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Singlet Methylcarbene: An Elusive Intermediate of the Thermal Decomposition of Diazoethane and Methyldiazirene[†]

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Abstract: *Ab initio* methods have been employed to study the decomposition pathways of diazoethane and methyldiazirene as two possible precursors for the formation of methylcarbene. Geometries have been optimized at the SCF, MP2, and CISD levels of theory using 6-31G*, DZP, and TZP basis sets. Final energies were obtained at the TZP CCSD(T)//TZP CISD+ZPVE(DZP CISD) level. Vibrational frequencies were evaluated up to the DZP CISD level. Two possible mechanisms were considered: (a) simultaneous breaking of the C−N bond and migration of a methyl hydrogen to form ethylene and N_2, and (b) stepwise formation of methylcarbene and N_2 followed by rearrangement to ethylene and N_2. For both starting materials only the stepwise pathway was found. The activation barriers for the decomposition of diazoethane and methyldiazirene are 26.9 and 30.1 kcal/mol at our highest level, respectively. The barrier for the reverse association from methylcarbene + N_2 to diazoethane is only 3.3 kcal/mol; this barrier is 11.7 kcal/mol for methyldiazirene. There is no indication that surface crossings with the first excited states (generally >60 kcal mol^{-1}) may occur. These results are in excellent agreement with experimental findings, and they nicely explain the difficulties involved in the isolation of methylcarbene, which lies on a small shoulder of the potential connecting the precursors and products. In view of further experimental work, methylcarbene should be more readily trapped using diazoethane as a precursor.

Introduction

Carbenes have long been of great synthetic utility and have also received considerable theoretical interest recently.[1] But apart from a few exceptional cases,[2] unstable carbenes cannot be isolated or even studied in the laboratory by conventional methods. For example, diazoethane (**1**) and methyldiazirene (**2**) both decompose readily into ethylene (**3**) and nitrogen. The most favored pathway involves methylcarbene (**4**) as the intermediate, but only a few studies have dealt with the classification of this mechanism.[3] Also, the existence of **4** as a true intermediate or transition structure and the preferred electronic state (singlet or triplet) has been a long-standing controversy. For thermal processes, Nickon *et al.* found that the high stereoselectivity of carbene products under mild conditions pointed to the singlet as the major intermediate.[4] However, using high levels of theory, Gallo and Schaefer placed the singlet 5 ± 1 kcal/mol above the triplet, making the triplet the ground state.[5] Earlier Evanseck and Houk had calculated an activation barrier for the rearrangement of **4** into **3** of only 0.6 kcal/mol (MP4/6-31G**//MP2/6-31G*+ZPE), low enough to make intersystem crossing to the triplet state, which would require more energy, unlikely.[3a] Recently, experimental data have reinforced Evanseck and Houk's conclusion and shown that the singlet should be the species involved in all major reactions. Seburg and McMahon, in agreement with Evanseck and Houk, reported no triplet products detected in ESR experiments as a photoproduct of **2**, conjecturing that the rate of the [1,2] hydrogen shift to **3** exceeds the rate of intersystem crossing from the singlet to the triplet. Using CO-doped argon matrices at 10 K, Seburg and McMahon indirectly pointed to the singlet state of **4** by trapping methylketene (**5**), reinforcing the existence of singlet **4** as an intermediate.[2a] Modarelli and Platz were unable to directly trap **4** using a pyridine ylide probe method but found evidence for the existence of **4** as a singlet intermediate. They predicted a possible calculated lifetime of less than 500 ps, also concluding that the [1,2] shift exceeds intersystem crossing.[2b] Furthermore, Ma and Schaefer, using high levels of theory [TZ2P(f,d) CCSD(T)], calculated an activation barrier from **4** to **3** of 1.2 ± 0.5 kcal/mol, suggesting that singlet **4** is a true intermediate.[3b] Thus evidence points to singlet **4** as a true minimum, albeit short-lived, rather than merely a transition structure.

This paper examines the singlet pathway in detail and also addresses the possibility of **1** and **2** reacting directly without cleaving to **4** and N_2 first. For **1** and **2** we have examined the two possible pathways illustrated in Scheme 1.

Computational Methods

Geometries were optimized by analytic gradient techniques utilizing the PSI[6] and Gaussian 92[7] programs using self consistent field (SCF),[8] second-order Møller−Plesset (MP2),[9] and configuration interaction with

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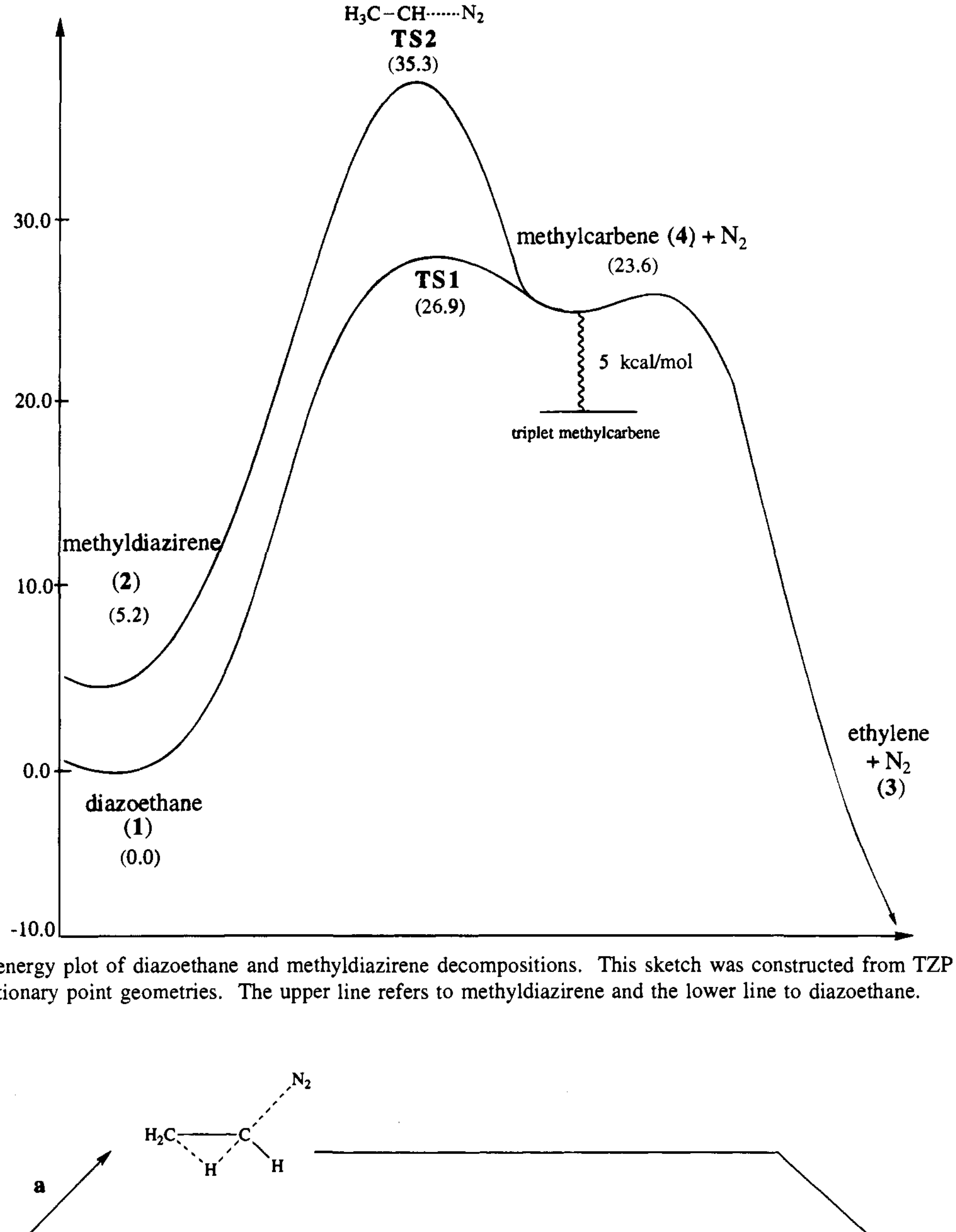
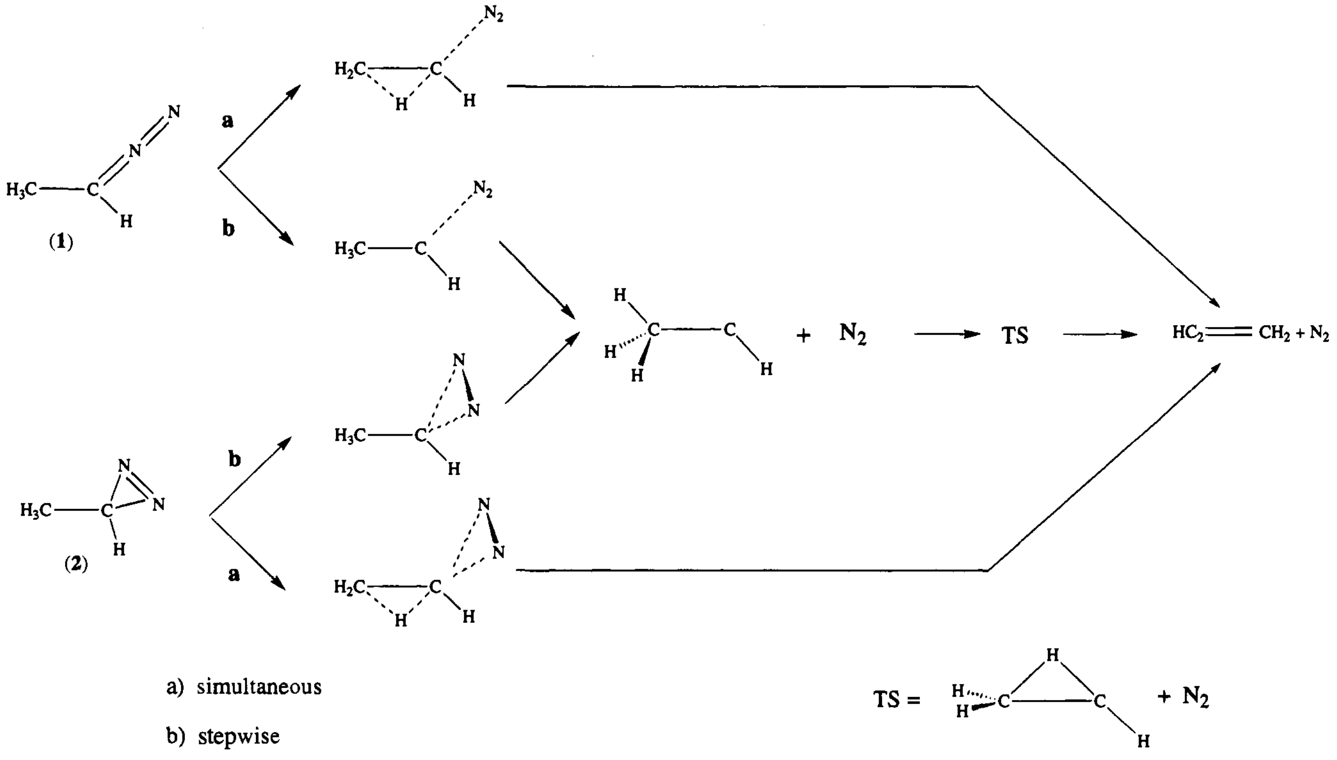
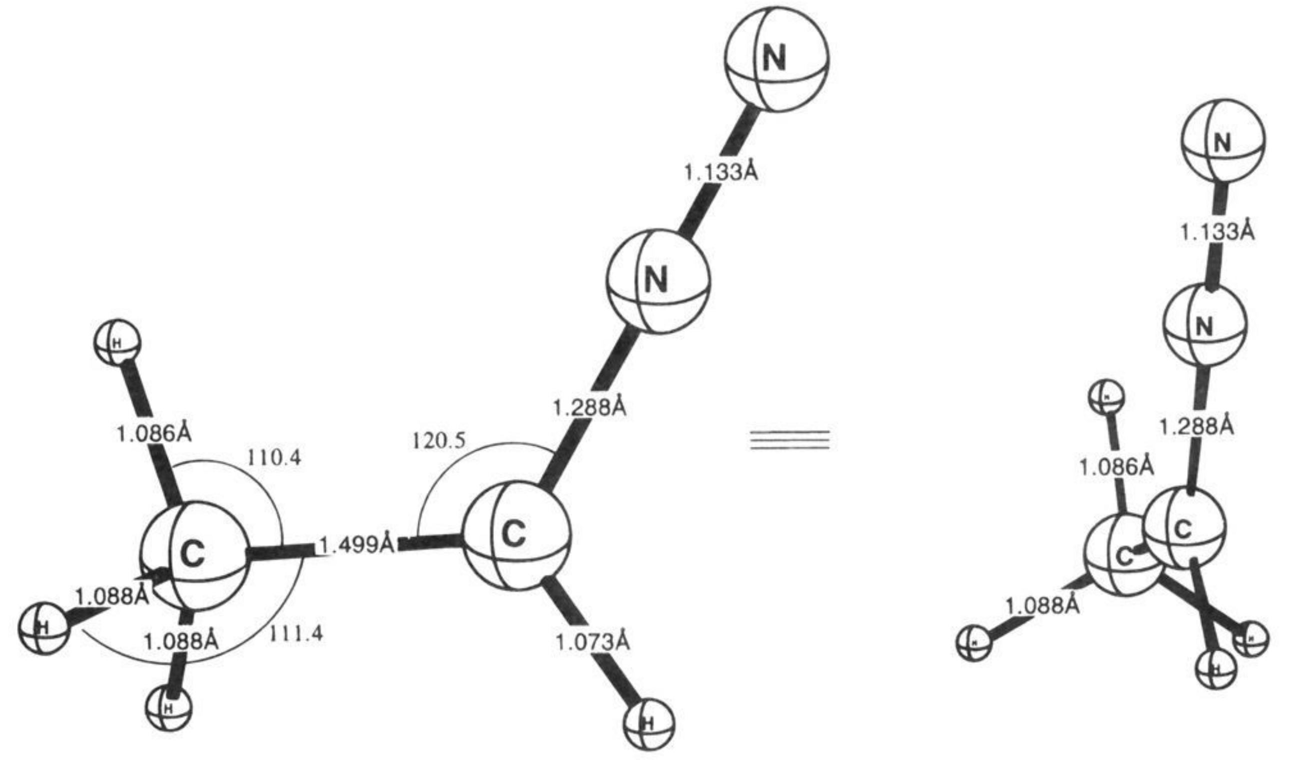


Figure 1. Relative energy plot of diazoethane and methyldiazirene decompositions. This sketch was constructed from TZP CCSD(T) energies using TZP CISD stationary point geometries. The upper line refers to methyldiazirene and the lower line to diazoethane.

Scheme 1



single and double excitation (CISD)[10] methods. The effect of unlinked quadruple excitations on the CISD energies was estimated by incorporating the Davidson correction,[11] and the corresponding energies are denoted CISD+Q. The basis sets employed were 6-31G(d), Huzinaga–



Diazoethane
(**1**, C_s)

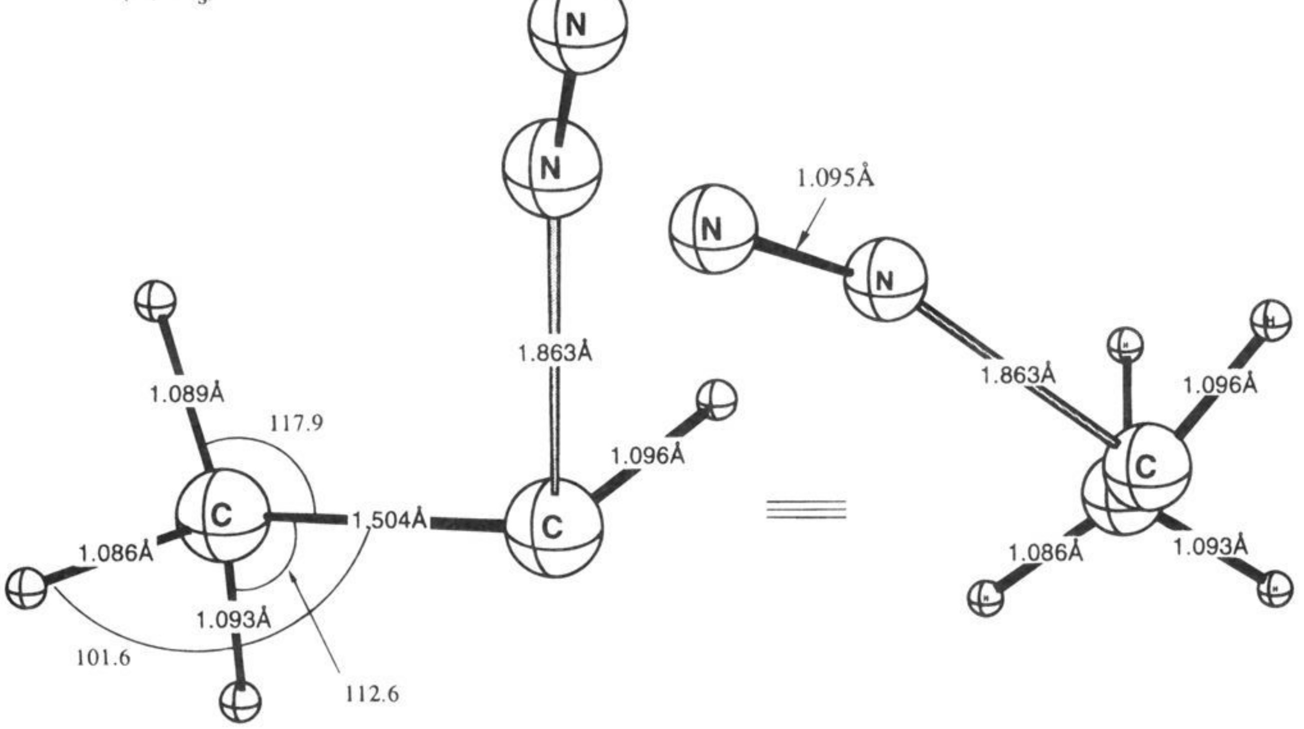


Figure 2. Optimized geometries for diazoethane (**1**-C_s) and for the transition structure (**TS1**) at the TZP CISD level. Bond lengths are given in angstroms and angles in degrees.

Table 1. Relative Energies (in kcal/mol) corrected for Zero-Point Vibrational Energies

species	HF 6-31G*	MP2 6-31G*	DZP CISD	DZP CISD+Q	TZP CISD	TZP CISD+Q	DZP CCSD//DZP CISD	DZP CCSD(T)//DZP CISD	TZP CCSD//TZP CISD	TZP CCSD(T//) TZP CISD
methylcarbene(**4**) + N_2	4.0	31.4	19.1	21.8	17.0	20.2	21.0	24.2	19.6	23.6
diazoethane (**1**-C_1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TS1	20.2	35.3	23.2	24.7	23.5	25.2	24.1	26.0	24.8	26.9
1-C_S(cis)	0.0	0.34								
1-C_S(trans)	−1.1	−2.7								
methyldiazirene (**2**-C_S)	2.7	0.2	0.8	1.0	3.0	3.5	1.4	2.5	4.0	5.2
TS2	36.0	41.6	36.4	35.9	36.1	35.9	35.0	34.9	35.3	35.3

Dunning double-ζ plus polarization (DZP)[12] [(9s5p/4s2p) contractions for C and N, (4s/2s) for H], and Huzinaga−Dunning triple-ζ plus polarization (TZP)[13] [(10s6p/5s3p) contractions for C and N, (5s/3s) for H)] basis sets. Single-point energies were calculated using the coupled cluster method including both single and double excitations (CCSD) and single and double excitations with the effect of connected triple excitations included perturbatively [CCSD(T)].[14] Zero-point vibrational energies (ZPVE) and frequencies were evaluated up to the

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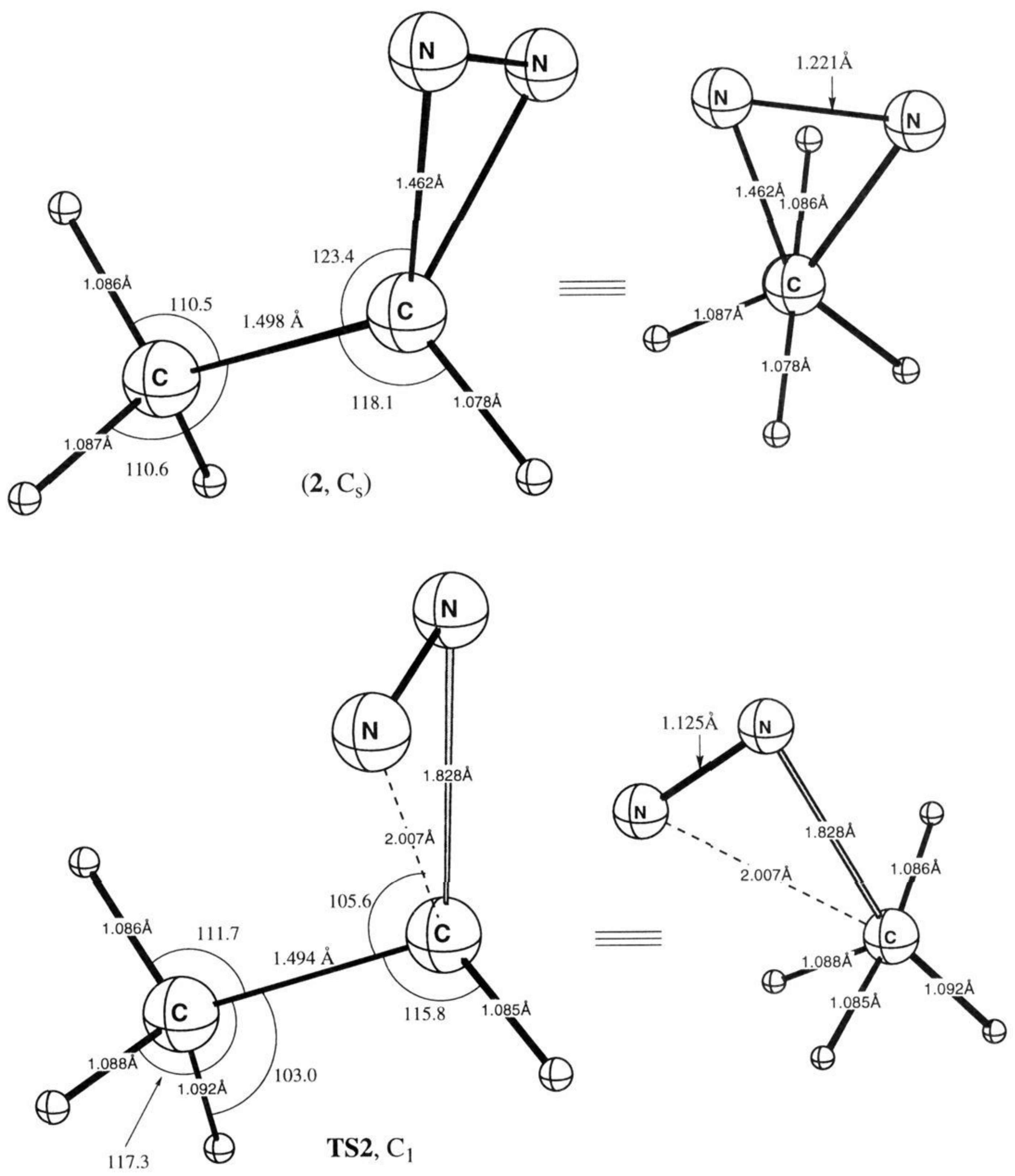

Figure 3. Optimized geometries for methyldiazirene ($\mathbf{2}$-C_s) and the transition structure (**TS2**) at the TZP CISD level. Bond lengths are given in angstroms and angles in degrees.

Table 2. Relative Energies (in kcal/mol) with Respect to the Appropriate Singlet Ground State

species	DZP CIS//DZP CISD 1st excited state (S_1)	TZP CCSD(T)//TZP CISD triplet (T_0)
diazoethane ($\mathbf{1}$-C_1)	67.2	58.9
TS1	85.4	43.7
methyldiazirene ($\mathbf{2}$-C_S)	92.3	78.4
TS2	85.6	46.2

DZP CISD level for all molecules. The ZPVE's were scaled by 0.91 at the SCF level, 0.93 at the MP2 level, and 0.95 at the CISD level.

Results and Discussion

Of our two initial structures, diazoethane (**1**) and methyldiazirene (**2**), **1** was examined first for the two competing decomposition mechanisms: (a) a simultaneous [1,2] hydrogen shift during the breaking of the C−N bond; and (b) a loss of N_2 and intermediate formation of methylcarbene (**4**) before rearrangement into ethylene (**3**) and N_2. The results are summarized in Tables 1−3 (Table 3 is in the supplementary material). Three conformers of **1** were initially considered: C_1, C_s(cis), and C_s(trans), all being very close in energy. At the MP2/6-31G(d) level the energy of $\mathbf{1}$-C_1 differed from that of the cis $\mathbf{1}$-C_s structure by only 0.1 kcal/mol and from the trans $\mathbf{1}$-C_s structure by 0.2 kcal/mol. Thus, the rotational barrier of **1** is very small. Although the C_1 structure had the lowest energy at the SCF and MP2 levels of theory, the energy of the trans structure with inclusion of zero-point vibrational energy (ZPVE) corrections was lower than that of C_1. This is due to the fact that the $\mathbf{1}$-C_s(trans) structure represents the transition structure for the methyl group rotation as determined by the presence of an imaginary frequency representing the aforementioned rotational mode. Therefore, it was intended to consider the cis and trans structures only up to the MP2/6-31G(d) level. However, at the DZP CISD level of theory the geometry of the $\mathbf{1}$-C_1 structure collapses to the cis structure. Thus, at the highest level of theory considered, the equilibrium geometry of diazoethane is the $\mathbf{1}$-C_s(cis) structure.

We located one transition structure (**TS1**) for the diazoethane dissociation belonging to the C_1 point group. The imaginary vibrational frequency corresponds to the C−N bond-breaking

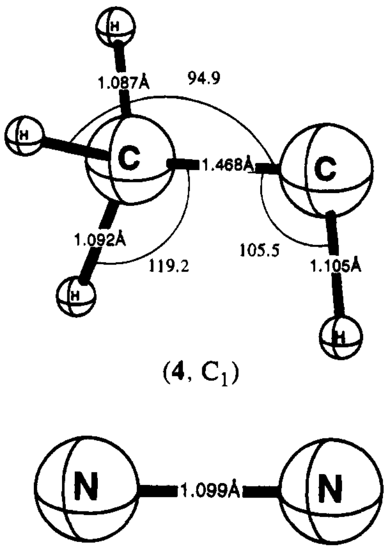

Figure 4. Optimized geometries for methylcarbene (**4**) and N_2 at the TZP CISD level. Bond lengths are given in angstroms and angles in degrees.

mode, derived from vibrational frequency analyses at the MP2/6-31G(d) and DZP CISD levels. There was no strong coupling between any of the methyl hydrogens and the C−N bond; **TS1** was found to be a true saddle point representing **b**, the stepwise pathway. This conclusion was confirmed by an intrinsic reaction coordinate (IRC) analysis (Figure 5). At all levels of theory, the methyl group remained fully intact and fairly unchanged. There were no extreme bond length changes or angle changes in the methyl group from **1** to **TS1** (Table 3, Figure 5). These findings can be illuminated by the analysis of the singlet−triplet gap in **4** by Khodabandeh and Carter.[15] Using Mulliken population analysis to determine the transfer of electron density, they found that the methylenic carbon molecular orbitals for the singlet state were unaffected by hyperconjugation; the CH_3 orbital donated practically no electron density in the singlet state to the methylenic sp^2 orbital. Based on the low rotational barrier of the methyl group, the extreme lack of hyperconjugation, and our vibrational frequency analysis, we thus ruled out the possibility of the direct pathway **a** using diazoethane as the starting material, due to the lack of interaction between the methyl hydrogens and the C−N stretch.

The reaction $\mathbf{1} \rightarrow \mathbf{4} + N_2$ through **TS1** is very endothermic at all levels of theory. Higher levels of theory give rather constant activation energies (ZPVE corrections included) around 25.0 kcal/mol and at our highest level [TZP CCSD(T)//TZP CISD] we determined a barrier of 26.9 kcal/mol.[16] The energy change from **TS1** to methylcarbene + N_2 is very small. The barrier for the reverse association is only 3.3 kcal/mol at the TZP CCSD(T)//TZP CISD level. The rearrangement of **4** into **3** thus is a very exothermic reaction and also has a very low barrier.

Another precursor studied was methyldiazirene (**2**), optimized in C_s symmetry. At our highest level of theory, TZP CCSD(T)//TZP CISD, the energy of **2** was 5.2 kcal/mol higher

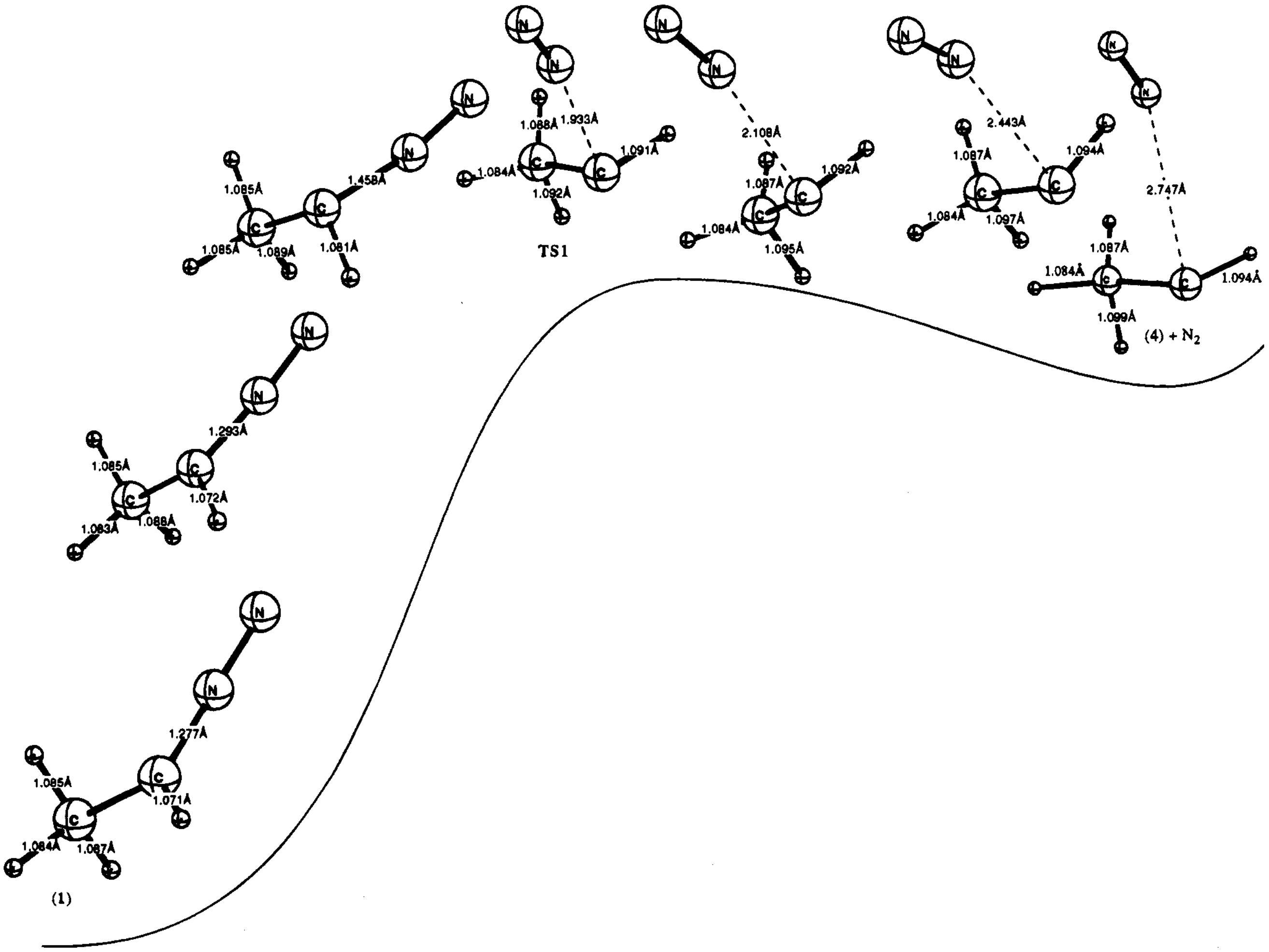

Figure 5. Schematic representation of pathway **b** with **1** as the precursor. Geometries were obtained from an intrinsic reaction coordinate (IRC) calculation at the HF/6-31G* level. Note the minimal change in the methyl group during the loss of N_2. Bond lengths are given in angstroms and angles in degrees.

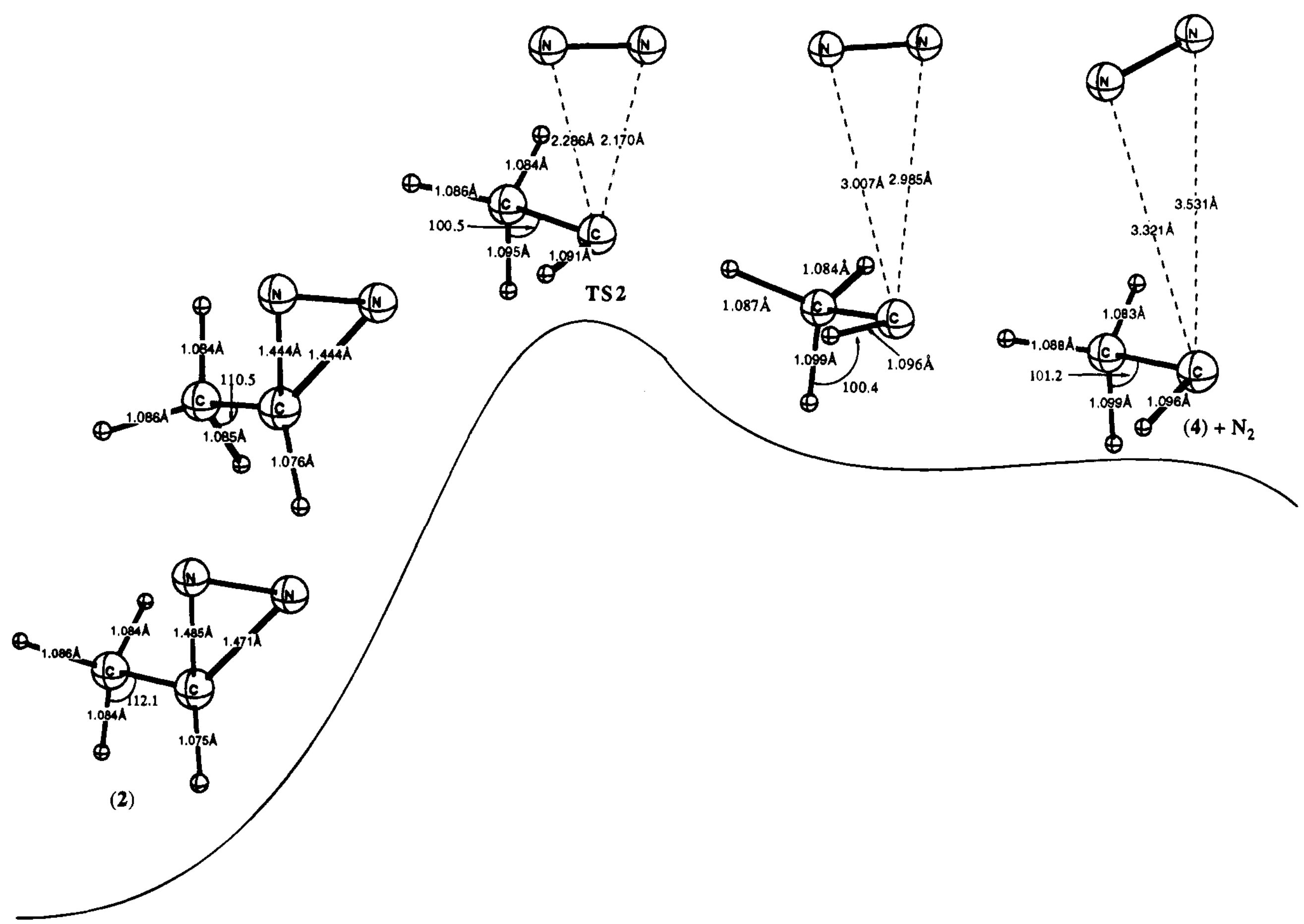

Figure 6. Schematic representation of pathway **b** with **2** as the precursor at the HF/6-31G* level. As for **1**, note the minimal change in the methyl group. Bond lengths are given in angstroms and angles in degrees.

than that of **1**. To maintain congruity with the study of **1**, we examined **2** for the existence of the two decomposition mechanisms. Using vibrational frequency analyses at the DZP CISD geometries we were able to determine that, as with **1**, the pathway is stepwise. There was little coupling evident between the C−N stretch and any of the C−H stretches or angles of the methyl group. An IRC analysis further confirmed that **2** and **4** are the educts and products connected by the methyldiazirene transition structure (**TS2**), respectively (Figure 6). **TS2** lies approximately 10 kcal/mol higher in energy than **TS1**, being 8.4 kcal/mol higher at the TZP CCSD(T) level (Figure 1). As observed before, the parameters of the methyl group are relatively unchanged in comparison to those of methyldiazirene, indicating no simultaneous (direct) rearrangement.

The section of the potential from **TS2** to **4** + N_2 is different from **TS1** to **4** + N_2. The potential surface of the pathway for dissociation of **2** is steeper than that of **1** because the activation barrier from **TS2** to methylcarbene plus N_2 is 8.4 kcal/mol higher than the barrier from **TS1**. With the higher energy drop from **TS2** the lifetime of methylcarbene would probably be even shorter still as the drop from methylcarbene to ethylene is strongly exothermic. Thus diazoethane would be more conducive to trapping methylcarbene.

Our findings appear to be consistent with experiment. Examining the high activation barriers of **TS1** and **TS2** while comparing them to the low barriers to both methylcarbene plus N_2 and ethylene plus N_2, it is easily seen that the reactants gain enough kinetic energy to pass the first and second barrier quickly. This very flat potential surface of **TS1** followed by a sharp drop nicely explains the low energy barrier (1.2 kcal/mol)[3] between methylcarbene and ethylene and the conjectured short lifetime of methylcarbene. The higher energy of **TS2** would cause methylcarbene to have an even shorter lifetime. We can also see that, since such a small amount of excess energy would rearrange methylcarbene into ethylene, the [1,2] hydrogen shift into ethylene would easily occur before methylcarbene could cross into the more stable triplet state. It is easily seen from the energy plot (Figure 1) that methylcarbene plus N_2 would very quickly and without difficulty rearrange into ethylene and N_2 due to the lower energy and much higher stability of the latter.

Following a referee's suggestion we have computed (DZP CIS//DZP CISD) the first excited states for **1**, **2**, and the corresponding transition structures (**TS1** and **TS2**); all relative energies (Table 2) are well above 60 kcal mol^{-1} vs the ground electronic states. Therefore, the possibility of an intersystem crossing is highly unlikely.

Conclusion

The role of the transition structures for the formation of methylcarbene starting with diazoethane and methyldiazirene has been thoroughly studied. After examination of the off-diagonal force constants from the vibrational frequency analysis, both transition structures show the stepwise mechanism for the formation of methylcarbene and N_2 to be operative. There is little to no evidence of participation by the methyl group in either transition structure. For diazoethane, the activation barrier

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(16) Both the Hartree−Fock and the MP2(6-31G*) methods seem to be inappropriate to study this problem computationally since Hartree−Fock (20.2 kcal/mol) underestimates and MP2 (35.3 kcal/mol) overestimates the decomposition (**1** → **4**) barrier significantly.

to **TS1** at the TZP CCSD(T)//TZP CISD+ZPVE level is 26.9 kcal/mol. The reverse activation barrier from methylcarbene and N_2 to **TS1** is only 3.3 kcal/mol. For methyldiazirene, the barrier to **TS2** was 35.3 kcal/mol and 11.7 kcal/mol from **TS2** to methylcarbene and N_2. This research illustrating the very flat potential surface of the mechanism for **TS1** and the somewhat steeper surface for **TS2**, combined with the known strong exothermicity of the methylcarbene to ethylene rearrangement, complements the experimental evidence.[2] This shows that (a) the [1,2] hydrogen shift will occur more quickly than the intersystem crossing to triplet methylcarbene and (b) the lifetime of methylcarbene will be almost negligible. From methyldiazirene, due to the higher energy of **TS2**, the chance of excess kinetic energy being present to drive the reaction from methylcarbene to ethylene is greater. Thus the lower reverse activation barrier in the diazoethane pathway indicates that there is a much greater chance of trapping methylcarbene when diazoethane rather than methyldiazirene is used as a precursor.

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Supplementary Material Available: Tables of optimized parameters of TZP CISD geometries and absolute energies and scaled zero-point vibrational energies of all structures studied (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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