



THEORETICAL INSIGHTS INTO THE CYCLOADDITION REACTION MECHANISM BETWEEN AZACYCLOPROPENYLIDENE AND FORMALDEHYDE

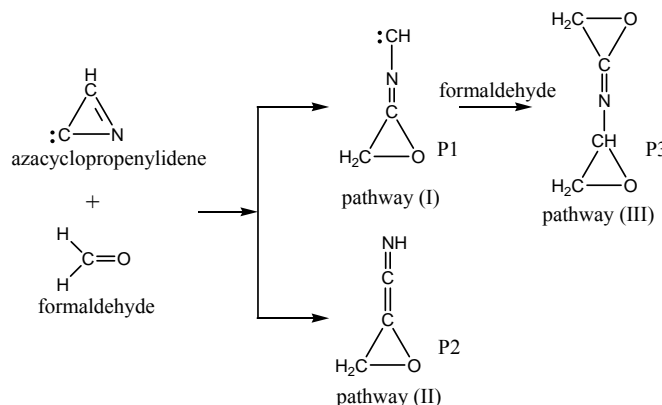
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The cycloaddition reaction mechanism between azacyclopropenylidene and formaldehyde has been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method in order to better understand the reactivity of azacyclopropenylidene with unsaturated compound formaldehyde. Geometry optimizations and vibrational analyses have been performed for the species involved in the title reaction. From the potential energy profile, it's predicted that the cycloaddition reaction has three competitive pathways: (I) the azacyclopropenylidene reacts with formaldehyde to form a carbene compound P1 through two steps; (II) the two reactants form an allenes compound P2 through three steps; (III) after formed P1 by the reaction of azacyclopropenylidene and formaldehyde, acting as the reactant, P1 further react with formaldehyde to form a stable bicyclic compound P3 via transition state with energy barrier of 14.7 kJ/mol. From the thermodynamics viewpoint, P3 is the dominating product, whose energy is 192.7 kJ/mol lower than that of the reactants.



INTRODUCTION

Cyanopolyenes molecules HC_nN have been detected in interstellar space by radio telescopes for a long time.¹⁻⁹ This class of molecules played an important role in astronomy and interstellar chemistry due to their astrophysical abundance and rather large dipole moments. One of the interesting cyanopolyenes, the molecule HCCN, has been studied by electron spin resonance and UV/IR spectroscopy from 1960s.^{10,11} For the first time, Guélin *et al.* detected HCCN with the IRAM 30 m telescope in the carbon star envelope IRC+10216,

and discussed its formation mechanism.¹² Later, HCCN has been observed in interstellar space in 1996.¹³ A lot of experimental and computational methods were carried out for the structures and the relative energies of some isomers of HCCN system. Many studies have revealed that there exist many isomers with different kind of geometries (linear, bent or cyclic) or different multiplicity (singlet or triplet) having similar energies for the HCCN molecules.¹⁴⁻²³ Lee *et al.* have characterized the quasilinear triplet, bent singlet, and cyclic singlet HCCN isomers and determined their molecular properties with a series of highly

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accurate *ab initio* level of theory.²⁴ The cyclic HCCN isomer, generally named as azacyclopropenylidene, is the most stable isomer of all singlet molecules. In addition, the cyclic HCCN isomer has been found to be an intermediate between the interconversion of other isomers on the hypersurface of neutral, anionic, and cationic species where the barriers are feasible.^{25,26} Recently, vibrational spectroscopic constants and fundamental vibrational frequencies for isotopologues of azacyclopropenylidene isomer has been investigated.²⁷

In 1998, matrix generations of singlet azacyclopropenylidene and singlet bromocyanocarbene (BrCCN) were reported by Maier and co-workers.²⁸ Casavecchia *et al.* reported the dynamics of a reaction of nitrogen atom with an unsaturated hydrocarbon by combining crossed molecular beam experiments and *ab initio* molecular orbital calculations. They found that azacyclopropenylidene is one of the products of the reaction of nitrogen atom with C₂H₂ in the upper atmosphere of Titan.²⁹ Thus, the azacyclopropenylidene seems to be a good candidate for astrophysical detection, considering these various possible formation pathways and its large dipole moment.³⁰ Computational investigation of HCCN molecules will be very helpful to elucidate the reactivity and kinetic stability of these molecules. We have studied the reactions between azacyclopropenylidene and small ring compounds.^{31,32} The calculational results demonstrated that azacyclopropenylidene can insert into small ring compounds to form ring-expanded products. However, no attention has been paid to the reactivity of azacyclopropenylidene with the active species containing double bond compounds until now. In the present study, we have performed comprehensive theoretical investigation of the reaction mechanism between azacyclopropenylidene and formaldehyde by employing the second-order Møller-Plesset

perturbation theory (MP2) method in order to better understand the azacyclopropenylidene reactivity. To the best of our knowledge, this study is the first report of the reaction mechanism between azacyclopropenylidene and unsaturated alkene compounds. The present results will enrich the available data for the relevant azacyclopropenylidene chemistry and discuss the possibility of formation of larger molecules by means of azacyclopropenylidene in interstellar space.

CALCULATION METHOD

The second-order Møller-Plesset perturbation theory (MP2) method³³ in combination with the 6-311+G* basis set has been employed to locate all the stationary points along the reaction pathways without imposing any symmetry constraints. Frequency analyses have been carried out to confirm the nature of the minima and transition states. Moreover, intrinsic reaction coordinate (IRC) calculations have also been performed to further validate the calculated transition states connecting reactants and products. Additionally, the relevant energy quantities, such as the reaction energies and barrier heights, have been corrected with the zero-point vibrational energy (ZPVE) corrections.

To further refine the calculated energy parameters, single point energy calculations for pathways (I), (II), and (III) have been performed at the CCSD(T)/6-311+G* level of theory based on the optimized geometries at the MP2/6-311+G* level of theory. As summarized in Table 1, both levels can give consistent results for the calculated reaction profile. For the sake of simplicity, the energetic results at the CCSD(T)/6-311+G*//MP2/6-311+G* level have been mainly discussed below if not noted otherwise.

All the calculations have been performed using Gaussian 98 program.³⁴

Table 1

The calculated relative energy (in kJ/mol) with respect to the isolated reactants^a

Pathways	Relative Energies			
Pathway (I)	TSa	IMa	TS1a	P1
	41.6/45.8	-121.7/-98.6	109.1/109.0	-9.8/-9.1
Pathway (II)	TS2a	IM2a	TS2b	P2
	162.3/178.3	24.5/31.2	94.6/99.3	-119.0/-106.8
Pathway (III)	TS3	P3		
	7.0/14.7	-218.6/-192.7		

^a The data after the slash refer to the results at the CCSD(T)/6-311+G*//MP2/6-311+G* level of theory.

RESULTS AND DISCUSSION

As displayed in Scheme 1, three possible pathways for the title reaction have been proposed. The geometric parameters for the reactants (azacyclopropenylidene (R1) and formaldehyde (R2)), transition states (TS), intermediates (IM), and products (P) involved in the pathways (I), (II), and (III) are displayed in Fig. 1. The calculated relative energies for the available stationary points have been summarized in Table 1. The corresponding reaction profile is illustrated in Fig. 2.

1 Pathway (I): the formation of a carbene compound P1

There are step (a) and step (1) along the reaction pathway (I), in which the step (a) is the common step for the pathways (I) and (II).

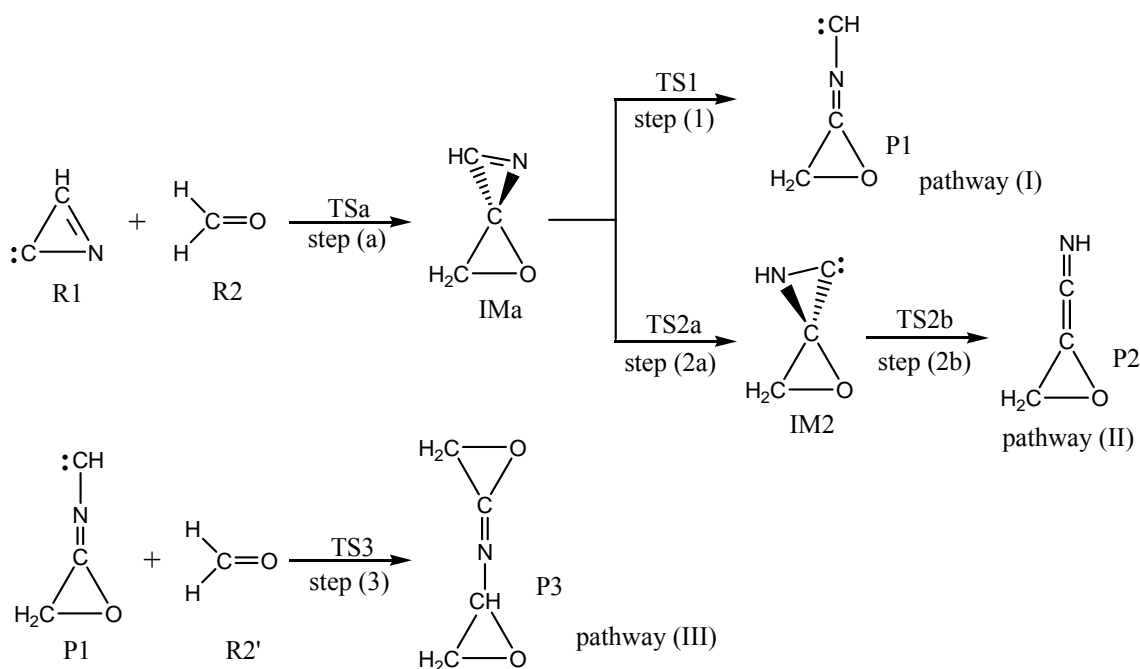
The first intermediate IMA has been formed along the reaction pathways (I) and (II) via a barrier of 45.8 kJ/mol. The calculated unique imaginary frequency of the transition state TSa in the cycloaddition process of the step (a) is $407i\text{ cm}^{-1}$ at the MP2/6-311+G* level of theory.

As shown in Fig. 1, in TSa, the distance of C^1-C^3 and C^1-O^1 is 1.828 and 2.282 Å, respectively. The distance of C^3-O^1 in R2 fragment is 1.263 Å, which elongated by 0.049 Å than that in isolated R2 molecule. Thus, in TSa, two new bonds of C^1-C^3 and C^1-O^1 are to be formed and the C^3-O^1 bond is to be transformed from double bond

to single bond simultaneously. As shown in Fig. 3, these changes can be further validated by the IRC calculations on the basis of TSa.

Qualitatively, the cycloaddition process can be understood from the frontier molecular orbital theory since the frontier orbitals (e.g., HOMO) of a chemical species are very important to define their reactivity and determine the way in which the molecule interacts with other species.³⁵ As displayed in Fig. 4, the weak strength of C^3-O^1 bond can be reflected from the HOMO of formaldehyde. Obviously, it's characterized by the π antibonding orbital. As for azacyclopropenylidene, the activity of C^1 site can be reflected from the largest contributions on the C^1 atom to the components of the whole HOMO. Therefore, C^1 atom of azacyclopropenylidene can react with the C^3-O^1 bond of formaldehyde to form spiro intermediate IMA.

As displayed in Fig. 1, compared with the isolated azacyclopropenylidene, the bond length of C^1-C^2 in IMA is extended by 0.006 Å. The angle of C^1NC^2 in IMA is 60.7° , which is decreased by 1.2° relative to that of the isolated azacyclopropenylidene. Therefore, the ring-tension of R1 fragment in IMA is larger than that of the isolated R1. Because of the existed large tension in the three-membered ring, the C^1-C^2 bond in IMA will be broken. Therefore, the second step of the pathways (I) is the C^1-C^2 bond cleavage, followed by the formation of P1.



Scheme 1 – The proposed three pathways for the reaction between azacyclopropenylidene and formaldehyde.

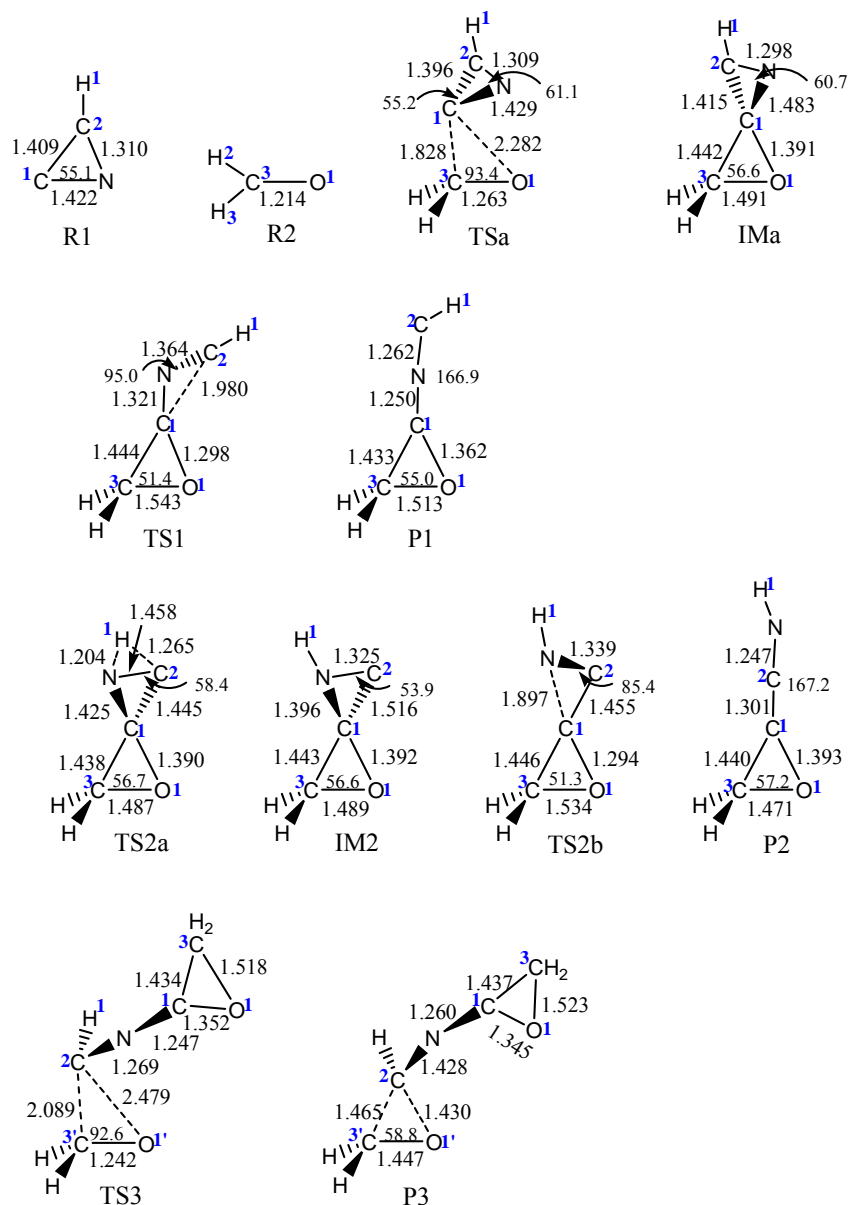


Fig. 1 – Optimized structures of the reactants (azacycloprenylidene and formaldehyde), transition states (TS), intermediates (INT), and products (P) in the reaction pathway (I), (II), and (III) at the MP2/6-311+G* level of theory, where the bond length and bond angle are in angstrom and degree, respectively.

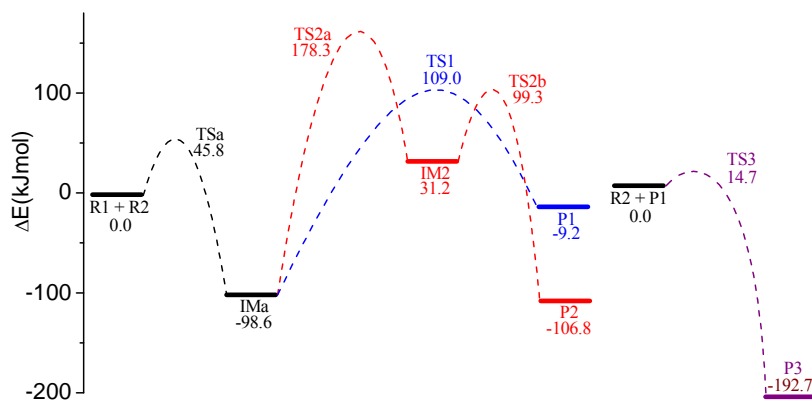


Fig. 2 – Reaction profiles for the cycloaddition reaction pathways (I), (II), and (III) between azacycloprenylidene and formaldehyde at the MP2/6-311+G* level of theory.

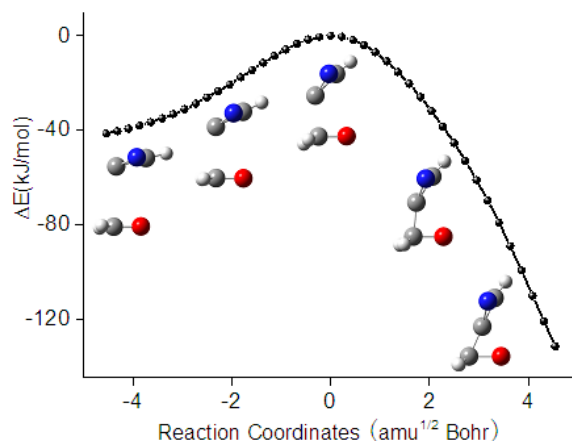


Fig. 3 – IRC of TSa and geometry evolution.

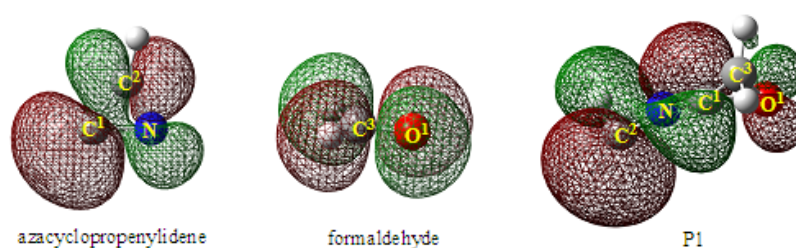


Fig. 4 – The calculated HOMO orbitals for azacyclopropenylidene, formaldehyde, and P1.

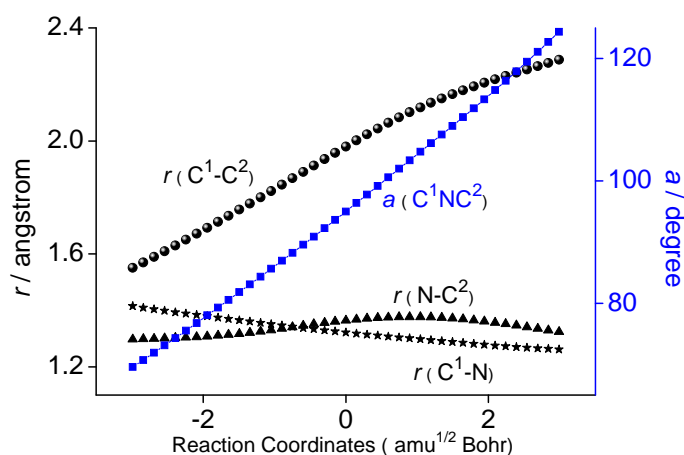


Fig. 5 – The selected bond lengths and angle changes along the reaction coordinates of the step (1) during the interconversion between IMA and P1.

Through the cleavage of the C^1-C^2 bond, IMA can be converted to P1 via TS1, where the barrier is 217.6 kJ/mol. The calculated unique imaginary frequency of TS1 is $563i\text{ cm}^{-1}$. IRC calculations have been performed on the basis of the calculated TS1 to investigate the interactions between IMA and P1 in the step (1) process (see Fig. 5).

As shown in Figs. 1 and 5, for the angle of C^1NC^2 in IMA, it increases along with the reaction. At the same time, the bond distance of C^1-C^2 increases along with the reaction process, implying the breakage of the three-membered ring involving C^1C^2N .

In P1, the C^2 adopts sp^2 hybridization, it has a pair of lone electrons, making the P1 exhibit the carbene character. Therefore, P1 is very active, it is not only the product of pathway (I), but also the reactant of pathway (III). In the following reaction process, P1 can further react with formaldehyde to form the product P3.

2 Pathway (II): formation of an allenes compound P2

As the common intermediate of pathway (I) and (II), IMA can transform to P2 via step (2a) and (2b).

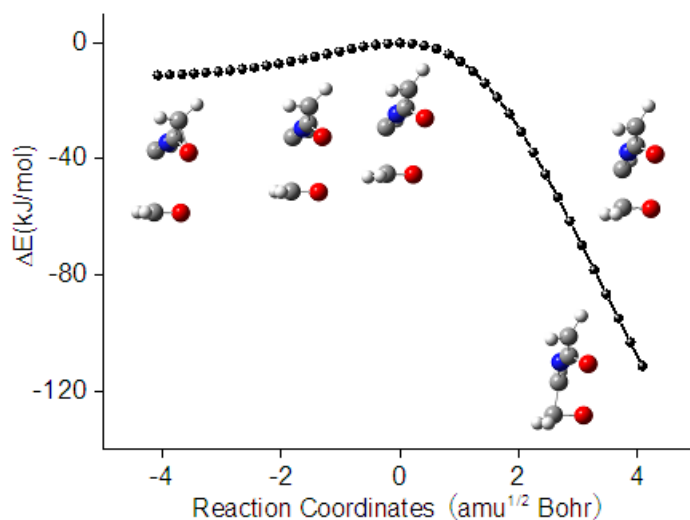


Fig. 6 – IRC of TS3 and geometry evolution.

The reaction step (2a) is the hydrogen transfer process from C^2 to the adjacent N, resulting in the conversion of IMA into IM2a via TS2a. Here, the calculated barrier is 276.9 kJ/mol and the unique imaginary frequency of TS2a is $1377i\text{ cm}^{-1}$. In details, as shown in Fig. 1, the distance of C^2-H^1 in TS2a has been elongated to 1.265 Å, and the distance of $N-H^1$ has also been reached to 1.204 Å, which indicate that the H^1 atom can be transferred from C^2 to N.

Similar to the C^1C^2N ring in IMA, the C^1C^2N ring in IM2a can be opened at its weaker bond. Through the break of the C^1-N bond, IM2a can be converted to P2 via TS2b, where the barrier is 68.1 kJ/mol. The calculated imaginary frequency of transition state TS2b is $301i\text{ cm}^{-1}$.

In P2, the bond length of C^1-C^2 is 1.301 Å, which fall in the range of the intermediate between $C=C$ and $C\equiv C$ bond length. Analogously, the bond length of C^2-N (1.247 Å) lies between the $C=N$ and $C\equiv N$ bond. The three atoms, C^1 , C^2 , and N, are approaching to the same line ($\angle C^1C^2N$ is 167.2°). Therefore, P2 is the allenes structure. Along the reaction profile, P2 is exothermic with the value of 106.8 kJ/mol comparison with that of the reactants.

3 Pathway (III): the formation of a bicyclic compound P3

As mentioned earlier, P1 exhibit the carbene characters, it can further react with formaldehyde to form the product P3, which is named as pathways (III). The geometric parameters for the species involved in the pathway (III) are displayed in Fig. 1. The calculated relative energies for the

available stationary points have been summarized in Table 1.

As shown in Fig. 1, in TS3, the distance of C^2-C^3 and C^2-O^1 is 2.089 and 2.479 Å, respectively. The distance of C^3-O^1 in R2' fragment (1.242 Å) is elongated by 0.028 Å relative to that in isolated R2' molecular. Thus, in the transition state TS3, two new bonds of C^2-C^3 and C^2-O^1 are to be formed and the C^3-O^1 bond is to be transformed from double bond to single bond simultaneously. As shown in Fig. 6, these changes can be further validated by the IRC calculations on the basis of TS3. Furthermore, similar with the explanation of R1 react with formaldehyde, the HOMOs of P1 and formaldehyde are displayed in Fig. 4. Along the reaction profile, P3 is the most stable species, which is exothermic with the value of 192.7 kJ/mol comparison with that of the reactants.

CONCLUSIONS

The cycloaddition reaction between azacyclopropenylidene and formaldehyde has three competitive pathway (I), (II), and (III), the corresponding products are carbene compound P1, allenes compound P2, and bicyclic compound P3, respectively. On the basis of the energy results obtained with the CCSD(T)/6-311+G*/MP2/6-311+G* method, it can be predicted that pathway (III) is the competitive dominant channel. The pathway (III) consist of three steps: (1) the two reactants (azacyclopropenylidene and formaldehyde) first form a spiro intermediate IMA via transition state TSa with energy barrier of 45.8 kJ/mol; (2)

IMa isomerize to a carbene compound P1 via transition state TS1a with energy barrier of 217.6 kJ/mol; (3) P1 further react with formaldehyde (R2') to form a bicyclic compound P3 via transition state TS3 with energy barrier of 14.7 kJ/mol. From the thermodynamics viewpoint, P3 is the dominating product, which energy is 192.7 kJ/mol lower than that of the reactants.

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