44)
TS1b-5	20.36	28.96	10.95	18.15	13.09	20.29 (18.70)
TS1b-2	35.47	34.35	21.84	19.13	24.06	21.35 (20.42)
TS1a-4	13.75	12.84	4.96	2.30	7.71	5.05 (5.02)
TS1a-6	42.33	35.85	22.75	12.03	27.34	16.62 (14.74)
TS1b-6	49.79	42.32	32.39	20.78	36.01	24.40 (22.83)
³1a	-20.95	-16.43	-9.71	-1.84	-8.64	-0.77 (-1.50)
³1b	-21.06	-16.77	-10.15	-2.31	-9.05	-1.21 (-1.70)
³TS1a-7	-12.23	-4.22	-0.84	9.80	-0.80	9.84 (7.54)
³TS1b-7	-11.79	-3.79	-0.38	10.27	-0.31	10.34 (8.06)
³7^b	-26.49	-16.96	-9.49	5.06	-11.41	3.14 (0.23)

^a The barrier for interconversion of **1a** → **1b** via an inversion barrier (rather than a rotational barrier) at this level of theory is 37.14 (36.42) kcal/mol. ^b The calculated orientation of the hydrogens around the double bond of the biradical is *cis*. The biradical triplet *trans*-7 (which was not calculated) would be expected to be similar in energy to 7.

rendering a biradical intermediate unlikely. Carbene **1** also undergoes an unusual fragmentation in which two bonds β to the carbene center are cleaved to produce ethylene (**4**) and acetylene (**5**).³ This fragmentation appears more pronounced as the energy of the carbene is increased,⁷ and in the gas phase⁸ it can account for more than 50% of the product yield in some cases.

The energies and geometries of various conformers of **1** have been calculated by both semiempirical and *ab initio* methods,^{1,2} and the energetics of the rearrangement of **1** to **2** have also been investigated computationally.² While it is clear that much of the unique behavior of **1** can be ascribed to the presence of the adjacent cyclopropane ring and that relief of the strain associated with this ring can explain the fragmentation and perhaps the C-C insertion, there has not been an examination of the factors dictating which of the various pathways available to **1** will actually be followed. In order to address this point, we have undertaken an extensive

ab initio investigation of the energetics of the plausible reactions of **1**.

Computational Methods. All calculations used the GAUSSIAN 82 or GAUSSIAN 86 program systems.⁹ Geometries were fully optimized at the HF/3-21G levels within the appropriate point group. Vibrational frequencies were calculated in order to confirm the nature of the stationary point and to correct relative energies for differences in zero-point energies. Single-point calculations were made at the MP2/3-31G* and MP4SDQ/6-31G levels¹⁰ and combined according to eq I in order to approximate relative

$$\Delta E[\text{MP4SDQ}/6-31\text{G}^*] = \Delta E(\text{MP2}/6-31\text{G}^*) + \Delta E(\text{MP4SDQ}/6-31\text{G}) - \Delta E(\text{MP2}/6-31\text{G}) \quad (\text{I})$$

energies at the MP4SDQ/6-31G* level.¹¹ Brackets are used

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(10) For a description of basis sets, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

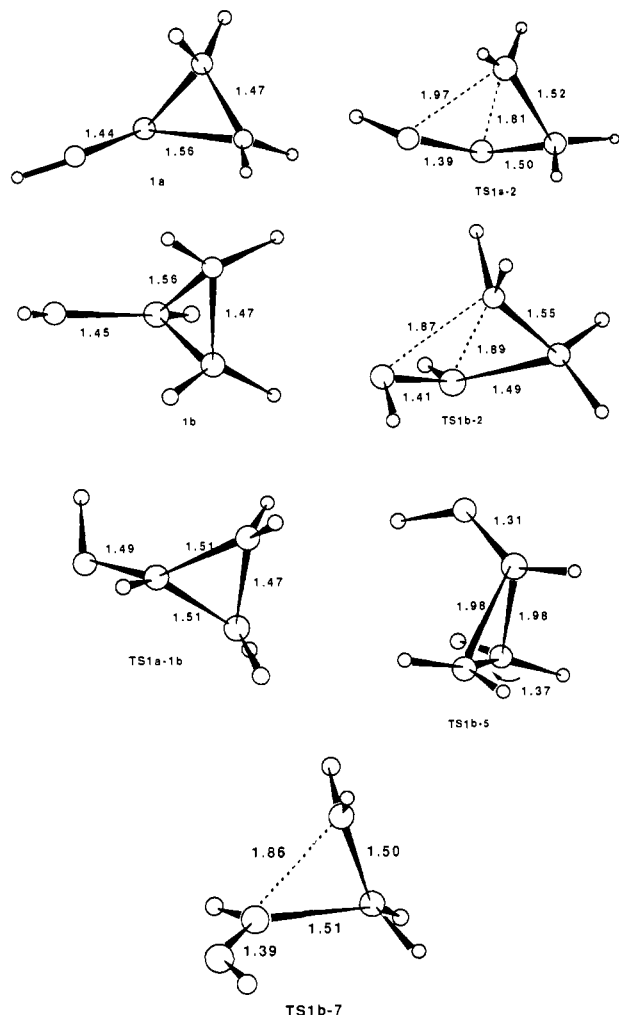


Figure 1. Geometries of relevant intermediates and transition states in the reactions of cyclopropylmethylene.

around a particular method when calculations have not actually been made at the level but rather approximated from lower level calculations. The effect of the largest spin contaminant was projected out of the correlation energies for open-shell systems. Total energies and zero-point energies are given in Table I, and relative energies are given in Table II. Calculated geometric parameters of relevant intermediates and transition states are shown in Figure 1, and Salem-Jorgenson plots of the molecular orbitals of some of these species are shown in Figure 2.

Results and Discussion

Conformational Preference of Cyclopropylmethylene. Previous calculations have demonstrated a preference for conformations of **1** in which the empty p orbital of the carbene is parallel to the C-C bonds of the cyclopropane ring.^{1,2} These conformations allow an overlap of the empty p orbital on the carbene carbon with the occupied antisymmetric Walsh orbital of the cyclopropane ring in the same manner as the cyclopropyl carbonium ion is stabilized by this interaction. The LUMO of **1a** in Figure 2b clearly shows the interaction between the empty p orbital and the ring while the HOMO is mainly the sp² orbital of the carbene (Figure 2a). The two stable conformations of **1** correspond to a cis and trans orientation of the hydrogen atoms on the carbene carbon and the methyne hydrogen on the ring. Conformer **1a** has a 0° dihedral angle between these hydrogens while the dihedral angle in **1b** is 180°.

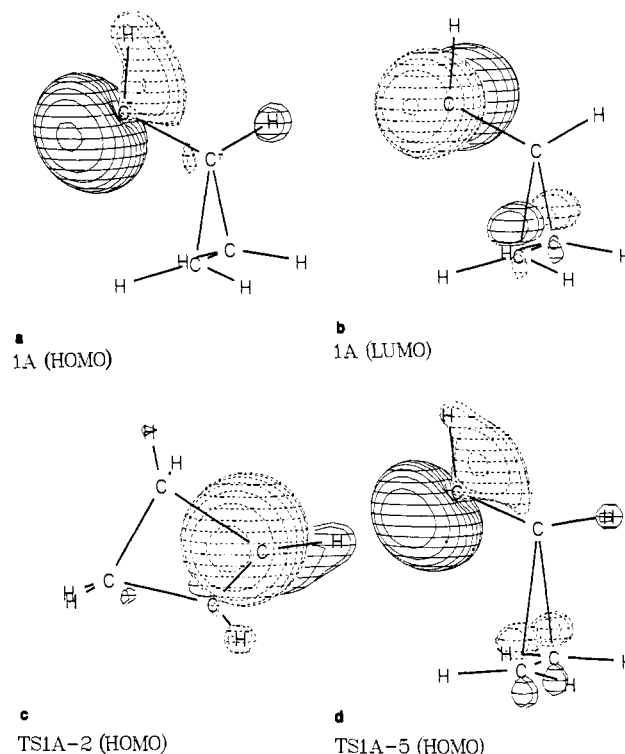
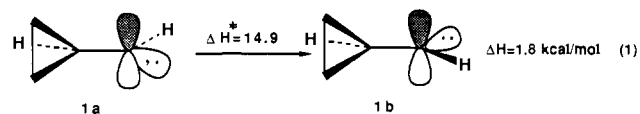


Figure 2. Salem-Jorgenson plot of the molecular orbitals of several species involved in the reactions of **1**.

Our calculations indicate that **1a** is more stable than **1b** by 1.8 kcal/mol while an enthalpy barrier of 14.9 kcal/mol is calculated for the conversion of **1a** to **1b** (eq 1). These values may be



compared to previously reported values of 2.6 and 10.1 kcal/mol for the relative energy and ΔH^\ddagger , respectively, at the HF/4-31G level.² Since conformers **1a** and **1b** are stabilized by delocalization of the electrons in a Walsh orbital into the carbene p orbital and the transition state for rotation in **1** is destabilized by the interaction of the filled sp² orbital on the carbene center with the antisymmetric filled Walsh orbital, it is not surprising that the rotational barrier is relatively large. The corresponding barrier in the cyclopropyl cation has been calculated to be 17.5 kcal/mol¹² with an experimentally measured value of 13.7 kcal/mol for the dimethylcyclopropyl cation.¹³ The close correspondence between the rotational barrier in carbene **1** and that in the carbonium ion indicates that the same factors are operative in stabilizing both types of reactive intermediates. As will be shown below, other reaction pathways exist which are lower than or comparable in energy to the rotational barrier in **1**.

Intramolecular Reactions of Carbene 1. In addition to the rotational interconversion of **1a** and **1b**, the energetics of the conversion of **1** to cyclobutene (**2**), methylenecyclopropane (**3**), and bicyclobutane (**6**), as well as the fragmentation to ethylene (**4**) and acetylene (**5**) were calculated. Table III shows the calculated enthalpies and entropies of activation and relative rates for the reactions of **1** by these various pathways. As a measure of the ability of our computational methods to reproduce energies of species along the C₄H₆ energy surface, we may compare experimental enthalpies with calculated values using **2** as the reference structure to relate the experimental and theoretical values.¹⁴

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(13) Namanworth, E.; Kabakoff, D. S. *J. Am. Chem. Soc.* **1970**, *92*, 2544.

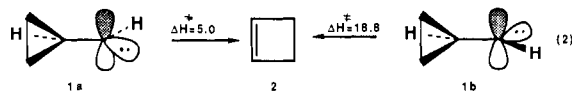
Table III. Calculated Activation Parameters and Relative Rates for Intramolecular Reactions of Carbenes **1a** and **1b**

starting carbene	product	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	relative rate ^c	
				25 °C	180 °C
1a	2	5.02	-2.57	1	1
1a	3	16.86	-1.48	3.3×10^{-9}	3.1×10^{-5}
1a	4 + 5	22.44	0.72	7.9×10^{-13}	1.9×10^{-8}
1a	6	14.74	-2.75	6.4×10^{-8}	1.8×10^{-5}
1a	1b	14.89	-1.29	1.0×10^{-7}	3.2×10^{-5}
1a	7/(4 + 5)^d	9.04 ^e	1.87 ^f	1.0×10^{-2}	1.1×10^{-1}
1b	1a	13.09	-1.9	1	1
1b	2	18.62	-2.65	5.9×10^{-5}	5.8×10^{-5}
1b	3	15.06	-2.09	3.2×10^{-2}	1.0×10^{-1}
1b	4 + 5	16.09	0.21	4.6×10^{-3}	4.1×10^{-2}
1b	6	21.03	-3.70	5.8×10^{-7}	5.8×10^{-5}
1b	7/(4 + 5)^d	7.96 ^e	1.36 ^f	3.1×10^4	1.5×10^3

^aIn kcal/mol. ^bIn cal/mol-deg. ^cRates are relative to the fastest concerted process for each carbene conformer. A different relative rate is calculated at each temperature. ^dThe estimated barrier is for the formation of the singlet biradical (i.e., ¹7) which is assumed to decompose with little or no activation barrier to **4 + 5**. ^eEstimated; see text. The barrier to decomposition of **1a** to the singlet biradical is assumed to be the same as the barrier for ³1 \rightarrow ³TS1a-7. Similarly, the barrier to decomposition of **1b** to the singlet biradical is assumed to be the same as the barrier for ³1b \rightarrow ³TS1b-7. ^fThese activation entropies were estimated by using the calculated entropy of the triplet ring-opening transition state.

This approach yields $\Delta H_{\text{exp}} - \Delta H_{\text{calc}}$ values of 2.8 kcal/mol for **3**, -4.3 kcal/mol for **4 + 5**, -0.5 kcal/mol for **6**, -2.0 kcal/mol for 1,3-butadiene, and -2.4 kcal/mol for the transition state connecting **2** and 1,3-butadiene.¹⁵

The fact that there are two conformations of **1** raises the possibility that each conformer could rearrange to **2** via transition states which have quite different geometries. This in fact appears to be the case with the rearrangement of **1a** to **2** via TS1a-2 (eq 2) which is calculated to have a barrier of 5.0 kcal/mol. In order



to examine the atomic motions necessary to transform **1a** to TS1a-2, a reaction cut was made between **1a** and the transition state. The distance between the carbene carbon and a methylene carbon on the ring was reduced in steps while all other parameters were completely optimized. An inspection of the geometries generated in this manner indicates that the C-C bond of the cyclopropyl ring migrates to the empty p orbital on the carbene center while the electron pair of the carbene remains nonbonding in the transition state. This is also illustrated by examining Salem-Jorgenson plots of TS1a-2 which demonstrate that the HOMO is localized on the carbene carbon with a great deal of s character (Figure 2c) while the LUMO is a combination of the carbene p orbital and orbitals on the migrating carbon. A similar conclusion regarding the orbital participation in the transition state for cyclobutene formation has been reached by Schoeller.²

The transition state which connects **1b** and **2** (TS1b-2) is 15.4 kcal/mol higher in energy than TS1a-2. The dihedral angle between the hydrogens on the incipient C=C in TS1b-2 is 152.5° while it is 7.3° in TS1a-2. Since TS1b-2 is 87.1 kcal/mol higher in energy than **2**, it could lead to *trans*-cyclobutene if such a species were an energy minimum. However, our calculations indicate

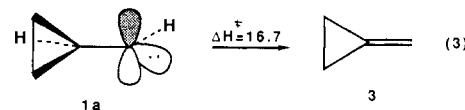
(14) Experimental heats of formation are taken from: Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(15) For the conversion of **2** to 1,3-butadiene, the experimental activation enthalpy¹⁶ has been compared to that calculated by: Rondon, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099, at the MP2/6-31G* level. For calculations at higher levels of theory see: Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412.

(16) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. Carr, R. W., Jr. *J. Phys. Chem.* **1965**, *69*, 1073.

that *trans*-**2** is not an energy minimum and the reaction path yields **2** directly. Nevertheless, it may be that the inherent high energy associated with *trans*-**2** is responsible for the higher barrier for ring expansion of **1b** as compared to **1a**. Attempts to rotate around the incipient double bond in TS1a-2 (or in geometries leading to it), in order to find a pathway from **1b** to TS1a-2, led to geometries in which the energy was substantially higher than in TS1a-2.

The rearrangement of **1** to **3** (eq 3) via TS1-3 requires an

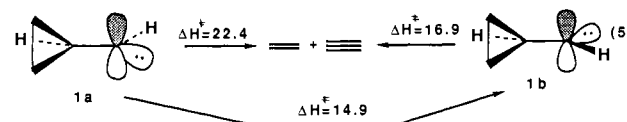


unfavorable conformation of **1**, and it is not surprising that this reaction proceeds via the rather high barrier of 16.7 kcal/mol (from **1a**) and has not been observed experimentally. The intramolecular insertion of either **1a** or **1b** into a β C-H bond to generate **6** (eq 4) is also calculated to have activation barriers



which render this process noncompetitive with cyclobutene formation. In this case, as in the ring expansion to **2**, there is a different transition state depending upon whether one starts from **1a** or **1b**. Rearrangement of **1a** via TS1a-6 has an activation enthalpy of 14.7 kcal/mol while **1b** must cross a barrier of 21.0 kcal/mol (via TS1b-6) to reach **6**. In both of these transition states connecting **1** and **6**, the C-H insertion occurs by the transfer of a methylene hydrogen on the ring to the empty p orbital on the carbene center.

The other reaction of carbene **1** which is observed experimentally is fragmentation to **4** and **5** (eq 5). For this process,



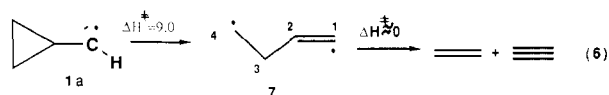
we have located two transition states whose participation depends upon which conformation of **1** is the starting point. From **1a** the reaction proceeds via TS1a-5 in which the dihedral angle between the carbene C-H and cyclopropyl C-H is 0° and the barrier is 22.4 kcal/mol. Carbene **1b** rearranges by crossing TS1b-5 in which the H-C-C-H dihedral angle is 180° and the barrier is 16.9 kcal/mol. The lowest energy concerted pathway to **4** and **5** from **1a** involves rotation to **1b** ($\Delta H^{\ddagger} = 14.9$ kcal/mol) followed by fragmentation of this species.

An inspection of the HOMOs of TS1a-5 and TS1b-5 shows why the concerted fragmentation in general has a high barrier relative to ring expansion and why this fragmentation is more favorable from **1b** than from **1a**. The HOMO of both transition states is made up of the antisymmetric combination of the developing π orbital on ethylene and a developing π orbital of the acetylene and is thus raised in energy due to four-electron closed-shell repulsions. However, these HOMOs still have a great deal of electron density in the carbene sp^2 orbital, and in TS1b-5, in which this orbital is anti to the developing ethylene orbital, this four-electron repulsion is less than in TS1a-5, in which the carbene sp^2 orbital and the developing π orbital are syn. This closed-shell interaction in the HOMO of TS1a-5 is shown in Figure 2d.

Table III demonstrates that these calculations identify cyclobutene formation as the only viable concerted pathway for carbene **1a**. The calculated relative rates listed in this table indicate that **2** will predominate over all the other possible products of the rearrangement of **1a** by a factor of at least 10^7 and over fragmentation to ethylene and acetylene by a factor of 10^{12} . In carbene **1b**, the calculations show no concerted pathway which is clearly favored over others. However, the data in Table III indicate that the most favorable concerted reaction of **1b** is simply rearrangement to **1a**. If this is the case, we expect either conformation

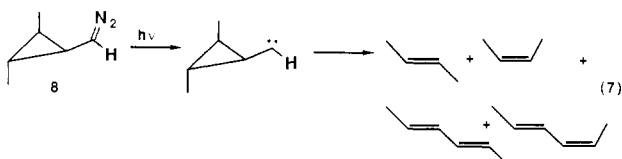
of carbene **1** to yield **2** as its major product along with small amounts of **3** and even smaller amounts of **4** and **5**. This conclusion is clearly not in accord with numerous experimental data which demonstrate that substantial amounts of **4** and **5** as well as **2** (but no **3** and **6**) are formed in the reactions of **1**. We are thus forced to search for a viable path to **4** and **5** from **1** and have considered several nonconcerted alternatives. As a starting point for this study we have investigated the position of triplet carbene **1** on the C_4H_6 energy surface.

The Chemistry of Triplet 1. As may be expected, triplet **1** was calculated to have a small barrier to rotation (0.2 kcal/mol). Triplet **1b** was calculated to lie 1.7 kcal/mol lower in energy than singlet **1a** giving a singlet-triplet splitting in **1b** of 3.5 kcal/mol. Since triplet **1** cannot give ground-state **2**, **4**, or **5** in a concerted reaction, it is logical to assume that this carbene will decompose to a biradical intermediate. Indeed this appears to be the case as cleavage of triplet **1b** to triplet biradical **7** is endothermic by only 1.9 kcal/mol and traverses a barrier of just 9.8 kcal/mol via **TS1b-7**. If we assume that triplet biradical **7**, with its separated spins, is comparable in energy to singlet **7**, intersystem crossing in the biradical followed by C-C bond scission could lead to **4** and **5**. Thus a possible route to **4** and **5** in this system would proceed via triplet **1** as shown in eq 6.



In order to assess the viability of the process in eq 6, we must consider the experimental evidence which bears on the mechanism of the formation of **4** and **5**. If triplet **7** were involved in this process, it is reasonable to expect that the formation of a substituted ethylene by cleavage of a suitably substituted **1** would be nonstereospecific. This expectation follows from the assumption that rotation about the C_3-C_4 bond in triplet **7** would be more rapid than intersystem crossing and subsequent cleavage.

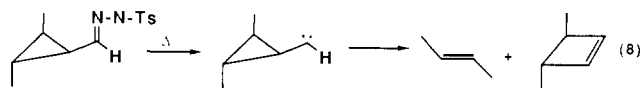
There have been several reports of the stereochemistry of the products when 2,3-dimethylcyclopropylmethylenes have been decomposed. A particularly interesting case in the study of the gas-phase photolysis of *trans*-2,3-dimethylcyclopropyldiazomethane (**8**) reported by Wolf and Guarino.¹⁷ The gas-phase chemistry of **1** differs from that in solution in that the initially formed **2** is created with excess energy and undergoes ring opening to 1,3-butadiene before it can dissipate this energy.^{8,17} This difference between the gas- and liquid-phase chemistry of **1** is not surprising when one considers that the rearrangement of **1** to **2** is exothermic by 66.7 kcal/mol and that the conrotatory ring opening of **2** must traverse a barrier of only 32.9 kcal/mol.¹⁶ Thus the gas-phase photolysis of **8** leads to acetylene, the 2-butenes, and 2,4-hexadienes (eq 7). The stereochemistry of the products



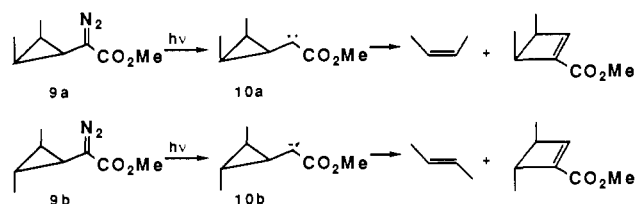
is pressure dependent with (*E*)-2-butene and (*E,E*)-2,4-hexadiene predominating at low pressures. However as the pressure is raised, the reaction becomes less stereospecific with close to a 1:1 ratio of (*E*):(*Z*)-2-butene and (*E,E*):(*E,Z*)-2,4-hexadiene formed at an added N_2 pressure of 739 Torr. The authors rationalize these results by proposing that, at the higher pressures, some of the carbene is degraded to its ground-state triplet which then undergoes nonstereospecific cleavage and ring expansion. The nonstereospecific ring expansion generates both *cis*- and *trans*-3,4-dimethylcyclobutene which undergo conrotatory ring opening to (*E,Z*) and (*E,E*)-2,4-hexadiene. Our calculations lend support to this proposal in that they indicate that triplet **1** is the ground state and that its cleavage is expected to be facile.

(17) Guarino, A.; Wolf, A. P. *Tetrahedron Lett.* **1969**, 655-658.

However, investigations of the reactions of substituted **1** in solution do not show any evidence for nonstereospecificity in either the cleavage or the ring expansion of the carbene. In fact, the ring expansion has been used by Berson, Bauer, and Campbell as a stereospecific synthesis of *trans*-3,4-dimethylcyclobutene with concurrent formation of (*E*)-2-butene stereospecifically (eq 8).⁵



Gallucci and Jones have examined the photochemistry of the *cis* and *trans*-dimethylcyclopropyl diazo esters **9a** and **9b** as precursors to the corresponding dimethylcyclopropylcarbomethoxy carbenes **10a** and **10b**.⁶ Direct photolysis of either **9a** or **9b** in



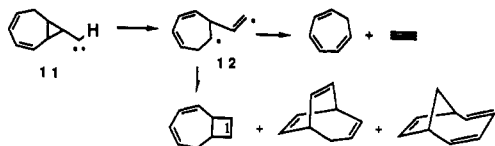
benzene solution gave stereospecific ring expansion and fragmentation. Irradiation with fluorenone sensitizer gave essentially the same ratio of cyclization to fragmentation with only a very slight loss of stereochemistry. To rationalize the fact that the reaction proceeded mainly along the singlet surface even in the presence of a triplet sensitizer, the authors favored a postulate that the singlet and triplet carbenes were in equilibrium but that the singlet simply reacted faster. Although carbenes **10a** and **10b** may have geometries quite different from that of **1**, our calculations indicate that singlet and triplet **1** are close enough in energy that they could be in equilibrium. It may be that the rate of this equilibrium is facilitated in solution.

Thus the experimental data concerning the reactions of **1** and its derivatives, especially those in solution, are not in accord with fragmentation proceeding exclusively along a triplet state. Since both fragmentation and ring expansion seem to proceed mainly along a singlet surface and we can find no concerted pathway to **4** and **5** competitive with ring expansion, we must consider the possibility of the reaction proceeding via singlet biradical **7** in which cleavage is faster than loss of stereochemistry.¹⁸ If we make the assumption that singlet and triplet **7** have similar energies and that the barrier to ring opening in singlet **1** is the same as that in the triplet (i.e., that the singlet-triplet splitting in the transition state for ring opening is the same as the singlet-triplet splitting in the carbene), then the process in eq 6 (in the singlet rather than the triplet state) will become competitive with ring expansion of **1**. This assumption has been included in the data in Table III which shows calculated rates and activation parameters for the formation of **7**/(**4** + **5**) from **1a** and **1b**. These data indicate that cleavage to a biradical may play a role in the chemistry of **1a** at higher temperatures and that this cleavage is the most favored process in carbene **1b**. If we use a two-configuration MCSCF¹⁹ treatment to calculate the difference between **1b** and ¹**TS1b-7** (2-MCSCF/6-31G), an activation enthalpy of 15.7 kcal/mol is obtained. Although this value is 5.9 kcal/mol larger than that calculated on the triplet surface at the [MP4SDQ/6-31G*] level, the difference may be due to the fact that insufficient correlation is included in the MCSCF treatment to describe the singlet. There is experimental evidence for biradical intermediates in reactions of derivatives of **1** in instances in which such biradicals would be stabilized by electron delocalization. Thus Jones, Reich, and

(18) In a calculation on an analogous biradical, CASSCF + CI calculations were used to conclude that the singlet *trans*-tetramethylene biradical is a "mechanistically insignificant intermediate" which fragments as soon as it is formed: Doubleday, C., Jr.; Page, M.; McIver, J. W., Jr. *THEOCHEM* **1988** 163, 331.

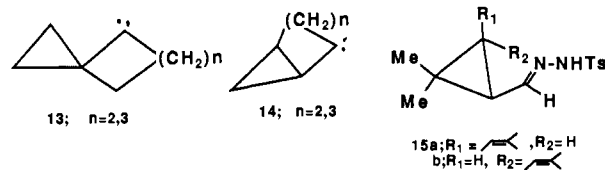
(19) Dupuis, M.; Sprangler, D.; Wendolski, J. J. GAMESS Q01, Program Library of Institute for Molecular Science. We thank Dr. M. Schmidt and Professor M. Gordon for providing us with this program.

Scott²⁰ have studied the reactions of carbene **11** and have observed products which may be rationalized by postulating the intermediacy of biradical **12**.



Since the calculated barrier to ring expansion in **1a** (5.0 kcal/mol) and the barrier to biradical formation in both **1b** (8.0 kcal/mol) and **1a** (9.0 kcal/mol) are lower than the barrier to interconversion of the carbene conformers (16.9 kcal/mol), we expect the chemistry of **1** to be determined by the conformer in which the carbene is born. When the carbene is formed in conformation **1a**, ring expansion should predominate while formation of conformer **1b** should lead to biradical **7**. It is difficult to predict which conformer should be formed preferentially in reactions leading to **1**. In most cases, the precursor to **1** is the corresponding diazo compound, and the conformational preference of this species has not been determined. However, the corresponding rotational isomers of vinylcyclopropane²¹ and cyclopropanecarboxaldehyde²² have been examined experimentally and theoretically, and the conformers have been found to have similar energies and to be separated by small barriers. Thus we would predict that both **1a** and **1b** are generally present in the reactions of **1** and that their ratio determines the ratio of ring expansion to fragmentation.

Although these calculations lead to the prediction that cis carbene conformations such as **1a** are likely to undergo ring expansion more readily than are trans conformations such as **1b**, it is difficult to design an experiment which substantiates this prediction. While carbenes such as **13** are locked into the cis conformation and rearrange by ring expansion,²³ the corresponding fragmentation is highly unfavorable as it would result in a strained cycloalkyne. Likewise carbenes such as **14** which are held in the trans conformation undergo predominate fragmentation^{24,25} due



to the fact that ring expansion places a bridgehead double bond in the fused cyclobutene ring of the product. Cyclopropanecarboxaldehyde tosylhydrazones in which large substituents on the ring force the tosylhydrazone group into trans position should favor generation of the trans carbene and consequent fragmentation. This effect may be operative in tosylhydrazones **15a** and **15b** in which the ratio of fragmentation to ring expansion is 2.7 and 2.1, respectively.²⁶

The fact that stereochemistry is generally conserved in the reactions of derivatives of **1** indicates that singlet biradical **7** must have a very short lifetime relative to cleavage to **4** and **5**. Of course, if this lifetime becomes vanishingly small, the singlet biradical is no longer an intermediate and disappears from the energy surface.^{18,27} This could be the situation for the cleavage of **1** in which case the energy barrier would correspond to the difference in energy between the carbene and **TS1b-7**. Although we have not conclusively demonstrated that this is the case, this assumption rationalizes the present computations with numerous experimental data regarding the reactions of **1**.

Conclusions

The course of intramolecular reactions of cyclopropylmethylene appears to be dictated by the conformation of the carbene. The fact that there is a substantial barrier to the interconversion of the conformers leads to the conclusion that the two conformers will react independently; the conformer in which the carbene and methyne hydrogens are cis favoring ring expansion and the trans conformer favoring fragmentation.

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(24) Freeman, P. K.; Kuper, D. G. *J. Org. Chem.* **1965**, *30*, 1047.

(25) The photochemical fragmentation of a singlet trans cyclopropylmethylene has been observed in a low-temperature matrix by: Kesselmayr, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 5029.

(26) Sasaki, T.; Eguchi, S.; Ohno, M.; Umemura, T. *J. Org. Chem.* **1973**, *38*, 4095.

(27) Our 2-MCSCF calculation¹⁹ of **TS1b-7** shows little biradical character with an electronic occupation in the HOMO of 1.915 and only 0.084 in the LUMO.